SERMACS 2019 – October 20-23, 2019
Hosted by: Coastal Georgia Local Section of the American Chemiccal Society
General Chair: Will E. Lynch
Program Chair: Brent Feske

SERMACS 1

Community outreach and its impact on science students

Carole Letson, *drletson@quail5.com. Science, Chattahoochee Technical College, Norcross, Georgia, United States*

“We should not teach children the sciences but give them a taste for them.” - Rosseau
Community outreach has a strong positive impact on science students. Volunteers return to class reinvigorated and with renewed confidence in their abilities. Participants also develop a sense of fellowship and teamwork as they work alongside their instructors; this dramatically enhances the classroom dynamic for everyone, including non-participants. Chattahoochee Tech’s (CTC) Science Division has a robust community outreach program dedicated to partnering with local schools to engage students and promote scientific literacy within our service area. We began partnering with the Atlanta Science Festival (ASF) 5 years ago, hosting an on-campus event as well as a booth at the Expo in Atlanta. The ASF events have grown steadily and now include 2 on-campus events, the Expo, and over a hundred student volunteers. For the past 4 years, we have conducted events in conjunction with National Chemistry Week. The publicity generated from our outreach events has led to regular visits at several local schools for anatomy curriculum, STEM nights, and Career Days.
This talk will discuss preparation, publicity, gathering volunteers, and successes and failures of outreach implementation. Because we get a wide range of ages with our participants, we must plan for a wide range of activities and demonstrations. Most of our students pursue healthcare professions so even our chemistry events lean toward human physiology while still remaining topical. For last year’s “Chemistry is out of this World” theme, students created displays relating life in space to the impact on the human body. This year, they submitted element posters to correlate with the Year of the Periodic Table. Part of our success is due to fostering student creativity and offering many ways to participate. We invite students to engage in a photo/art contest with prizes. Student submissions are then used to educate our visitors.
Community outreach helps to promote our College and remove the stigma associated with the Technical College system. We ask that representatives of our programs be present so that our visitors can see what CTC has to offer. Having visitors on campus allows us to showcase our lab materials as well as our best assets: our people.

SERMACS 2

Employability skills through critical thinking

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Savannah Technical College is the “College that Works!” As part of the Technical College System of Georgia, the college’s mission is to train the workforce by providing a world class education, skills training and lifelong learning opportunities. As a partner in the community, Savannah Tech works closely with leading businesses and industries to know what skills they need in their employees. We found that their greatest need in employees is in “soft” skills including attitude, professionalism, teamwork, problem solving, critical thinking, planning and organization, social skills, media rules and communication. In 2018, Savannah Tech had fully implemented their Quality Enhancement Plan, where every course contains a graded assignment that helps to develop these soft skills for employability. This presentation will highlight some examples of different assignments used in the various disciplines taught at the college, the assessment process, and the impacts this plan has had on our students.

SERMACS 3

Why is chemistry so hard (to teach)? Exploring strategies for the chemistry courses at Gwinnett Technical College

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Chemistry is one of the most challenging courses for technical college students for a variety reasons. It is the first critical thinking encounter for some and others either never liked word problems in math or had very traumatic experience in a previous chemistry course. All of the fears, rumors and anxieties that come with the students to the college chemistry course presents a new challenge every term for the chemistry instructors. This presentation will focus on the strategies that the chemistry faculty use at Gwinnett Technical College to help overcome some of the fears and engage the students in an active learning environment. With the institution of mandatory workshops (recitations), instructors have time to create activities and model positive learning behaviors. The outcome of the talk will be to present, discuss and generate ideas and exercises that are useful in your endeavor to overcome some of the challenges that you may be facing in your courses.

SERMACS 4

Teaching STEM classes at the technical college level

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Abstract

Teaching STEM classes at the technical college level can be challenging. Technical colleges tend to have a more diverse population than a typical university. In general, the students enrolled in chemistry are focused on applying to their various programs and are taking chemistry because it is a prerequisite for nursing, dental hygiene or respiratory therapy. Most have had chemistry in either high school or during a prior college experience but very few relate the experience as positive. The onus is on the instructor to engage, inspire, and hopefully excite these students to make learning chemistry and other STEM classes a more positive experience. As instructors, how can we create an environment which embraces the diversity of our students and focuses them on the common goal of learning? By over-coming fixed mind sets, peaking student interest by making lessons more relevant to their own lives, and by building a sense of belongingness versus intimidation, we can create an environment of learning rather than having to pass a class for the credit and then forgetting the information once the class is completed.

SERMACS 5

Shaken, not stirred: Exploration into the synthesis of group 2 amide compounds

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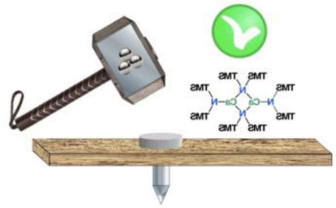
Ball milling calcium iodide with potassium bis(trimethylsilyl)amide in a 1:1 ratio without solvent and then extracting the ground material with toluene yields the synthetically valuable neutral amide calcium bis(trimethylsilyl)amide in good yield, without contamination by calciate species that complicates solution metathesis. The effects on yield of grinding time, milling frequency, and calcium halide identity will also be discussed.



SERMACS 6

Catalytic application of cobalt complex bearing a tetradentate tripodal ligand for the homo-coupling of secondary alcohols

Lucas Bryant[1]*, lpb2x@mtmail.mtsu.edu, Daniela Taylor*[2]*, Keying Ding*[3]*. (1) Chemistry, Middle Tennessee State University, Alpharetta, Georgia, United States (2) Middle Tennessee State University, Murfreesboro, Tennessee, United States (3) Chemistry Department, Middle Tennessee State University, Murfreesboro, Tennessee, United States*

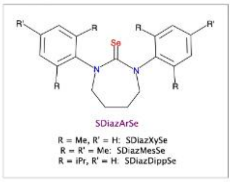
The replacement of rare, expensive, and toxic metals such as Ru, Rh, Pt, Pd, and Ir with earth-abundant metals is an appealing target in the field of catalysis. A cobalt complex bearing a novel tetradentate tripodal ligand has been synthesized and used for the homo-coupling of secondary alcohols to form ketones. Along with a wide variety of both aliphatic and aromatic secondary alcohol substrates, a strong base is introduced into the reaction for the activation of the cobalt catalyst. Without the presence of both the cobalt complex and strong base, no coupling reactions occur. These reactions take place under inert atmosphere with the use of argon flow to allow the dehydrogenated products to form. Coupled products are assessed using NMR with an internal standard to determine yield as well as GCMS to confirm structure. These reactions provide high yields of ketone products using catalyst loadings as low as 3.5 mol%.

SERMACS 7

Synthesis and reactivity of expanded-ring heterocyclic selones

Keri Dowling*, kdowling@uncc.edu, Daniel Rabinovich. UNC Charlotte Chemistry, Charlotte, North Carolina, United States*

The synthesis, characterization, and coordination chemistry of three new N-heterocyclic selone (NHSe) ligands containing a saturated 1,3-diazepine ring and bulky aromatic substituents on the nitrogen atoms is described in this presentation. A series of closed-shell (d^{10}) metal complexes have been synthesized in order to understand the effect that the size of the heterocyclic ring has on the Lewis basicity of the ligands, particularly relative to analogous ligands based on five- and six-membered heterocyclic rings. More specifically, several cadmium(II) and mercury(II) complexes (SDiazArSe)MX_2 (M = Cd, Hg; X = Cl, Br, I) and group 15 derivatives (SDiazArSe)MX_3 (M = Sb, Bi; X = Cl, Br, I) have been isolated and characterized by a combination of analytical and spectroscopic techniques. This presentation will also outline our preliminary exploration of the reactivity of the selone ligands towards elemental halogens such as bromine and iodine, which lead to the formation of simple adducts of general formula (SDiazArSe)X_2 (X = Br, I). In addition, several homoleptic two-coordinate cationic silver(I) complexes will be described, with a brief discussion of their potential anticancer properties.

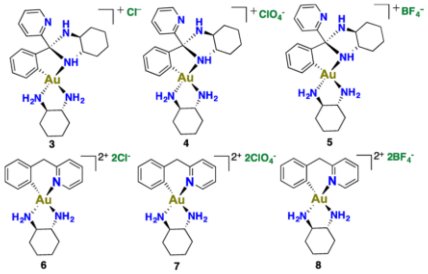


SERMACS 8

Synthesis, structure and anticancer activity of organometallic gold(III) complexes bearing dach ligands

Sailajah Gukathasan, *sgu269@uky.edu, Sean Parkin, Samuel G. Awuah. Chemistry, University of Kentucky, Lexington, Kentucky, United States*

A novel class of six cyclometalated gold(III) complexes has been prepared by the reaction between (C,N) cyclometalated gold(III) compounds and (1R,2R)-(+)-1,2-Diaminocyclohexane ligand in the presence of different counter ion and their structures characterized by X-ray crystallography. The structural scaffold of the complexes were of the type $[Au(C\hat{}NH)DACH_2]^+$ (**3-5**) and $[Au(C\hat{}N)(DACH)]^{2+}$ (**6-8**). The solution studies under physiological conditions revealed that these complexes are stable. The electrochemical characterization also proved the stability of these complexes. The in vitro anti-cancer activities of complexes **3-8**, cisplatin and auranofin were studied in A2780, OVCAR8, RPE-MYC and MCF7 cancer cell lines by crystal violet assay. Complexes **3-5** exhibited more potency towards A2780 and OVCAR 8 cell lines (IC_{50} ~ 4.0 μM), while complexes **6-8** were more potent against MCF7 and RPE MYC (IC_{50} ~ 4.0 μM). All the complexes showed selectivity over normal healthy cells, MRC5. Both complex types do not show interaction with DNA except at very high concentration >500 μM. The cellular uptake of these complexes was 200-700 picomol /million cells in OVCAR8 cell line. Overall, this study proved that tuning the gold(III) center with DACH and [C^N] cyclometalated gold ligands can increase the stability of gold(III) complexes and contribute to novel anticancer drug design.



SERMACS 9

Activation of terminal alkynes by trimethylamine: Synthesis and reactivity of zwitterionic aminoalkyne ligands in pentaruthenium carbonyl cluster complexes

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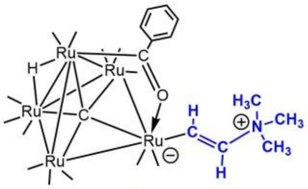
Alkyne-substituted cluster complexes are key intermediates in the catalytic reactions such as carbonylation, hydrogenation, hydroformylation, hydroamination and cyclotrimerization. The reaction of cluster complex $Ru_5(m_5\text{-}C)(CO)_{14}(m\text{-}h^2\text{-}O{=}CC_6H_5)(m\text{-}H)$, **1** with the alkynes C_2H_2 and $HC_2(CO_2CH_3)$ in the presence of $(CH_3)_3NO$ yielded the complex $Ru_5(m_5\text{-}C)(CO)_{13}[N(CH_3)_3][(m\text{-}h^2\text{-}O{=}CC_6H_5)(m\text{-}H)$, **2** and the zwitterionic $N(CH_3)_3$-alkyne addition products: $Ru_5(m_5\text{-}C)(CO)_{13}(m\text{-}h^2\text{-}O{=}CC_6H_5)(m\text{-}H)[C_2H_2N(CH_3)_3]$, **3** and $Ru_5(m_5\text{-}C)(CO)_{13}(m\text{-}h^2\text{-}O{=}CC_6H_5)(m\text{-}H)[HC_2(CO_2CH_3)N(CH_3)_3]$, **4**, respectively at room temperature. It was found that compound **2** can be converted to **3** by reaction with C_2H_2 at room temperature. A cyclotrimerized product $Ru_5(m_5\text{-}C)(CO)_{12}(m\text{-}h^2\text{-}O{=}CC_6H_5)(m\text{-}H)(H_2C_6C_3O_6C_3H_9)$, **5** was also obtained from the reaction of **1** with $HC_2(CO_2CH_3)$ and $(CH_3)_3NO$. All the new compounds were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses.



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$Ru_5(\mu_5\text{-}C)(CO)_{13}(\mu\text{-}\eta^2\text{-}O{=}CC_6H_5)(\mu\text{-}H)[C_2H_2N(CH_3)_3]$, **3.**

SERMACS 10

Modelling the H-cluster subsite of [FeFe]-hydrogenases: Catalysts for hydrogen production

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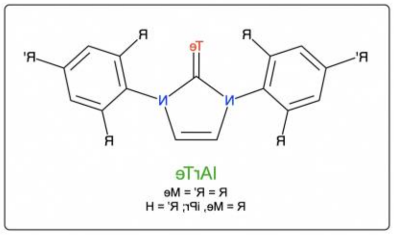
[FeFe]-hydrogenases efficiently catalyze the reduction of protons to H_2 which is a clean and primary energy carrier of the future. The active site of [FeFe]-hydrogenases consists of an H-cluster connected by a cysteinyl ligand to a tetrairon cluster. The H-cluster, which is the catalytically active center, is a diiron cluster containing a bridging dithiolate cofactor and ligated by diatomic CO/CN^- ligands. This study involves the design and synthesis of diiron-carbonyl complexes containing poly-aromatic thiolate groups in order to mimic the structural and functional attributes of the H-cluster of [FeFe]-hydrogenases. These compounds have been structurally (X-ray crystallography) and spectroscopically (IR, UV-visible and NMR) characterized, and examined as catalysts for the electrochemical reduction of proton to hydrogen. Our catalysts generate hydrogen from acidic water at milder reduction potentials than similar complexes reported in the literature.

SERMACS 11

Synthesis of the first heterocyclic telone complexes of silver and mercury

Kirk John V. Arcena, *karcena@uncc.edu, Daniel Rabinovich. UNC Charlotte Chemistry, Charlotte, North Carolina, United States*

We have prepared in the past a variety of metal complexes supported by N-heterocyclic thione (NHT) and selone (NHSe) ligands. In particular, two-coordinate cationic complexes $[Ag(IArE)_2]^+$ (E = S, Se) exhibit potent anticancer activity. We have now extended the scope of this project by preparing the corresponding tellurium analogues, namely the N-heterocyclic telone (NHTe) ligands IArTe (Ar = Xy, Mes, Dipp). Significantly, the coordination chemistry of NHTe ligands is virtually unknown, being limited only to the preparation of a chromium(0) complex and a handful of bismuth(III) derivatives. Initial reactivity studies with our IArTe ligands have led to the isolation of several silver(I) and mercury(II) complexes of general formulas $[Ag(IArTe)_2]X$ (X = NO_3, BF_4, ClO_4) and $(IArTe)HgX_2$ (X = Cl, Br, I), respectively. Not surprisingly, the telone derivatives appear to be more thermally sensitive than their sulfur and selenium analogues. In addition, the telone ligands react cleanly with elemental iodine to form the adducts $(IArTe)I_2$. This presentation will also include a comparison of these results with previous work completed for the thione and selone analogues.



SERMACS 12

Phosphonium ionic liquids: Versatile platform for future applications

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Phosphonium-based ionic liquids (ILs) have garnered interest in recent years due their high thermal stability, whe compared to many of the common ammonium/imidazolium based ILs. Especially stable are tetraaryl phosphonium ionic liquids, the synthesis of these compounds has proven to be sensitive. This talk will discuss the synthesis and characterization of a new class of pyridyl phosphonium salts, ([Mopyphos]X), which show promise as ILs for both high temperature and room temperature applications.

SERMACS 13

Harnessing light and proton-coupled electron transfer to drive dinitrogen reduction at rhenium

Quinton J. Bruch[1], *qjbruch@live.unc.edu, Gannon Connor*[2], *Chun-Hsing Chen*[1], *Patrick L. Holland*[2], *James M. Mayer*[2], *Faraj Hasanayn*[3], *Alexander J. Miller*[1]. *(1) Dept of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States (2) Yale University, New Haven, Connecticut, United States (3) American University of Beirut, Beirut, Lebanon*

The reliance of the Haber-Bosch process on hydrocarbon steam reforming and the associated environmental costs have long motivated research into sustainable alternatives. In this research, molecular rhenium complexes are investigated as a platform for ammonia synthesis using discrete electron equivalents and water as a proton source. Mechanistic investigations show that $(PONOP)Re(Cl)_3$ binds N_2 upon reduction and halide abstraction to form the bimetallic complex *trans,trans*- $[(PONOP)Re(Cl)_2]_2(m\text{-}N_2)$. Photolytic cleavage of N_2 was observed, with striking isomer-dependent reactivity. The nitride product releases ammonium ions when treated with proton-coupled electron transfer reagents.

SERMACS 14

Electrochemical analysis of nickel dithiocarbamate complexes for redox flow battery applications

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Energy storage is a vital aspect for the successful implementation of renewable energy resources on a global scale. Arguably the best method of energy storage is within small molecules via the formation of chemical bonds coupled to multi-electron redox reactions. Herein, we investigated the redox cycle of 2e$^-$ redox couples based on nickel dithiocarbamates for potential use as catholytes in non-aqueous redox flow batteries. To gain mechanistic insight into the Ni^{II}(Et$_2$dtc)$_2$ redox cycle we studied the addition of different pyridine based ancillary N-donor ligands (L) into the Ni^{II}(Et$_2$dtc)$_2$ in CH$_3$CN. The irreversible Ni(II) oxidation peak shifted cathodically with increased [L] and the highest shift was observed for 4-Dimethylaminopyridine. Pyridines functionalized at the 2 position did not show any effect on peak potential shifting due to steric hindrance for coordination to nickel. Overall, the pyridine coupled oxidation process was determined to be 1e$^-$ in nature, yielding 5-coordinate [Ni^{III}(dtc)$_2$py]$^+$ and 6-coordinate [Ni^{III}(dtc)$_2$(py)$_2$]$^+$ species. The equilibrium constants for pyridine coordination were determined and found to increase with larger pK$_a$ values. Further mechanistic insight of the Ni^{II}(Et$_2$dtc)$_2$ redox cycle was found when we added Zn^{2+} and Ni^{2+} ions in the system. The addition of either divalent cation resulted in improved 2e$^-$ reduction of [Ni^{IV}(Et$_2$dtc)$_3$]$^+$. This enhancement is belived to be due to chemical assistance in removing a dtc$^-$ ligand from a Ni^{III}(Et$_2$dtc)$_3$ intermediate, allowing for easier reduction to Ni^{II}(Et$_2$dtc)$_2$.

SERMACS 15

New molecular and ionic actinide fluorides: Simple systems, complex chemistry

***Garret Gotthelf**, ggotthelf12@gmail.com. Chemistry and Chemical Biology, Rutgers University, Somerset, New Jersey, United States*

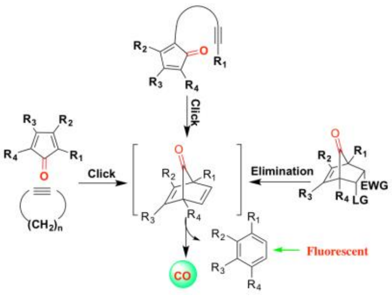
Actinide metal undergoes a redox reaction with CuX$_2$ (X= Br, Cl, F) in organic solution to form assorted new molecular compounds. Uranium metal reacts with Copper (II) Fluoride to primarily form monomeric compounds like py$_4$UF$_2$I$_2$. Thorium will dimerize with those same condition, py$_7$Th$_2$F$_5$I$_3$, but will form a monomer py$_4$ThFI$_3$ when conditions are changed. Changing the solvent environment causes signifcant changes in the resulting compounds. In acetonitrile Uranium prefers to crystallize as a cation anion pair with the oxidizing agent. All compounds have been characterized by X-ray crystallography.

SERMACS 16

Click, fluoresce, and release: Tracking drug delivery through the concomitant generation of a fluorophore

***Binghe Wang**, wang@gsu.edu. Dept of Chem, Georgia State University, Atlanta, Georgia, United States*

Carbon monoxide is an endogenous signaling molecule with pleiotropic pharmacological effects including cytoprotection and anti-inflammation. Animal model studies have demonstrated CO's effect against colitis, systemic inflammation, ischemia reperfusion injury, and chemically induced liver injury, among others. However, CO delivery is difficult to measure and quantify *in vitro* and *in vivo*. We have developed organic CO prodrugs that are capable of CO delivery with tunable release rate, triggered release, and generation of a fluorophore for easy monitoring of CO release. This presentation will discuss our work in this area.



SERMACS 17

Assessment of liposome triggered release and lipid metabolic labeling using fluorescence techniques

***Michael Best**, mdbest@utk.edu, Jinchao Lou, Xiaoyu Zhang, Tanei Ricks, Daiane Alves, Chelsi Cassilly, Francisco Barrera, Todd Reynolds. The University of Tennessee, Knoxville, Tennessee, United States*

This presentation will highlight different projects in which fluorescence microscopy and other fluorescence techniques have proven to be invaluable tools for probing biological applications involving lipids. One aspect that will be discussed is triggered release of cargo from liposomes, which is being pursued for drug delivery applications. The goal of this project is to develop stimuli-responsive lipids that drive release of encapsulated contents from liposomes upon reaching diseased cells. In particular, lipid switches that promote release of contents by undergoing conformational changes following molecular recognition events will be discussed. The design of these systems, as well as their evaluation using fluorescence dye leakage assays, dynamic light scattering and electron and fluorescence microscopy, will be presented. In an additional project, the metabolic labeling of lipids that play important biological roles will be presented, which is conducted through the development of clickable analogs of substrates that produce tagged lipid products using normal cellular biosynthetic machinery. This allows for tracking of the biosynthesis of key lipids in cells. Lipid labeling has been assessed by fluorescence microscopy, fluorescence-based TLC experiments and mass spectrometry lipidomics.

SERMACS 18

Aurones as a scaffold for fluorescent probes and sensors

***Scott T. Handy**, shandy@mtsu.edu. Chemistry, MTSU, Murfreesboro, Tennessee, United States*

As part of our ongoing interest in the Chemistry and Biochemistry of aurones, we have initiated an effort to make use of their intrinsic fluorescent behavior both as sensors as well as probes. While aurone fluorescence is known, it has been only studied in a few reports and most of these have focused on very similar systems. In our efforts, we have opted to study the tunable nature of the absorption and emission by varying the exocyclic benzylidene group to develop a predictable family of fluorescent compounds for a variety of applications. Separately, we have also synthesized a fluorescent sensor for detecting hydrogen sulfide based upon the reduction of an azido-substituted aurone and determined that substitution of the benzofuranone portion can greatly influence the solubility properties of the aurones, while leaving their photophysical properties largely unchanged. The results of these studies as well as applications in progress will be discussed.

SERMACS 19

Metal ion-responsive ratiometric fluorescent probes for two-photon microscopy

***Christoph J. Fahrni**, fahrni@chemistry.gatech.edu. Georgia Inst of Techlgy, Atlanta, Georgia, United States*

The identification and quantification of transition metals, ideally within the context of their native physiological environment, is of critical importance for a comprehensive understanding of metal homeostasis in cells, tissues, and whole organisms. To this end, we developed a suite of fluorescent probes for interrogating the nature of labile zinc pools in live cells by two-photon excitation microscopy (TPEM). To achieve both a balanced two-photon absorption cross-section as well as a chromatic shift in the fluorescence emission upon metal binding, we employed a design strategy where the metal ion receptor serves as an acceptor rather than donor moiety within a push-pull fluorophore architecture. As coordination of the metal cation to the receptor site increases the degree of intramolecular charge transfer (ICT) upon photoexcitation, the two-photon cross-section is rendered more favorably, and the fluorescence emission is shifted towards longer wavelength compared to the free probe. Based on this approach, we devised a Zn(II)-responsive fluorescent probe, chromis-1, and visualized temporal changes of buffered Zn(II) levels in live cells as well as developing zebrafish embryos. Additional efforts focused on tuning the photophysical properties to develop a dual mode probe that can be used with both TPEM and conventional confocal fluorescence microscopy. Altogether, the combination of molecular tools with advanced fluorescence imaging techniques revealed intriguing insights into the nature of labile zinc pools and the dynamics of their regulation in live cells and developing zebrafish embryos.

SERMACS 20

Lessons from super-resolution microscopy: Choosing the right method and sample preparation considerations

***John Allen**, spectre3301@gmail.com. Nikon Instruments Inc., Durham, North Carolina, United States*

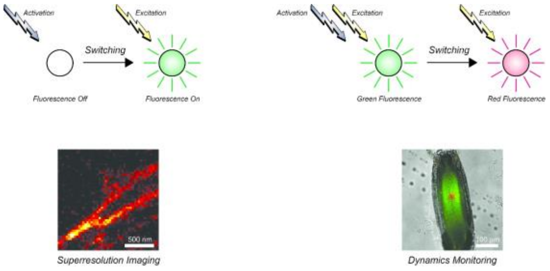
Super-resolution light microscopies, including STochastic Optical Reconstruction Microscopy (STORM) and Structured Illumination Microscopy (SIM), surpass the resolution limit for optical systems as described by Ernst Abbe. However, realization of spatial super-resolution requires compromise in other areas. Reduced signal-to-noise, temporal resolution, and phototoxic levels of illumination are common challenges and vary considerably with super-resolution method, of which a large variety now exists. These methods also have different sample preparation requirements. This presentation will include a concise survey of mainstream super-resolution microscopies and the major advantages and disadvantages of each for biological imaging applications. Information on fluorophore selection, compatible labeling methods, and imaging buffer systems/mounting media will also be provided, with an emphasis on STORM and related single molecule localization microscopies. STORM poses especially stringent requirements with regard to sample preparation. The reason for this is two-fold. First, it requires inducing blinking behavior from fluorophores, which requires matching specific fluorophores and buffer conditions. Second, the especially high-resolution capability of STORM (even compared to other super-resolution microscopies), with XY resolution of ~20 nm being routinely realized. There are concerns such as fluorophore-target linkage error that did not have to be considered when developing the standard immunohistochemical staining protocols for lower resolution techniques, such as confocal or widefield epifluorescence microscopy.

SERMACS 21

Photoswitchable fluorophores for bioimaging applications

***Francisco M. Raymo**, fraymo@miami.edu. Department of Chemistry, University of Miami, Coral Gables, Florida, United States*

The goal of our research program is the development of operating principles to switch fluorescence under the influence of external stimulations. We design molecules capable of switching from a nonemissive to an emissive state, upon illumination at an appropriate activation wavelength and then produce fluorescence after irradiation at a given excitation wavelength. The resulting compounds permit the confinement of fluorescence within a defined region of space at a specific interval of time, relying exclusively on the interplay of beams illuminating the sample at the activation and excitation wavelengths. Such level of spatiotemporal control offers the opportunity to overcome diffraction and reconstruct fluorescence images with spatial resolution at the nanoscale. We also design molecules capable of interconverting between emissive states with spectrally-resolved fluorescence, upon illumination at an appropriate activation wavelength. The resulting compounds allow the switching of the fluorescence color with spatiotemporal control in a given sample of interest and the subsequent monitoring of dynamic events in real time with the sequential acquisition of fluorescence images. We are particularly interested in exploring these operating principles for fluorescence switching to visualize intracellular substructures with nanometer resolution as well as track the translocation of species within living organisms. Thus, our fundamental investigations on molecular switches can eventually lead to the realization of innovative imaging probes for a diversity of bioanalytical applications.



SERMACS 22

Conjugated oligomers for fluorescent live cell imaging

__Joong Ho Moon__, jmoon@fiu.edu, Hooman Torabi, Alfonso Barrios, Abdul Halim, Sabbir Sarker. Chemistry and Biochemistry, Florida International University, Miami, Florida, United States

Owing to high brightness, photostability, and nontoxicity, various conjugated polymers (CPs) and conjugated polymer nanoparticles (CPNs) have been developed and used for fluorescent labeling of live cells and tissues. Despite the excellent photophysical properties, the relatively large sizes and size distributions of CPs are problematic for intracellular labeling and monitoring of organelles, proteins, or nucleic acids. Meanwhile, molecularly defined conjugated oligomers (COs) are better suited for intracellular labeling applications due to fast cellular diffusion, although tedious synthesis and relatively poor photophysical properties have been issues. To overcome the issues, we recently developed biodegradable CPs showing efficient live cell entry and mitochondria labeling. CPs were converted to pentameric COs upon cellular entry followed by intracellular reduction, which the resulting COs efficiently traffic to the mitochondria. To combine the advantages of both CPs (i.e., more chromophores per molecule) and COs (defined molecular weights and faster cellular entry) avoiding extensive synthetic procedures, we recently synthesized a macrocyclic system using the imine bond formation between aldehyde end-capped phenyleneethynylene trimer units and flexible diamines. The resulting fluorescent macrocycles exhibit higher quantum yields than the corresponding trimer and selective nucleic acid labeling in live cells. In this presentation, our recent efforts to develop CO-based materials for intracellular fluorescent labeling and sensing in live cells will be discussed.

SERMACS 23

Photo-click strategies for selective substrate labelling with 4D resolution

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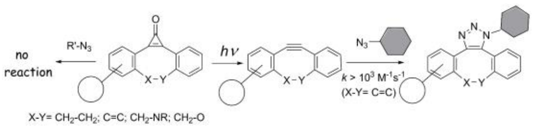
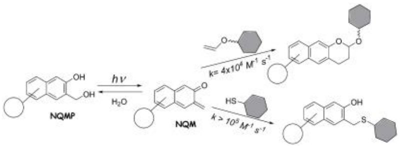
Photochemical triggering of “click” reactions permits the spatial and temporal control of the derivatization, labelling, cross-linking and patterning of various substrates. Two-photon excitation – induced click ligations allows for achieving 3-D resolution of the process. The absence of potentially detrimental catalysts and/or activating reagents, as well as high stability of “photo-click” reagents in the dark provide additional benefits to this strategy. Three photo-click techniques have been recently developed in our laboratory:

1. “Photo-SPAAC” click strategy is based on the photo-decarbonylation of cyclopropenone moiety incorporated into an 8-membered ring.
2. “Photo-Diels-Alder” derivatization technique relies on a very rapid and selective cycloaddition of photogenerated *o*-naphthoquinone methides (NQMs) to vinyl ethers producing photostable benzochroman derivatives.
3. “Photo-Michael” reaction allows for selective and reversible modification of thiol groups in biological or synthetic polymers, as well as write-erase-write process on the thiolated surfaces. This method makes use of a very facile reaction between NQM and thiols to give hydrolytically stable thioether.





SERMACS 24

Beneficial effect of deionized collagen in the properties of biocomposites prepared from the reinforcement of a tung oil-based thermosetting resin

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A free radical thermosetting resin containing 40 wt.% of tung oil, 30 wt.% of *n*-butyl methacrylate (BMA), 20 wt.% of divinylbenzene (DVB), and 10 wt.% of asolectin has been reinforced with 0.5-10 wt.% of collagen Type I extracted and purified from waste beef tendons. It has been observed that the introduction of sodium ions during the purification process has a direct impact in the secondary structure of collagesn, and that their removal after collagen purification favors the formation of a typical triple helix structure, as determined by circular dichroism (CD) spectroscopy. The main focus of the work described herein is to determine the effects of excess sodium ion content on collagen structure and final composite properties.All purified collagen samples obtained in this study were characterized by matrix-assisted laser desorption/ionization time-of-flight (MALDI-tof) mass spectroscopy for molecular weight determination.A thorough comparison of the properties of tung oil composites reinforced with sodium-containing and sodium-free collagen reveals that sodium removal enhances the thermo-mechanical properties of the final materials, as the structural properties of collagen are directly connected with its triple helix structure. The properties of the collagen composites prepared were assessed by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and scanning electron microscopy (SEM). The composites studied in this work show potential for biomedical applications as implants and in tissue engineering due to the biological nature of the material's components and their comparable properties to high-density polyethylene (HDPE).

SERMACS 25

Monomer from abietic acid and tung oil

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Most current research in the area of sustainable environmentally friendly materials relate to the use of renewable sources for the fabrication of bio-based polymers and composites. Using plant-based derivatives is a common strategy. Pine sap can be distilled into turpentines (light fraction) and pine rosin (heavy fraction). Pine rosin is obtained as a brittle solid. The major component is abietic acid. This project aims at investigating different approaches for the synthesis of pine rosin-based polymers and composites that can be potentially used for manufacturing a collection device for pine sap. To begin, the approach was to take pine rosin to synthesize through bulk homo-/copolymerization with a free radical. Three free radicals used at the time to find the best fit were Azobisisobutyronitrile and two forms of peroxide based Luperox DI polymer initiators. Homopolymerization was not complete alone, but the samples provided enough physical data to show there was potential in another direction. It was quickly understood that there would be need for other reactive species beyond the addition of the reactive comonomer for polymerization. It is understood from past research that tung oil has shown potential co-polymerization with the stated free radicals. There was noticeable reaction for polymerization. From prior literature, it was calculated a need for a 3:2:1 ratio of abietic acid, tung oil and glycerine respectively. After fabricating the glycerol abietate from a glycerine and two tung oil fatty acids with modified tung oil by transesterification, the next step is to modify and attach the abietic acid through an acid cross-esterification process. To calrify and find the hydroxyl within abietic acid and characterization of glycerol abietate, Nuclear Magnetic Resonance (NMR), Fourier Transmission Infrared Spectroscopy (FTIR) and Raman spectroscopy were used.

SERMACS 26

Synthesis and characterization of UV resistant castor wax-based polyurethane coatings

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Polymeric coatings, especially polyurethane coatings, are used to protect the underlying materials from damage caused by abrasion, UV exposure, water damage, and/or corrosion. Polymeric coatings containing carbon-carbon double bonds are known to be more susceptible to degrading when exposed to elevated temperatures and/or UV exposure. Castor wax, also known as hydrogenated castor oil, is a sustainable bio-based polyol without carbon-carbon double bonds. Castor wax is frequently added to cosmetic formulations to increase the viscosity and act as an emollient. In this study, a series of castor wax-based polyurethane dispersions that are less susceptible to UV degradation were synthesized by varying the molar ratios of the polyol (castor wax), ionomer (dimethylolpropionic acid), and the isocyanate (isophorone diisocyanate). As a control, a corresponding series of polyurethane dispersions were prepared using castor oil instead of castor wax. The thermal and mechanical properties of the resulting films were subsequently characterized by and number of techniques including thermogravimetric analysis, differential scanning calorimetery, dynamic mechanical analysis, and tensile testing.

SERMACS 27

Non-isocianate polyurethanes (NIPUs) obtained from fatty acids

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The vegetable oils and their fatty acids are considered an excellent resource to produce polymers. They are renewable resources with great properties, low cost, easy processing and can form materials that are able to degrade faster. In this context, esterification, epoxidation and hydroxylation of oleic and linoleic acids were realized in order to increase their reactivity and to produce non-isocianate polyurethanes (NIPUs). The esterification reaction used methanol with acid catalysis, during 48 hours.

Epoxidation/hydroxylation reactions occurred in one step, using performic acid originated *in situ*. From the reactions were obtained the esters and the polyols of the esters of the oleic and linoleic acids. These materials were used to obtain the NIPUs. The materials were analyzed by Fourier transformed infrared spectroscopy (FT-IR) and ^{1}H nuclear magnetic resonance (^{1}H NMR), indicating that the reactions occurred. In addition, the samples were characterized by thermogravimetry (TG)/derivative thermogravimetric (DTG), using inert atmosphere. TG/DTG curves showed different thermal stabilities, also confirming the occurrence of the reactions.

SERMACS 28

Controlling macromolecular topologies towards sustainable bioplastics

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Sustainable chemicals, polymers and materials have received tremendous attention since the beginning of the 21st century. However, biobased plastics, elastomers and advanced materials are still many steps from being competitive with petrochemical counterparts. We have led efforts on the conceptualization of novel macromolecular topologies and compositions in converting renewable biomass into sustainable monomers and polymers using eco-friendly, atom-efficient and economy-viable chemistry. A few case studies are given to illustrate the precise control of macromolecular structures toward tough bioplastics and elastomers.

SERMACS 29

Enzymatic ring-opening polymerization of ε-caprolactone: Effect of organic solvents and ionic liquids

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Aliphatic polyesters including polylactones and their derivatives play a crucial role in biodegradable materials. These biodegradable polyesters are thermoplastic, renewable and biocompatible polymers with mechanical properties that are comparable with those of polystyrene or polyethylene terephthalate (PET or PETE). Although a few lactones are naturally occurring as saturated or unsaturated γ- and δ-lactones, most lactones are synthesized; for example, ε-caprolactone is produced from the oxidation of cyclohexanone by peracetic acid. Conventional methods for preparing polylactones, such as direct polycondensation, azeotropic condensation, solid state polymerization, and ring-opening polymerization (ROP) using metal or organic catalysts, suffer from different drawbacks. Enzymatic ROP reaction is becoming a benign approach to the production of polylactones. Our group carried out the polymerization of ε-caprolactone catalyzed by immobilized *Candida antarctica* lipase B at 70 °C, and found that different organic solvents and ionic liquids showed considerable impact on the polymerization outcomes. Poly(ε-caprolactone) can be synthesized with high molecular mass ($M_w > 20\ 000$ Da), relatively low polydispersity index (PDI < 1.8), and moderately high yield (up to 60%).

SERMACS 30

Polymeric memory resistive devices from poly(*N*-alkyl methacrylate)s as an artificial synapse

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Memory devices based on organic materials are a promising alternative towards the next generation of nonvolatile nanoelectronics. Memory resistive devices, or memristors, are defined as any two-terminal electronic device that alters its conductivity based on its electric history. In this effort, a methacrylate polymer is derivatized with an electronically active carbazole moiety. Under an applied electric field, the carbazole group rearrange their alignment, thus facilitating easier electron carrier delocalization and charge transport through molecular conformational changes. By tuning the structure of the polymer, the chain flexibility and number of conductivity states can be further modified. The ability to have a multitude of conductivity states according to applied voltage makes the memristor a major candidate for emulating synapses in artificial neural networks – offering both high connectivity and the high density required for efficient computing. Memristors, with a simple sandwich device architecture of ITO/Poly(*n*-(9H-carbazol-9-yl)*n*-alkyl methacrylate)/Al, exhibit essential synaptic plasticity and learning behaviors, including short-term plasticity and spike-timing-dependent plasticity, through programmed waveforms inspired by neuronal action potential. Variations to length of side chains that attach the carbazole moiety to the polymer backbone were studied for their effects on the optical and electrical properties of these materials.

SERMACS 31

Thermo-mechanical, rheological, physical and chemical characterization of poly(lactic acid)/poly(hydroxybutyrate)/lignin coated cellulose nanocrystals nanocomposites prepared by high torque melt mixing

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Poly(hydroxybutyrate) (PHB)/poly(lactic acid) (PLA) blends have previously been studied as environmentally friendly options to replace petroleum based plastics for certain applications. PLA and PHB are both semi-crystalline polyester thermoplastics. We have found that incorporation of lignin coated cellulose nanocrystals (L-CNCs) in various grades of PLA and by high torque melt mixing leads to improved mechanical properties. We have prepared various PLA/PHB polymer blend ratios and incorporated 0.2 wt % to 2 wt % loadings of L-CNCs in the nanocomposites. The thermal mechanical, rheological, physical, and chemical properties of new materials produced will be described. The results of this work will be reported.

SERMACS 32

Sonochemically functionalized boron nitride nanomaterials as reinforcement for aerogels

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Boron nitride nanomaterials (BNNTs) and hexagonal boron nitride platelets (h-BNs) have received considerable attention for composite and aerospace applications due to their exceptional properties. Likewise, polymer aerogels provide a great opportunity for use as aerospace insulation materials, but their practical use is limited. Boron nitride nanomaterials, if adequately stabilized in compatible solvents, can be used as reinforcement for aerogels, expanding their practical use. Aerogel matrix compatibilization of BN nanomaterials remains difficult as h-BN can be hydrophilic or hydrophobic depending on orientation, and due to chemical stability, BNNTs are difficult to covalently functionalize. To address these challenges, we present a novel sonochemical technique to covalently attach alkoxy and fluoroalkoxy substituents to the surface of BN nanomaterials. Attachment is confirmed via FT-IR, and the use of x-ray photoelectron spectroscopy (XPS). Solvent compatibility, particle size and stability in solution are evaluated using DLS and UV-Vis spectroscopy. Once the BNNTs have been functionalized, sol-gel polymerization is used to incorporate functionalized boron nitride nanomaterials (f-BNs) into the aerogel matrix as reinforcement materials. The resulting aerogel surface chemistry and pore structure are characterized by FT-IR, TEM, Nitrogen adsorption, and NMR.

SERMACS 33

Phase transferable polymer encapsulated metallic nanoparticles

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Polymer encapsulated nanoparticles (NPs) have potential applications in devices, biomedical nanotechnology, and catalysis. It is known that such particles retain their catalytic activity in solution as pseudo-homogeneous catalysts, effectively bridging homogeneous and heterogeneous catalysis. Here, a method to separate NP catalysts from a reaction mixture is demonstrated which involves making the encapsulating polymer phase transferable between immiscible organic and aqueous phases. Polyethyleneimine, a water soluble cationic polymer, was modified to be soluble in a water immiscible organic phase (hexane) via partial monoalkylation by reductive amination of terminal amines using aldehydes. The product has secondary amines which are protonatable to allow for shuttling between phases. Polyethyleneimine encapsulated Pt NPs were synthesized by chemical reduction and are phase transferable catalysts. These particles can catalyze both aqueous phase reactions (e.g. dehydrogenation of ammonia borane) and organic phase reactions (e.g. hydrogenation). The polymer encapsulated Pt NPs have been evaluated for activity, separation efficiency, and reuse in reactions in either phase.

SERMACS 34

Hydrophobic ligands influence the structure, stability, and processing of the major cockroach allergen Bla G 1

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Rational: The cockroach allergen Bla g 1 forms a novel fold featuring an exceptionally large 3758 Å^3 hydrophobic cavity enclosed by 12 amphipathic alpha-helices. This cavity allows Bla g 1 to bind a range of hydrophobic ligands. Given the ability of such ligands to enhance sensitization against numerous other allergens, understanding the structural basis of this interaction and its implications for Bla g 1 structure, stability, and processing could yield insights into the molecular determinants of allergenicity.

Methods: The effect of various fatty-acid, phospholipid, and lipotechchoic acid (LTA) cargoes on Bla g 1 structure and thermostability was assessed using circular dichroism coupled with solution-NMR, and molecular modeling, while proteolytic assays were used to probe for changes in its susceptibility to cleavage by the endosomal protease cathepsin S, a key player in the antigen processing pathway.

Results: Binding of fatty-acids enhanced the stability of Bla g 1. This effect was dependent on alkyl chain length, with longer-chain cargoes providing up to a ~20°C increase in melting temperature while simultaneously eliminating cathepsin cleavage. Phospholipid and LTA's provided similar enhancements to thermostability. However, the former yielded only a modest (0-2 fold) reduction in cathepsin proteolysis while the latter showed a strong dependence on the source organism, with more pathogenic species exerting a strongest (>2-fold) protective effect.

Conclusions: Binding of lipid cargoes can enhance the stability and proteolytic resistance of Bla g 1. We hypothesize that this hinders endosomal processing and antigen presentation, skewing the TH1/TH2 response to favor allergy.

SERMACS 35

Deciphering the biophysical effects of glycosylation on membrane proteins

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Glycoproteins play an important role in essentially every biological process and, as a result, can be linked to nearly every known disease. A better understanding of how glycosylation affects and regulates these proteins could help in the development of treatments aiming to control the progression of a number of diseases and aggressive cancers. The structural and dynamic characterization of membrane proteins that have been glycosylated can be an incredibly useful step toward understanding how they are modified in human cells. By using model peptides and recombinantly expressed glycoproteins we will make membrane-like samples to be studied by Mass Spectroscopy and Nuclear Magnetic Resonance (NMR) Spectroscopy. Mass Spec has used to confirm glycosylation of proteins in a lipid environment and provide a constrained template for refinement using NMR data. As we have shown previously, NMR is a powerful technique for determining the high-resolution structure and dynamics of membrane proteins, as recent developments in the field allow us to look at these proteins in environments that resemble membrane bilayers.

SERMACS 36

Novel peptide protects mitochondrial structure-function: Implications for cationic, lipophilic peptides as endogenous assembly factor mimetics

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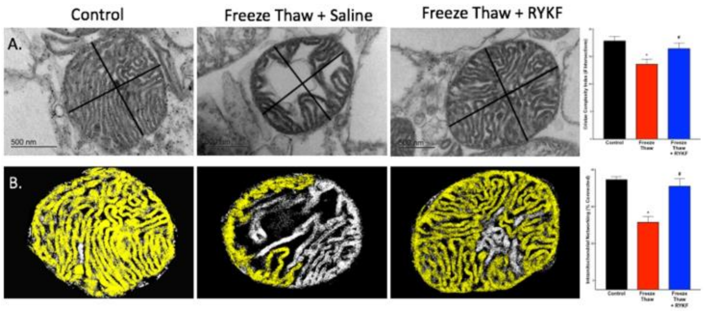
Mitochondrial structure and function are inextricably linked, with decrements in structure-function noted across diseases. Alternating cationic, lipophilic motifs are known to stabilize mitochondrial protein assembly, and are a shared feature of many mitochondria-targeted peptides. In this study, we determined if a new peptide, RYKF, restored mitochondrial structure-function in pathological mitochondria. We then complemented these studies with biomimetic mitochondrial membrane models to test RYKF-cardiolipin interactions. Vector-mediated RYKF expression in C2C12 myoblasts significantly improved maximal mitochondrial respiration after a metabolic stressor. In contrast, exogenous RYKF peptide treatment did not protect maximal respiration from peroxide injury. Transmission electron microscopy was employed to study isolated mitochondria from rat left ventricle treated with RYKF after a freeze thaw injury. Decrements in cristae complexity and mitochondrial networks were observed with injury, and RYKF pre-treatment significantly improved these morphological deficits. Synthetic lipid membranes were constructed to model healthy and diseased inner mitochondrial membranes and test for RYKF-cardiolipin interactions. Confocal imaging of lipid membranes suggested RYKF aggregates cardiolipin. In diseased membranes containing 25% less cardiolipin, RYKF restored the biophysical integrity of the membranes toward the healthy control. These data suggest RYKF may be aggregating CL-containing membranes, and in turn, mimicking an endogenous mitochondrial assembly factor that stabilizes cristae ultrastructure and bioenergetic function. Mitochondria-targeted peptides represent a promising therapeutic approach to treat diseases characterized by mitochondrial dysmorphology.



TEM images of mitochondria illustrating the effects of RYKF on mitochondrial structure. (A) Mitochondria were analyzed for cristae complexity by counting the number of cristae intersections along the horizontal and vertical axes. (B) Intramitochondrial networking was calculated using the yellow flood fill tool. *, P

SERMACS 37

VGSC blockers with cell invasion inhibitory activity in breast cancer cells

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Currently, there is no therapeutic strategy for metastasis and current treatments rarely lead to long-term survival of patients without disease recurrence. Hence, there is an immediate need to develop new drugs for the treatment of metastasis. Our increased understanding of the metastatic process has resulted in the discovery of several potential drug targets to prevent metastasis. One such target is the voltage-gated sodium channel (VGSC). VGSCs are well-established drug targets for anti-epileptic, anti-arrhythmic and pain medications due to the crucial role the play in cellular excitability. Recently, VGSC expression has been recognized in non-excitable cancer cells and their over-expression has been associated with cell invasion properties in a variety of human cancers. For example, the neonatal isoform of the VGSC subtype Na$_V$1.5 subtype (nNa$_V$1.5) is over-expressed in human breast cancer and its activity has been associated with metastasis and poor patient prognosis. We have discovered a number of small organic molecule blockers of this channel in MDA-MB-231 breast cancer cells and shown that they inhibited the invasion of these cells at low micromolar concentrations. Design, synthesis and biological evaluation of these compounds will be presented.

SERMACS 38

Peripheral protein unfolding drives membrane bending

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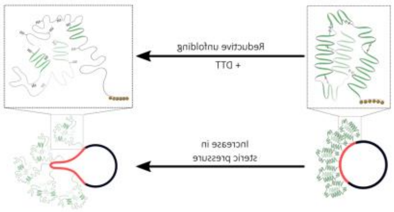
Generation of membrane curvature is essential to cell function. Important cellular processes, such as cell signaling, vesicle trafficking, membrane fusion, endocytosis, and many others depend on protein structural dynamics at the membrane interface and coupled membrane responses. Modulation of lipid membrane curvature can be achieved by a number of peripheral protein binding mechanisms such as hydrophobic insertion of amphipathic helices and membrane scaffolding. Recently, an alternative mechanism was proposed in which crowding of peripherally bound proteins induces membrane curvature through steric pressure generated by lateral collisions. This effect was enhanced using intrinsically disordered proteins that possess high hydrodynamic radii, prompting us to explore whether membrane bending can be triggered by the folding–unfolding transition of surface-bound proteins. We utilized histidine-tagged human serum albumin bound to Ni-NTA-DGS containing liposomes as our model system to test this hypothesis. We found that reduction of disulfide bonds in the protein resulted in HSA unfolding, which subsequently led to membrane tubule formation, indicated generation of membrane curvature. The frequency of tubule formation was found to be significantly higher when the proteins were unfolded while being localized to a phase-separated domain as opposed to randomly distributed in fluid phase liposomes, indicating that the steric pressure generated from protein unfolding can drive membrane deformation. Our results are critical for the design of peripheral membrane protein-immobilization strategies and open new avenues for exploring mechanisms of membrane bending driven by conformational changes of peripheral membrane proteins.



SERMACS 39

Uncovering the many roles of Stk1 in MRSA virulence and resistance gene regulation

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The *S. aureus* regulatory kinase Stk1 is a master regulator of virulence gene expression. Stk1 is a **p**enicillin binding protein **a**nd **s**erine/**t**hreonine **a**ssociated (PASTA) kinase that senses changes in cell wall homeostasis through the extracellular penicillin binding domain and phosphorylates substrates that control downstream gene transcription. In virulent and antibiotic resistant strains, Stk1 also controls genes involved in antibiotic resistance, biofilm formation, and toxin expression. Inhibition of Stk1 *in vitro* potentiates methicillin-resistant *S. aureus* (MRSA) to β-lactam antibiotics and inhibits biofilm formation, making it an attractive target for the development of novel antibiotic adjuvant and antibiofilm therapies. In an effort to more fully understand the roles Stk1 plays in MRSA gene regulation, we used small molecule Stk1 inhibitors as chemical probes to explore how Stk1 functions under medically relevant conditions such as biofilm formation and antibiotic treatment. Our results revealed interesting strain-specific differences in the genes regulated by Stk1, despite having similar phenotypic responses to treatment with these probes. Our results and a working model of the role of Stk1 in MRSA gene regulation will be presented.

SERMACS 40

Concept for a cell-based biosensor for early Alzheimer's disease detection

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Alzheimer's disease (AD), a neurodegenerative disease characterized by progressive cognitive decline, is a leading cause of dementia in people over the age of sixty. Evidence has shown that an earlier diagnosis leads to more effective treatment, in part as a result of the irreversible death of neurons. However, a cost-effective method for early diagnosis does not exist. The 2019 Alzheimer's Facts and Figures Report states if an early diagnostic tool became available, $7.9 trillion is the estimated potential cost savings for the current US population. In addition to neuronal death, accumulation of amyloid plaques comprised of aggregated amyloid-β protein (Aβ) and breakdown of the blood brain barrier (BBB) characterize AD. The BBB is formed by a tight monolayer of endothelial cells, which is characterized by tight junctions, the absence of openings, and few pinocytotic vesicles. These characteristics render high transendothelial electrical resistance (TEER). AD-associated breakdown of the BBB is correlated with vascular Aβ deposition, suggesting that pathological Aβ can modulate TEER. This research considers how this physiological response might be leveraged for early disease detection.

Primary human brain microvascular endothelial cells (HBMVECs) were cultured on a suspended membrane to mimic the BBB. Once TEER values reflected physiological conditions, HBMVECs were treated with varying Aβ aggregation states, and TEER measurements were monitored over time. Treated HBMVECs were also stained and imaged to observe localization of tight junction proteins. Oligomeric Aβ, but not Aβ monomer or fibril, induced a reduction of TEER and movement of tight junction proteins away from cell borders. These results demonstrate that Aβ oligomers, the proposed pathogenic species in AD, are uniquely responsible for inducing endothelial monolayer permeability. This data provides a conceptual basis for the design of a cell-based biosensor for early AD detection that leverages selective BBB breakdown by pathogenic forms of Aβ.

Future work will translate this experimental system to a cell-based biosensor platform capable of detecting the presence of Aβ oligomers. Investigations will entail identifying the lowest Aβ oligomer concentrations which affect TEER measurements to establish sensor sensitivity. Our project lays the groundwork for the development of cost-effective, early AD detection.

SERMACS 41

Crystallographic and analytical characterization of an enzyme catalyzed transformation of a conjugated polymer

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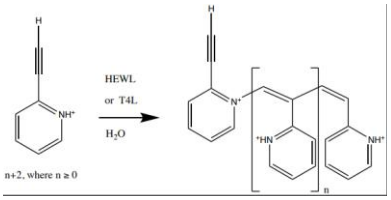
Hen egg white lysozyme's (HEWL) natural role is as a peptidoglycan hydrolase. However, this enzyme has been observed to mediate polymerization of 2-ethynylpyridine, which is the first example of hydrolase-meditated formation of a conjugated polymer. Proteins are favorable in polymer synthesis because some can be easily acquired from biological sources and renewably produced. This project is an integration of biochemistry and material science that will guide green chemistry in the use of biological catalysts in polymer formation as opposed to metal catalysts, which produce harsh organic wastes. The three primary aims of this project are first to identify the structure of the reaction products by LC-MS, NMR, and IR. Next is to obtain crystal structures of the ligand-enzyme complex and purified products. crystal structures of protein grown with 2EP-polymer and inhibitors of polymerization will be presented. The final aim is to determine the product structure of the HEWL reaction with different monomers. This information will impact future 2-EP polymerization by providing a reference point so that other hydrolase polymerization products may be predicted. This work will broaden green chemistry's understanding of enzyme function in polymerization and how they may be used by industrial chemists to eliminate current methods, which produce harsh organic waste.



SERMACS 42

Micro-technique isolation of insect binding proteins as an antibody assay source

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Micro-techniques were used in the isolation of binding proteins from *Manduca sexta*. These low-cost biochemical procedures may serve as a possible replacement for mammalian antibody production used in analytical assays or antibody technologies.

SERMACS 43

Photodynamic inactivation of antibiotic-resistant bacterial strains using lignin-photosensitizer conjugates

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The transmission of pathogens from improperly sterilized surfaces poses an escalating risk to human health. Towards our overall objective of developing potent antimicrobial materials to combat this threat, we have focused on photoactive materials in which photosensitizers have been tethered or embedded to renewable polymer scaffolds. As one such example, here we have covalently appended thionine, a phenothiazine-based photosensitizer, to lignin using a cyanuric chloride coupling strategy. While lignin is the second most abundant renewable biopolymer, with millions of tons of lignin produced by the paper industry as a waste or byproduct annually, its use as a platform for antimicrobial materials has been limited given its heterogeneous structure. The resultant lignin-thionine conjugate was characterized by a number of physical and spectroscopic methods, including diffuse-reflectance UV-visible spectroscopy that demonstrated the absorption properties of the material, thermogravimetric analysis (TGA) that showed an increase in the thermostability of the lignin-thionine conjugate compared to pure lignin, and elemental analysis that demonstrated a photosensitizer loading of 72 nmol thionine/mg material. The lignin-thionine conjugate was found to be highly effective in mediating the antimicrobial photodynamic inactivation of bacteria, achieving a 5 log unit inactivation of Gram-positive methicillin-resistant *Staphylococcus aureus* and vancomycin-resistant *Enterococcus faecium* upon illumination (60 min; 400–700 nm, 100 ± 5 mW/cm^2), and a 6 log unit reduction against Gram-negative multidrug-resistant *Acinetobacter baumannii*. Photodynamic inactivation studies against viral pathogens will also be presented. Taken together, these results demonstrate the utility of lignin as the polymer backbone of photodynamic materials for use against microbial pathogens.

SERMACS 44

Molecular tetravalent lanthanide complexes

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My group has developed a new class of bulky imidophosphorane ligands. The coordination chemistry and spectroscopy of lanthanide complexes supported by these ligands will be presented focusing on the design, isolation, and characterization of a molecular tetravalent terbium complex. These studies will serve as a reference point for work-in-progress on the coordination chemistry and reactivity of the early actinides, thorium and uranium, supported by this ligand class.

SERMACS 45

Thermodynamics and stability studies of actinide-based metal-organic frameworks

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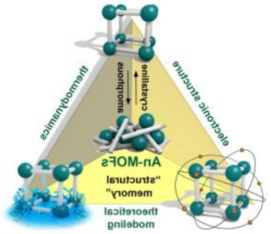
The devastating effects of nuclear waste spill in the environment have prompted ongoing investigations for more comprehensive and desirable nuclear waste administration techniques. Metal-organic frameworks (MOFs), which are well-defined and porous hybrid materials constructed from organic linkers and inorganic building units, have been demonstrated to be practically applicable in areas such as heterogenous catalysis, gas adsorption and separation, and very recently, nuclear waste administration. However, for effective nuclear waste management, structural stability and dynamism, as well as electronic structures of actinide-containing architectures should be extensively studied. Current research on MOFs have revealed their potential application as novel waste forms due to their porosity, modularity, tunability, crystallinity, flexibility, and long-term stability.

In this talk, I will focus on: (i) thermochemical and electronic structure studies of actinide-containing heterometallic MOFs, (ii) mechanistic insights into "capping linker" installation in An-MOFs, and (iii) unique long-term stability of actinide-containing MOFs. We envision that this work will reveal fundamental knowledge for the development of novel hierarchical forms for effective actinide detection and sequestration.



An overview of the thermodynamics, electronic structure, and "structural memory" effect of An-MOFs

SERMACS 46

Catch-and-release trivalent americium oxidation electrocatalysis using a ligand-modified electrode

Matthew V. Sheridan[1], Jeffrey R. McLachlan[1], Alejandro Hernandez[1], Johan R. Gonzalez-Moya[1], Travis S. Grimes[2], ***Christopher Dares***[1], *cdares@fiu.edu. (1) Chemistry and Biochemistry, Florida International University, Miami, Florida, United States (2) Aqueous Separations & Radiochemistry, Idaho National Laboratory, Idaho Falls, Idaho, United States*

Access to high valent actinides has the possibility of facilitating closing the nuclear fuel cycle by enabling the separation of U, Np, Pu, and Am from the fission products. The key holdout in this regard is the generation of Am(VI) which is challenging due to the high one-electron oxidation potential for Am^{3+} ($E(Am^{IV/III})$ = 2.62 V vs. SCE). A variety of efforts made to effect this oxidation, including the development of chemical oxidants such as bismuthate, persulfate, more recently – periodate, and other exotic oxidants including noble-gas oxidants. Recently, we developed a Ligand Modified Electrode (LME) electrochemical approach, which involves derivatizing the surface of electrodes with ligands that bind Am^{3+}, and adjust the electrochemical potential required for oxidation to $Am^{V}O_2^{+}$ and $Am^{VI}O_2^{2+}$. This has included the use of organic ligands covalently attached to surfaces, as well as lacunary polyoxometalates. These LMEs have successfully generated a mixture of $Am^{V}O_2^{+}$ and $Am^{VI}O_2^{2+}$ at potentials as low as 1.8 V. Unfortunately, attempts to quantitatively generate $Am^{VI}O_2^{2+}$ have failed with these LMEs.
We present here, a new set of LMEs which quantitatively convert Am(III) to $Am^{VI}O_2^{2+}$ at 1.9 V. The electrochemistry of these LMEs provide insights into the nature of the interaction between the ligand and americium in a variety of oxidation states. We envision that others may be able to take advantage of this work to perform studies involving $Am^{VI}O_2^{2+}$.

SERMACS 47

Preparation of novel complex uranium oxides via exploratory crystal growth methods

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Considerable research efforts have focused on creating and characterizing new materials suitable for nuclear waste storage applications. While borosilicate glasses have been found to be a suitable matrix for the majority of chemical components in nuclear waste streams, minor problematic species present in the waste which are prone to unfavorable processes such as volatilization and partial crystallization must be handled differently. To investigate viable alternatives, we have utilized exploratory crystal growth methods including high temperature flux and hydrothermal synthesis to prepare hierarchical materials conducive to the sequestration of radionuclides.

This presentation will focus on the exploratory crystal growth of novel complex uranium oxides exhibiting three-dimensional framework structures, and the existing structure-property relationships will be emphasized. Among those to be discussed, the hydrothermal synthesis of the first uranium borosilicate will be presented, and, in addition to our group's research on uranium salt-inclusion materials, efforts to extend these systems to incorporate heavier actinides such as neptunium and plutonium will be highlighted.

SERMACS 48

Tailoring redox active ligands for probing the reactivity of actinides

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Increasing percentage of power generation derived from nuclear fuels is one means to address the demands of our highly energy dependent society while still reducing global dependence on fossil fuels. The potential for detrimental environmental effects from contamination due to a spill or radiological event limits public acceptance of the use of 5f elements, the actinides. Because of this, we have been interested in the unique properties of the actinides, their coordination behavior, and distinctions that can be made between the 5f actinides and the 4f lanthanides or transition metals in the development of selective means for sensors or extractions. New materials are required that can coordinate, sense, and isolate actinides. Here, we introduce a new series of ligands called pyrrophens – an open pyrrolic macroacyclic system that is capable of hexadentate binding of U(VI) as the uranyl (UO_2^{2+}) ion species. The interaction of the pyrrophen with uranyl in solution a stable hexagonal bipyramidal complex with all of the equatorial coordination sites fulfilled by the ligand interactions and no coordination from solvent. We compare coordination behavior with that of first row transition metals and look at structure and selectivity. Research in this area will allow us address probative questions about the nature of actinide bonding, the validity of models for the actinides, hard-soft interactions, and interactions between metals in bimetallic complexes.

SERMACS 49

“Soft spot” for uranyl: Derivatization of a soft-donor hexadentate ligand for UO_2^{2+} recognition

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The development of oxo-donor ligands for the selective sensing and extraction of uranyl has been studied for its applications in nuclear waste remediation. The highly Lewis-acidic nature of UO_2^{2+} predispose it to favorable interactions with such ligands. We have previously characterized salen-type systems, which are synthetically available and somewhat tunable, but their utility can be hindered by competition from other metal ions, in particular Cu^{2+}. Soft-donor frameworks, with the exception of expanded-porphyrin macrocycles, remain largely underutilized in this respect. While pyrrole-based systems have been somewhat successful, they are limited by their challenging syntheses and slow binding kinetics. We have recently reported a new macro*a*cyclic ligand system, “pyrrophen” which borrows the large, soft-donor pocket from expanded porphyrins, and the synthetic route of simple salens. These ligands feature imine, pyrrole, and ester donor atoms which effectively satisfy the equatorial plane of uranyl; however, two ligands are required to satisfy the coordination sphere of transition metal ions such as $Cu^{2+}$and Zn^{2+}, leading to the formation of M_2L_2 helicates resulting in a colorimetric response distinct from that of uranyl. Additionally, pyrrophen preferentially binds uranyl over other ions, and shows no affinity for Ln^{3+} species. Here, we exploit the modularity of this ligand system and preferred binding geometries of metal cations to explore the effects of structural and electronic changes to the ligand architecture.

SERMACS 50

Tripodal CMPO ligands for selective f-element extraction

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The increasing use of rare earth elements in modern high-tech devices has encouraged the development of efficient *f*-element extraction methods in recent years. The ability to selectively bind and extract lanthanide (Ln) and, in the case of raw source processing, certain actinide (An) metals remains an important goal as new applications emerge. Our group has been examining ligand systems for such *f*-element extraction and separations based on the carbamoylmethylphosphine oxide (CMPO) chelator that is well documented for its application in the TRUEX process for nuclear waste remediation. We have developed several classes of ligands that tether three CMPO units to a central capping scaffold. This approach creates tripodal ligands that are pre-organized for metal binding, and the modular syntheses allow for straightforward variation of the ligand cap and CMPO substituents for further tuning of the molecular architecture. Upon identifying promising ligands for selective lanthanide or actinide extraction, more recent efforts have been focused on variation of the extraction protocol (e.g., varying ligand concentration and mixing times). This presentation will highlight some of the recent results from these studies, including an observed increase in Ln extraction upon decreasing mixing times from 20 to 1 hour for a trialkylphosphine oxide capped CMPO ligand. Finally, the observation of enhanced thorium(IV) extraction relative to Lns will be detailed for another CMPO agent based on a longer, more flexible alkyl amine cap that appears well-suited to encapsulate the charge dense actinide ion.

SERMACS 51

Incorporation of new secondary building units into uranium framework materials by flux crystal growth

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Actinide chemistry attracts attention in the scientific community due to its importance in understanding and developing separation and disposal of nuclear waste, as well as preventing migration of radionuclides in the environment. Many known classes of inorganic materials have been proposed as nuclear waste-storage materials, particularly mineral based ones due to their stability in harsh natural environments; however, no universal storage material has been found so far and the important task to develop and evaluate new candidates for waste-storage remains. By using exploratory crystal growth, the number of known actinide materials can be increased, and with it our understanding of uranium coordination chemistry which will aid in the design of the next nuclear waste form. For nuclear waste storage applications, porous 3D structures are promising and can lead to higher density storage of several different types of radionuclides; however, the tendency to form 2D sheets in U(VI) containing materials arises from the preference of the uranyl ion to bond through the equatorial oxygens rather than the strongly bonded axial oxygens. In order to obtain 3D structures using U(VI) building blocks, it is advantageous to introduce secondary building blocks such as oxyanions, including silicates and phosphates, that can help overcome the tendency of U(VI) to form 2D sheet structures. While U(VI) silicates and phosphates are plentiful, both naturally occurring and synthetically obtained, other similar tetrahedral building units such as germanates and aluminates are under explored. This seminar will focus on the molten flux synthesis, structure, and ion-exchange properties of new U(VI) materials that contain oxyanions such as silicates aluminates, gallates, and aluminophosphates

SERMACS 52

Tridenate and tetradentate N-donor extractants for minor actinide separations

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Considerable effort over several decades has been focused on development of neutral N-donor extractants for minor actinide solvent extraction and separation from trivalent lanthanides. In particular, the group actinide extraction concept has heralded the possibility of simplified separation schemes, with neutral solvation as the central mechanism. Candidate compounds have arisen from bis-trazinyl-substituted pyridines, bipyridines and phenanthrolines. The advantages of a single highly selective neutral extractant is the ease by which the separations can be rendered through simple acid swings to control solvation complexation and minimize the components in a system. However, several challenges must be faced to realize their utility. These include low solubility of polyaromatic structures, hydrolytic and radiolytic stability, the balance between N-donor basicity and acid competition, and related low capacity and extraction efficiencies using a minimally modified solvent phase.

With these challenges in mind, this project is focused on the design, synthesis and characterization of new N-donor compounds. The synthetic approach is to develop convergent methods for both symmetric and non-symmetric tridentate and tetradentate structures. This talk will focus on the efforts of the radioanalytical laboratory. Screening of compounds for relevant solvent solubility, solution stability, and Am/Eu extraction efficiency/selectivity is benchmarked by the tridentate compound 3,3'-dimethoxy-phenyl-bis-1,2,4-triazinyl-2,6-pyridine (MOB-BTP), which was previously reported. Selected candidates undergo more systematic characterization to understand their extraction/complexation equilibria and kinetics using, slope analysis from radiotracer experiments and spectroscopic evaluation. Preliminary results indicate that minor changes, such as a 3,3'- to 4,4'-substitution of distal phenyl rings results in drastically diminished solubility and decreased Am/Eu separation factors on account of higher Eu(III) extractability. Evaluation of N-donor relative basicity, along with extractant and acid dependencies will provide data to model phase transfer reactions. Optical spectroscopy is employed to estimate stability constants and interpret interactions in the first coordination sphere.

SERMACS 53

Large area airborne contamination monitoring

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Current decontamination and decommissioning operations at Hanford have demonstrated a flaw in the current state-of-the-art capability of defining airborne contamination boundaries. Airborne particulate emissions of Pu-239 from these operations on the Hanford Pu Finishing Plant were detected well beyond areas controlled for airborne Pu, putting numerous workers at risk for radiological assimilations. Forty-two Hanford workers had positive bioassay results for plutonium uptake. Work areas determined to be free of airborne contamination as measured by state-of-the art continuous alpha monitoring (CAM) systems were later discovered to be contaminated. Airborne contamination was scattered to such a degree that CAM systems were surveying insufficient volumes of air to accurately predict where respiratory protection was required. The state-of-the art portable CAM system used at both Hanford and at SRS screens air for alpha activity at the rate of 1 CFM. This research has explored the feasibility of using commercially available air purifying systems to screen significantly larger volumes of air (300 CFM) for airborne actinide contamination at

significantly lower cost. A detection system has been designed and built to screen the air purifier system pre-filters and HEPA filters for any actinide bearing particles that have been captured. The detection system is based primarily on x-ray/low energy gamma ray spectrometers, because actinides typically have higher x-ray vs gamma emissions. Sensitivities have been compared to conventional screening by alpha spectrometry.

SERMACS 54

Complexation thermodynamics between cyclodextrins and fatty acids

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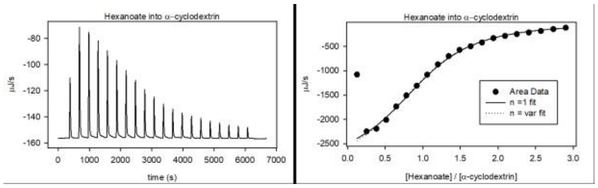
Cyclodextrins (CD) are a family of compounds made up of sugar molecules bound together in a ring. Cyclodextrins can self-assemble with fatty acids in aqueous solutions. These processes have relevance in food science and technology, e.g. for the encapsulation and delivery of lipid-soluble nutrients and additives. To study the driving forces behind this self-assembly process, we are using isothermal titration calorimetry (ITC) to determine the thermodynamic parameters of this reaction.

Our purpose is to correlate the affinity trends observed in a series of fatty acids of varying size with the structures of these acids, with the cavity size of the cyclodextrin hosts, and with the properties of the aqueous solvent. We conduct these studies using unmodified α-CD, β-CD and γ-CD to combine with different carboxylic acids in Tris buffer (10 mM, pH=7.4, water solution). We will report on results obtained with hexanoate and octanoate anions, used here as soluble models for fatty acids. According to our results, their affinity largely depends on their fit to the cavity size of the host and their hydrophobicity. The stoichiometry of these interactions is typically 1:1; however, guests with longer hydrophobic tails give rise to more complex interactions, including e.g. 1:2 guest:cyclodextrin combinations.



SERMACS 55

Synthesis and antimicrobial activity of *n,n'*-bis-substituted triazolium salts with lipophilic substituents on 1,2,3- and 1,2,4-triazole rings

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Triazoles have been researched extensively for their medicinal properties as a scaffold for their investigation as potential drug therapeutics. However, N,N-bis substituted triazolium salts, a class of compounds derived from triazole systems, have yet to be investigated for their structure-activity relationship (SAR) between substituents and antimicrobial activities. Azoles that are similar in structure, such as imidazolium and benzimidazolium salt compounds, have been extensively utilized, due to their promising biological activities. The non-water soluble nature of imidazolium and benzimidazolium compounds has substantially decreased their viability in the clinical atmosphere. The SAR of a substituted class of triazolium-based compounds has corroborated the claim that triazole rings would provide the greatest water solubility. To further the understanding of triazolium salts as antimicrobial agents, we present a structure-activity relationship (SAR) focued on N,N-bis substituted triazolium salts, which were synthesized from 1,2,3- and 1,2,4-triazole rings.

SERMACS 56

Identification and development of antifungal peptoids

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A comparative lack of clinical antifungals are available to those dealing with deadly fungal infections and those that are available are wrought with toxicity issues. In an effort to expand the antifungal arsenal, our lab has developed a high-throughput phenotypic assay to identify peptoids with antifungal activity. Specifically, we have identified lead compounds effective against *Cryptococcus neoformans* and *Candida albicans*. The detailed characterization of a compound with good efficacy against *C. neoformans*, including potency, cytotoxicity, and *in vivo* characteristics will be discussed, as will our efforts to improve upon this lead compound through modular structure activity relationship studies.

SERMACS 57

Evaluation of peptoid derivatives of ultra short antifungal peptides

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Candia albicans is the most prevalent nosocomial infection with a high mortality and morbidity rate in immunocompromised patients as well as 40-60% mortality rate in healthy individuals if infection spreads to the blood stream. Depending on the environment, *C. albicans* can switch their morphology from budding yeast to hyphae that form biofilms. These biofilms can proliferate on either mucus membranes or plastic surfaces such as catheters or prosthetics making the yeast more resistant to host defenses such as antimicrobial peptides as well as antibiotics. With the rise in antimicrobial resistance, the need for more effective and stable drugs are a must. A series of ultra-short peptides with varying degrees of potency against *C. albicans* has been reported, however, peptides make poor drugs due to short half-lives resulting from protease degradation. Peptoids, N-substituted glycine, have improved half-life, bioavailability, and are protolytically stable while retaining many of the same characteristics of peptides such as diverse functional side chains, similar mechanism of action, and facile synthesis. A series of peptoid mimics of anti-*Candida* peptides have been synthesized. The therapeutic properties of these peptoids will be discussed, including the antifungal and antibacterial efficacy, the mammalian cytotoxicity, and the hemolytic activity.

SERMACS 58

Design, synthesis and biological evaluation of some novel oxazolidinone derivatives as potential anti-mycobacterial and antibacterial agents

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ITB disease which is one of the leading causes of globally infectious diseases deaths by pulmonary infection, is caused by a bacterial pathogen *Mycobacterium tuberculosis*. Although many therapeutic agents were developed for tuberculosis and non-tuberculosis mycobacterial infections, no standard treatment protocol was approved due to their natural multi-drug resistance.

Linezolid can be considered as the first member of the class of oxazolidinone antibiotics and linezolid-containing regimens have been suggested as a promising potential alternative to treat patients with multidrug-resistant tuberculosis (MDR-TB) or extensively drug-resistant TB (XDR-TB) by inhibiting bacterial protein synthesis through binding to rRNA.

In the present research work, a series of novel de-acetyl linezolid-amino acid conjugates were synthesized using benzotriazole chemistry. Drug-amino acid conjugates are used because of increased tissue delivery, in which the amino acids act as pro-drugs or effective carriers of these agents while maintaining and even amplifying their bioactive integrity. Amino acid conjugates can increase the bioavailability and quantitatively decrease the required amount of active drug thus preventing toxic undesired side effects.

All the synthesized compounds were fully characterized by NMR, IR, and HRMs and these synthetic specimens are currently undergoing further testing to evaluate their biological activity.

SERMACS 59

Synthesis approaches 4,6-diaryl- and 4,8-diarylquinoline-methylcarboxylate scaffolds as inhibitors of the HIV-1 integrase in enzyme

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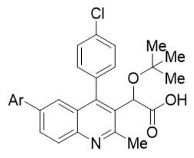
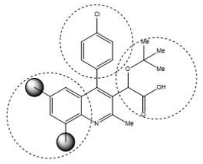
AIDS, an often fatal disease in humans is caused by the fast spreading immunodeficiency virus (HIV), was first discovered in 1981. Currently, Highly Active Anti-Retroviral Therapy (HAART) is an effective treatment method which employs several drugs in combination to target the various steps of the HIV replication cycle. However, it is not well-tolerated in patients due to the harsh side effects. This has led to the study of integrase (IN) inhibitors. HIV-1 IN not only catalyzes the insertion of viral DNA into the genome of a human cell, but studies have shown, through allosteric HIV-IN inhibitors, it also interacts with high affinity with viral RNA and binds the viral genome in virions.

The current goal is to design a set of compounds with a unique structure that have higher affinity and specification for HIV-1 IN enzyme. LEDGF/P75 binding of these molecules will also be examined to confirm their selectivity for integrase multimerization. Synthetic approaches to 4,6-diaryl- and 4,8-diarylquinolines-3-methylcarboxylates will be investigated as viable inhibitors for the HIV-1 IN enzyme. Our newly synthesis compounds would be sent and tested directly by our University of Southern Mississippi colleagues for their biological activities against HIV-1 IN. A highly selective allosteric inhibitor of HIV-1 IN would be a valuable chemical probe to investigate further the role of HIV-1 IN in biology and disease. We hypothesized that derivatives of this molecule with various (hetero)aryl groups may help to increase the affinity of the molecules to target HIV-IN binding site.





SERMACS 60

Uncouplers of oxidative phosphorylation as obesity therapeutics

***José A. Santiago-Rivera**, santiago.ja4@gmail.com. Chemistry, Virginia Tech, Blacksburg, Virginia, United States*

Obesity has become a serious health concern in the US as two thirds of the population are considered either overweight or obese. Targeting the mitochondria shows promise for the treatment of obesity and obesity-related diseases. ATP production takes place in the mitochondria with nutrient oxidation being coupled to oxidative phosphorylation. A small molecule capable of shuttling protons from the mitochondrial inner membrane space to the mitochondrial core, in favor of the electrochemical gradient of the proton motive force, can decouple nutrient oxidation to ATP production. This renders oxidative phosphorylation inefficient, requiring more nutrient oxidation. Previous small molecule mitochondrial uncouplers have shown weight-loss properties, but their benefits have been overshadowed by side effects resulting from poor selectivity towards the mitochondrial inner membrane. Recently, the discovery of mitochondrial uncoupler BAM15 opened a field for the study of compounds that lack off-target effects and exhibit a broader therapeutic window. Herein, an SAR study was conducted using imidazole-pyrazine derivatives as potential mitochondrial uncouplers. Compounds were initially screened using an oxygen consumption assay and results were obtained with compounds displaying favorable uncoupling capability and pharmacokinetic properties in mice. These discoveries provide a field for the treatment of obesity that can be further explored.

SERMACS 61

Mitochondrial uncouplers as disease therapeutics

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Mitochondria are responsible for the generation of ATP by coupling nutrient catabolism of dietary carbohydrates and fats with oxidative phosphorylation. Small molecules capable of shuttling protons from the mitochondrial inner membrane space to the mitochondrial matrix, known as mitochondrial uncouplers, make ATP production inefficient in that more nutrient oxidation is required. Uncouplers have shown promise in treating metabolic diseases such as obesity, type 2 diabetes, ischemia-reperfusion injury and neurodegenerative diseases. Small molecule uncouplers, such as 2,4-dinitrophenol, have been previously shown effective as weight loss agents, but they suffer from deleterious off-target effects and non-selective membrane depolarization limiting their therapeutic application.

A recently discovered compound, BAM15, has been shown to be a selective mitochondrial uncoupler ($EC_{50} = 0.27\ \mu M$) with a desirable therapeutic profile. A small molecule library was synthesized and an SAR study was conducted to investigate the protonophoric activity of BAM15, illuminating the importance of cLogP and pK_a in maintaining uncoupling activity. Compounds displaying favorable uncoupling activity were further evaluated for their pharmacokinetic properties ($t_{1/2,}$ %F) in mice. Our investigations resulted in compounds with desirable therapeutic profiles, making mitochondrial uncouplers a promising and underexplored approach to treating metabolic diseases.

SERMACS 62

Total synthesis and biological investigation of metal-binding natural products as bacterial inhibitors

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Antibacterial resistance represents an impending crisis, draining agricultural, industrial, and healthcare resources. Clinical antibiotics act on the same primary microbial targets and are decreasingly effective against multi-drug resistant pathogens. Thus, there is urgent need to develop antimicrobials with new mechanisms of action. One such strategy is the inhibition of virulence factors, molecules produced by the bacteria that confer the ability to infect the host. Our lab is specifically interested in investigating the antibacterial potential of metal-binding secondary metabolites (siderophores). We are currently engaged in the diverted total synthesis of three related thiazoline siderophore natural products and analogs thereof: the ulbactins, the watasemycins, and the thiazostatins. Previously we reported the first total synthesis of ulbactin F and *epi*-ulbactin F by mimicking the proposed biosynthetic pathway. We have since improved the diastereoselectivity, allowing for rapid synthesis of Ulbactin analogs. This diverted total synthesis strategy has been applied in parallel to the watasemycins and the thiazostatins to further elucidate antibacterial activity and structure-function relationships. The synthesis of these natural products and select analogs will allow for the continued characterization of their biological impact on pathogenic bacteria with the ultimate goal of developing virulence inhibitors as antibiotics.

SERMACS 63

Design, synthesis and antimicrobial evaluation of new fluoroquinolone-dichloroacetic acid conjugates as a potential DNA gyrase inhibitors

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Infectious diseases were the most common cause of human illness leading to death. Quinolones and fluoroquinolones are a class of synthetic, broad-spectrum antibiotics with potent bactericidal activity. The fluoroquinolones are indicated in the treatment of local and systemic diseases caused by a wide range of gram-positive and gram-negative. Because of its valuable pharmacological activities, fluoroquinolones have attracted a lot of attention in the field of medicinal chemistry.

In this project, we focus on the second-generation fluoroquinolone that inhibits DNA gyrase and topoisomerase IV. A series of new hybrid structures containing fluoroquinolone (ciprofloxacin and norfloxacin) and dichloroacetic acid were designed and synthesized. Synthesized analogs exhibited significant antibacterial properties and some of them were significantly more potent than the parent drugs against *E. coli* and *S. aureus* via in-vitro bioassay method.

SERMACS 64

pH responsive colloidal gold nanoparticle catalysts for recovery and reuse

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The distinct optical, electronic and catalytic properties of colloidal gold nanoparticles (AuNPs) which are not seen in bulk gold have made them an attractive research subject in the past few decades. Oxidation of alcohols, reduction of nitroarenes, hydrogenation of quinolone and carbon - carbon coupling reactions are the reactions catalyzed by AuNPs. The preference for supported catalysts in industry over colloidal catalysts is due to their usability in continuous reactors and simplicity in recovery through simple separation methods like centrifugation, sedimentation and filtration for reuse. In comparison, recovery of homogeneous catalysts is more complex. Colloidal catalysis is a potential intermediate that can take advantage of the reaction benefits of homogeneous catalysts but must employ catalyst recovery methods like temperature, magnetic, or pH induced aggregation, solvent extraction, etc. The proposed advantages of colloidal AuNPs over supported catalysts lie in improved catalytic activity, selectivity and milder reaction conditions with applications in chiral catalysis. To achieve this, the colloidal nanoparticles must be stabilized with ligands to retain dispersion and function as a catalysts. This causes surface passivation and reduces catalytic activity. We are exploring the effects of the organo-thiol stabilizing ligands on the catalytic activity of colloidal (AuNPs). Reduction of 4-nitrophenol to 4 -aminophenol with sodium borohydride ($NaBH_4$) as a reducing agent catalyzed by colloidal (AuNPs) is our model reaction. Effects of the chain length of ligands and surface coverage of nanoparticles on catalytic activity are studied. Studying the relationship between the molecular structure of the stabilizing agents and the surface coverage of the nanoparticles is vital for understanding the mechanism of the catalytic rate of colloidal (AuNPs) for redox reactions. The use of pH sensitive ligands for pH triggered recovery and reusability of colloidal (AuNPs) catalysts is also being studied.

SERMACS 65

Magnesium oxychloride formation kinetics and enhanced water stability for sustainable building materials applications

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Magnesium oxychloride (MOC) is a ceramic material with significant fire resistant properties and growing potential as a light-weight, structurally strong alternative building material. Despite many advantages, MOC has limitations as a construction material, particularly water stability. While researchers have explored solutions to these shortcomings, fundamental understanding of this material is still urgently needed. Thus we have investigated the fundamentals of the formation cure reaction and mechanisms of water stability enhancement reactions. The formation cure reaction kinetics for magnesium oxychloride 5-phase was monitored from 35 to 55°C using time-resolved quantitative x-ray diffraction and differential scanning calorimetry (DSC). The reaction was characterized as a two-step process: dissolution of magnesium oxide into a gel state followed by crystallization of magnesium oxychloride. Assuming first-order kinetics for both MgO dissolution and MOC crystallization, a kinetic model predicts 42.4 kJ/mol and 26.1 kJ/mol for dissolution and crystallization activation energies respectively. Alternatively, the Avrami nucleation and growth model was fit to DSC measurements predicting diffusion controlled, one-dimensional growth with an activation energy of 72.4 kJ/mol, accounting for both dissolution and crystallization.

For the water stability enhancement, two methods of water stability enhancement have been explored: chlorartinite formation from CO_2 exposure and phosphoric acid addition. The conversion of magnesium oxychloride to chlorartinite by CO_2 forms a protective, semi-insoluble chlorartinite layer on the surface of the magnesium oxychloride crystals, which improves water stability. Phosphoric acid (2.5 to 10 wt. %) was added to the MOC slurry before the cure reaction. Additions of 2.5 wt. % and above had positive impacts on the water stability, preserving ~50 wt. % crystalline MOC after the water stability test, but has a significant impact on the MOC formation kinetics. This is achied via. the formation of an amorphous phase on the MOC crystal surface that contains structural motifs related to insoluble MgHPO4×3H2O (newberyte) and Mg2P2O7×3.5H2O (magnesium pyrophosphate) phases. Results from this work are significantly impactful for the use of MOC in more sustainable alternatives for conventional materials in residential and commercial building applications.

SERMACS 66

Photoswitchable nanoparticle ligands to modulate and control catalytic reactivity

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Traditional ligand-passivated metal nanoparticles have demonstrated remarkable catalytic reactivity for a variety of reactions ranging from C-C coupling to hydrogenation. The reactivity arises from the metallic core of the material where the ligands are mainly required to ensure colloidal stability and prevent aggregation of the particles to the bulk. Most commonly, the ligands do not participate in the catalytic process beyond stabilization; however, the ligands present great potential in controlling the overall catalytic process. To achieve this capability, research in the Knecht group has focused on employed materials binding peptides with integrated azobenzene photoswitches, which provide for an optical handle to control the catalytic reactivity of the materials. In this regard, the peptides bind to the growing metal nanoparticles in solution, arresting their growth at sizes <5 nm. From this structure, the azobenzene photoswitch is in direct contact with the metallic surface. Upon optical activation, photoisomerization of the azobenzene occurs, resulting in a complete reconfiguration of the peptide overlayer structure, which can be readily reversed through isomerization of the photoswitch back to the initial state. As a result, two different ligand conformations can be reversibly achieved, presenting unique and different catalytic properties. This photoswitching event, and resultant catalytic properties, are controlled as a function of the peptide sequence, photoswitch positioning in the sequence, and metallic composition of the inorganic core. By having switchable control over the catalytic properties, this paves the way towards achieving remotely stimulated catalytic property control that could be harnessed to achieve on/off reactivity. Such capabilities could prove to be highly important for multistep reactions.

SERMACS 67

Nickel nanoparticles supported on multi-walled carbon nanotubes as an effective catalyst in Suzuki cross coupling reactions

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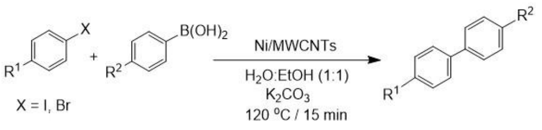
Nickel (Ni) nanoparticles supported on multi-walled carbon nanotubes (Ni/MWCNTs) were synthesized by mechanical grinding of a sample of nickel salt and MWCNTs using a ball-mill mixer. The preparation method allows for bulk production of Ni nanoparticles at room temperature without the necessity of any solvent or chemical reagent. The nanoparticles prepared by this method exhibit small particles size of 5-8 nm with uniform dispersion of Ni nanoparticles on the surface of multi-walled carbon nanotubes. The Ni/MWCNTs demonstrated remarkable catalytic activity for Suzuki cross coupling reactions of functionalized aryl halides and phenylboronic acids with excellent turnover number and turnover frequency (e.g. 72000 h^{-1}) using Monowave 50 conventional heating reactor at 120 ^{o}C within a very short reaction time of 15 minutes. The catalyst is air-stable and exhibits easy removal from the reaction mixture, recyclability with no loss of activity, and significantly better performance than the well-known commercial Pd/C catalyst. The Ni/MWCNTs nanoparticles were fully characterized by a variety of spectroscopic techniques including X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), and Scanning Electron Microscopy (SEM). Since nickel offers similar properties compared to other more expensive transition metals including the most widely used palladium counterpart in cross coupling catalysis, this work demonstrates a promising lower-cost, air-moisture stable, and efficient alternative catalyst based on Ni nanoparticles for cross coupling reactions.



SERMACS 68

Molecular/heterogeneous catalyst for the selective hydrodeoxygenation of oxygenated aromatics related to lignin biomass

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A molecular palladium complex was synthesized and attached to the surface of amorphous silicon dioxide to generate a molecular/heterogeneous catalyst motif. This catalytic system exhibited excellent selectivity (>99 %) for hydrodeoxygenation (HDO) of oxygenated aromatics under mild reaction conditions. HDO reactivity is an important aspect for the catalytic conversion of biomass to fuels and value-added chemicals. A kinetic analysis showed that this new molecular/heterogeneous catalyst is as kinetically active as metallic nanoparticle catalysts. Characterization techniques such as XRD and solid-state NMR, in conjunction with ICP-MS, indicate that the molecular catalyst is present on the surface of SiO_2 and the formation of unwanted metallic Pd nanoparticles can be avoided. Post reaction analysis confirmed prolonged molecular integrity of the catalyst and sustained binding of the catalyst to the oxide surface when nonpolar solvents were employed for reactions. These surface-attached molecular catalysts thus were recycled through multiple catalytic reactions.

SERMACS 69

Continuous flow system for the heterogeneous catalytic production of advanced biofuels

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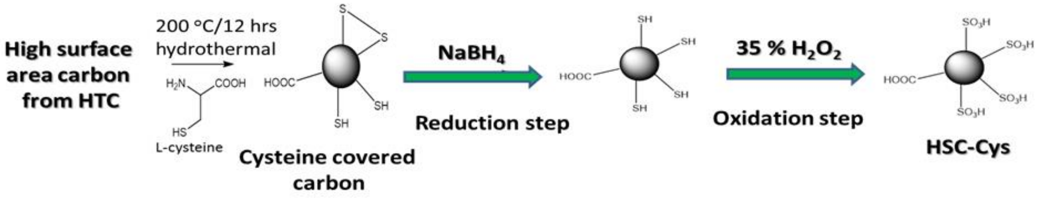
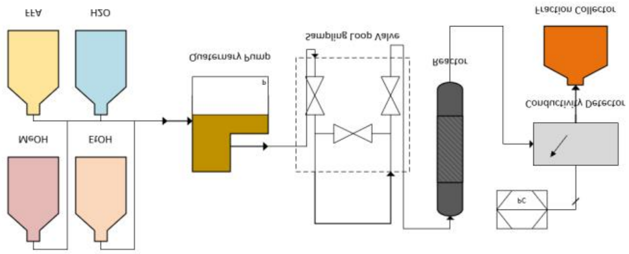
A continuous flow system was designed to incorporate high productivity and completely green chemistry for the creation of advanced biofuels. Sulfonated carbon catalyst was successfully prepared from hydrothermal carbonization of biomass (HTC) (Scheme 1). The HTC was converted to catalytically active carbon using a novel, environmentally benign process involving the use of L-cysteine followed by reduction with $NaBH_4$ or dithiothreitol (DTT) and oxidation with H_2O_2. The catalytic performance was first confirmed in a batch reaction system before continuous flow studies. The system reliably operates at relatively low temperatures (<120ºC) and pressures (<100 barr) to produce high quality biofuels from waste containing free fatty acids at conversions greater than 95% in 10% of the time required for traditional batch reactions. This enhanced performance appears to be the result of the creation of heterogeneous nanoparticles behaving in a homogeneous manner. Catalyst characterization, conversion chemistry, system performance and scale-up insights will be presented.





SERMACS 70

Plasmon drag effect pinning and molecule adsorption

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This talk will describe the recent progress in plasmon drag effect studies and the possible applications in chemistry. Recently, we have predicted that illumination of metals by light induces a new force on electrons – which we called the spin force. This force should result in pinning of the net plasmon-induced electromotive force to an atomically thin layer at the metal interface [Phys. Rev. B 96, 195411 (2017)]. Consequently, the plasmonic group at NIST conducted experiments that show that plasmon drag effect (light-induced current) is different in ambient air and in 10^{-3} Pa vacuum and depends on the molecules adsorbed at the metal interface [arXiv:1812.01673 (2018)], confirming our prediction about the plasmon drag pinning to the atomic layer at the metal interface.

SERMACS 71

High-impact undergraduate research experiences through the eyes of the undergraduate scholar

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Systematic data underscores the positive effects of undergraduate research experiences on learning and attitude towards a career in the sciences, as well as a variety of other personal and professional benefits. Here, I will discuss anecdotal evidence on these effects and present insights learned through my experiences in undergradaute research and mentorship programs such as the McNair Scholars Program, National Science Foundation Research Experiences for Undergraduates, industrial research internships, and the aspects of these programs which I found were the most impactful.

SERMACS 72

MAP (mentorship advancing to Ph.D.): Role mentorship played in a McNair program scholar's life

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This presentation will highlight the role mentorship played on a McNair Scholar's decision to pursue a Ph.D. As a sophomore in college, I applied for the new Ronald E. McNair Postbaccalaureate Achievement Program at Middle Tennessee State University (MTSU). The Ronald E. McNair Postbaccalaureate Achievement Program is U.S. Department of Education funded TRiO program designed to prepare first-generation students from disadvantaged backgrounds with strong academic potential for doctoral studies through research and other scholarly activities. The goal of the Ronald E. McNair Postbaccalaureate Achievement is to increase the attainment of Ph.D. degrees by students from underrepresented segments of society. I became one of the first ten McNair Program Scholar at MTSU. My experience as a McNair scholar provided me with GRE prep, research opportunities in chemistry, and other educational activities, but it also provided me with quality mentorship preparing me for doctoral studies. I believe the knowledge, skills, and abilities gained through my McNair scholar experience has provided me the foundation I needed to obtain my Ph.D. and become the research professional that I am today.

SERMACS 73

Mentors matter for all students from high school to graduate school and beyond

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Move forward and reach back. This quote from Donne Dean, ACS career consultant and past president of the Association for Women in Science, AWIS, is always on my mind when I mentor students. I would not be a professor of chemistry today if my Upward Bound director, my community college chemistry professor, my research advisors and others helped me succeed as a first-generation college graduate. Mentors are critical to one's success. I will present key strategies that I have learned from my mentors that enable me to reach out to students today as they move up the career ladder in the chemical sciences.

SERMACS 74

Mentoring high school students in nanoscience research at Hampton University

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The Nanoscience Transforming STEM (Science, Technology, Engineering and Mathematics) Education at Hampton University (NanoHU) Program has played a prominent role in exposing underrepresented minority high school students to nanoscience research. Rising 10th and 11th graders were selected for a six-week non-residential, research-intensive program where they were actively engaged in Interdisciplinary Nanoscience projects under supervision of faculty mentors. Performing research alongside a faculty mentor helped students better understand design of experiments, interpretation of data, exploration of scientific literature, communication and teamwork. These are all highly valuable and transferable skills that are necessary for success in the modern workforce and in higher education. This presentation describes three summers' research work conducted by six underrepresented minority high school students at Hampton. The students synthesized gold and silver nanoparticles using conventional heating and microwave irradiation techniques. Compared to conventional heating method, microwave irradiation provided shorter reaction times, better reproducibility and enhanced reaction control. These nanoparticles were used to study their transformation and stability in an aquatic environment. The students learned to use UV-Vis spectrophotometer to characterize nanoparticles, search literature and prepare PowerPoint presentation. The summer program culminated with a mandatory poster session where students presented their results. This research experience has motivated the high school students to pursue STEM disciplines with three of the students having transitioned to Hampton, John Hopkins and Rensselaer universities where they are pursuing STEM studies and coursework.

SERMACS 75

SciWrite: Workshop development and mentorship in scientific writing for summer undergraduate researchers

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Scientific writing is an essential communication tool serving to disseminate novel research advances and innovative ideas with the scientific community. As undergraduates, budding scientists are taught to keep good lab notebooks and write lab reports for the sciences courses. While these provide good learning and assessment tools, they do little to bridge the gap between written communication for science classes and scientifically writing manuscripts for publications. Currently, courses in the latter are rare. Students typically learn to write scientifically in graduate school through repeated edits and revisions from their research mentor. This process can be frustrating and time consuming for many first time manuscript writers, and their mentors. To reduce such stressors and bridge the gap in scientific writing from undergraduate to graduate levels, an intensive SciWrite professional development workshop was developed for undergraduates involved in summer research in the chemistry and biochemistry department at Georgia Southern University (GS). SciWrite is now in its fifth year benefitting diverse groups of students not only from the department, but also undergraduate researchers from the CEMITURE (NSF-REU) and McNair programs. Our SciWrite program utilizes guided mentorship from faculty through technology and face to face interactions. Although different concerns and issues arise each year, SciWrite has had many successes. These include students submitting their own written abstracts to various conferences and writing manuscripts for publication.

SERMACS 76

Integrating scientific research to create meaningful undergraduate experiences

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Savannah State University (SSU) has enhanced significantly its undergraduate research training capacity through a number of STEM training and mentorship programs. Many STEM disciplines such as the life science, physical sciences and interdisciplinary domains such as forensic science and marine science are recognized for the under representation of African Americans and also women. The goal of undergraduate research experiences is to produce STEM graduates with the internal drive to serve the wider community through pursuit of careers in thebiomedical sciences, broadly defined. They must also nurture passion by revealing the significance of varied scientific disciplines to important human or societal concerns. Furthermore, research experience creates learning communities, safe spaces, where students are encouraged to challenge themselves as young scientists. Our approach expands, and improves upon a previously successful research education model (NIBIB-EDEPS) conducted at Savannah State University, which resulted in 92% graduation rate in 4.5 years, and over 46% of the EDEPS cohort transitioning directly into biomedical related post graduate studies, and an additional 39% conducting post baccalaureate work. Students are exposed to the associated ethical context and quandaries. For these high-achieving student participants, such research experience nurtures creativity with capacity to innovate and teaches teamwork, as well as, ethical conduct. Through these efforts, we improve future human health and well-being by leading the development and acceleration of scientific technologies. Our approach is of scientific relevance to continuously improve the student learning experience in a dynamic environmentwhilesustaining scientific rigor.

SERMACS 77

REU Site that recruits faculty-student teams

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The NSF-REU site at Furman University recruits and accepts faculty-student teams from other institutions for our summer program. Visiting teams are accepted to the REU program from institutions that currently lack the infrastructure, support or culture of an undergraduate research program. Inclusion of visiting research teams promotes education of the student scientist and lays the groundwork for faculty members to build independent research programs that will positively serve countless undergraduate students in the future. Teams can work on their own projects or develop collaborations with Furman faculty.

To support the long-term development of visiting research teams, we often accept applications from a single visiting faculty mentor over multiple summers. Visiting faculty members typically participate in the REU program for 3-6 summers, working to build their own research program. The faculty mentors are expected to develop research programs and collaborations, in addition to writing proposals and articles for publication.

There are many benefits to REU students by being part of these visiting teams. For example, students will already know the faculty member with whom they are working and often other lab members as well (faculty may bring 2-4 students). Particularly for students who went to college close to home and have never traveled very far, it can be personally challenging to travel to distant REU programs. By having familiar faces, the student can enter the new situation with a sense of belonging and understanding. This support is particularly important for students from minority serving institutions (MSI) and two-year institutions. In addition, MSIs are often heavily recruited by REU programs with little long-term benefit to the students' home institutions. The most talented students will often go elsewhere, making it harder for faculty members to build a sustained research program. By providing a research environment and stipend for the faculty member and research students, it is easier for the faculty member to recruit top students to work with over the summer. Finally, the faculty members choose and recruit their own research students. Faculty members are the best judges of who will excel and benefit from the research experience.

SERMACS 78

Mentoring and support for the REU-INFEWS: Food, energy, water security program at Mississippi State University

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The NSF-funded REU-INFEWS program at Mississippi State University emphasizes entrepreneurship and small business in addition to a research focus related to environmental sustainability through biofuels and biochars. The program has recruited and included additional students beyond the NSF-funded participants through additional research grants, and support programs from HBCUs to participate in the mentoring and advising activities. Summer research students at Mississippi State University are also included so our summer cohort each year includes 30-45 students. Our program puts heavy emphasis upon mentoring through research. Undergraduate participants are encouraged to create Individualized Development Plans that support them to identify goals and skills useful for their future careers. Renewed and expanded through 2022, this program will continue to support students toward careers and small business opportunities in the chemical sciences.

SERMACS 79

Assessing the quality of undergraduate research experiences: Perspectives of in-lab mentors

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This work focuses on the experiences of undergraduates, graduate students, and post docs in curiosity driven laboratory research settings. In this study, undergraduates were engaged in laboratory-intensive academic research experiences through independent study, volunteering, or work study employment. They were interviewed in several focus groups at the conclusion of the academic year. Some of the topics probed included the lab affiliation process, student motivations, authority versus approachability of their mentors, communication skills, and time management. In-lab mentors, the graduate students or postdoctoral researchers who work most closely with undergraduates on research projects, were also interviewed in separate focus groups. A subset of the graduate students and postdoctoral researchers then used a reflection guide to record weekly audio logs about their experiences working with the undergraduates over the course of the following fall semester. Themes that emerged from the qualitative analysis of 130 of these logs will be reported; coding and queries were conducted using NVivo software. This is new, on-going, unpublished research.

SERMACS 80

Kennesaw State University chemistry and biochemistry summer undergraduate research experience

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The goal of the Kennesaw State University Chemistry and Biochemistry Summer Undergraduate Research Experience (CBSURE) is to provide underrepresented students in science who attend smaller schools with little to no access to research experiences the opportunity to conduct state-of-the-art research across various disciplines in chemistry and biochemistry one-on-one with our faculty. This program just completed its third year hosting a total of 25 students over this time resulting in numerous presentations and several manuscripts. An additional outcome of this program is to showcase KSU as a research destination to complete a Masters degree in the Chemical Sciences. To date, we have had 2 students attend our Masters program as a result of participation in the CBSURE program and another student from this summer's cohort is very excited to apply for next year.

SERMACS 81

Novel ionic rectification based on functionalized silica nanoparticle and track-etched nanopores for switchable drug delivery

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Recently, ionic rectification through nano-pores has attracted much research attention. Ionic rectification is characterized by an increase in ion conduction for one voltage polarity but a decrease for the opposite polarity, producing an asymmetric mass transport of ions through nanopores. Most ionic rectifications reported in literature require the fabrication of extremely small single nano-pore, which is formidably challenging for most laboratories. Furthermore, the pore size and density of functional groups at the pore entrance must be strictly controlled to obtain the desired rectification. Noteworthy this exciting discovery hasn’t found practical applications in biomedical science yet. In this study, we propose a novel approach to realize ionic rectification by using chemically functionalized silica nano-particles and nano-porous membranes. When one side of a U-tube is filled with negatively charged silica nanoparticles and another side is filled with positively charged silica nanoparticles that are functionalized with 3-aminopropyltriethoxysilane (APTES) through a conventional silanol chemistry, a dramatic ionic rectification can be realized applying voltages of different polarities across a track-etched nanoporous membrane (15 nm in pore size). The ionic rectification system has been well characterized using scanning electron microscope, transmission electron microscopy, Dynamic Light Scattering, and FTIR. It was found that the on/off ratio of the ionic rectification system can be affected by a variety of factors such as membrane pore size, silica particle size, surface chemistry, buffer ionic strength, buffer pH value, applied voltage and distance between two electrodes. By optimizing these factors, the on/off current ratio of our rectification system can reach as high as 20. The system was also utilized for controllable drug delivery of ibuprofen, whose dosing rate was quantified using high-performance liquid chromatography.

SERMACS 82

Evaluation of metal–organic framework as sorbents for the BTEX family of compounds

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Metal-organic frameworks (MOFs) are a class of highly porous materials that can be synthesized using a variety of inorganic nodes and organic linkers. These customizable features make MOFs desirable for gas sensing, gas storage, and gas separation. In this study, MOF thin films of the UiO-66-X family, where x = -H, $-NH_2$, and $-NO_2$ were grown on Au-coated Si wafers and Au coated quartz microbalance crystals using a vapor-assisted conversion method. The thin films were characterized by XPS, XRD, RAIRS, and SEM. The thin films were activated by heating under high vacuum then exposed to a saturation pressure of benzene, toluene, ethyl benzene, and xylene isomers (BTEX) while recording the frequency change of the crystal. The Sauerbrey equation was used to convert the frequency change of the crystal to the accumulated mass, followed by calculation of the Henry’s constant. The results indicate that the UiO-66-NO_2 and UiO-66-NH_2 thin films have the largest (and similar) Henry’s constant for the xylene isomers. In general, the UiO-66-H thin films have the smallest Henry’s constant. The results suggest that dipole-dipole interactions between the organic linker in the MOF and aromatic compound is the important factor governing the extent of adsorption.

SERMACS 83

Electrochemical monitoring of the thermal sintering behavior of electrode-attached 1.6 nm diameter gold nanospheres

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Here, we report the thermal sintering behavior of 1.6 nm diameter tetrakis(hydroxymethyl)phosphonium chloride (THPC)-stabilized Au nanospheres (NSs) chemically-attached to a glass/indium tin oxide (glass/ITO) electrode as compared to 4 and 15 nm diameter citrate-stabilized Au NSs. The peak oxidation potential (E_p) in anodic stripping voltammetry (ASV) is indicative of the size, which is at 0.45 V for the as-prepared 1.6 nm diameter THPC Au NSs. ASV shows that the onset of sintering in these NSs occurs as low as 80 ºC based on the presence of the peak at 0.45 V but also a new oxidation peak at 0.70 V in the ASV, which correlates to 1.6 nm and ~4 nm diameter Au NSs, respectively. The ratio of the peak current at 0.70 V relative to that at 0.45 V increases with an increase in temperature and duration of thermal treatment. The peak at 0.45 V completely disappears after treating at 150 ºC for 60 mins. In contrast, 4 and 15 nm Au NSs are completely stable under the same thermal treatment. UV-vis spectra of 1.6 nm Au NSs chemically-attached to amine-functionalized glass/ITO also confirmed that sintering occurred based on the appearance of a well-defined localized surface plasmon resonance (LSPR) band after 60 min at 100 ºC, which is initially absent. The electrochemically-determined surface area-to-volume ratio (SA/V) decreases with an increase in temperature and heating time, consistent with an increase in NS size upon thermally-induced sintering. A plot of NS size versus heating temperature shows that a dramatic size transformation occurs in the temperature range of 100-150 ºC for 1.6 nm NSs while 4 nm and 15 nm Au NSs are stable up to 400 ºC. Scanning electron microscopy (SEM) images confirm the electrochemical and UV-vis size analysis. The thermal stability of metal NSs is important to better understand in order to improve long-term stability for catalysis applications.

SERMACS 84

Synthesis and characterization of radioluminescent $NaGdF_4$: EU nanoparticles as a potential light source for optogenetics studies

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Rare earth doped phosphors can produce bright luminescence with narrow spectral features under irradiation from UV-Vis, IR, and X-ray photons as well as electrons, and other energy sources. They are widely used in lighting, X-ray imaging, and bio-labeling applications. Controlling particle size is important for bio-labeling applications, and a challenge is to develop brighter luminescent particles with well annealed crystal structure to avoid quenching by defects, while at the same time preventing aggregation and fusion during annealing. To address this, we encapsulated $NaGdF_4$ phosphors in a silica shell, which could also be subsequently functionalized using target ligand. We synthesized Eu doped $NaGdF_4$ nanoparticles using a co-precipitation method followed by hydrothermal synthesis upon addition of NaF. The synthesized nanoparticles were coated with a silica shell using a mixed TEOS, ethanol and NH_4OH solution. Next, the nanoparticles were annealed at high temperature (600-1000 °C) to increase the emission intensity by removing defects that can quench luminescence. Nanoparticles with no silica coating were annealed as a control that can be resulted in sintered particles and high luminescent intensity. The synthesized $NaGdF_4$: Eu were characterized using powder XRD, TEM imaging, DLS and XEOL spectroscopy. TEM images show nanoparticles with diameter around 100 nm. Eu doped $NaGdF_4$ nanoparticles were synthesized by varying the amount of dopant (Gd: 0.1, 1, 15, 20, 100 mol% Eu). According to the XEOL spectroscopy measurements, at low and high dopant levels, they show low emission intensity, likely due to lack of luminescent centers and self-quenching, respectively. After hydrothermal treatment, the intensity of most samples increased by factor of 2-2.5; another factor of 5 is gained by annealing the particles at high temperature, though this causes them to fuse, negating their bio-application. Sintering of nanoparticles during the annealing process is addressed by coating with silica. However, increase in luminescent intensity is limited by size of the nanoparticles and boundary defects due to silica coating. In future, we plan to optimize the synthesis, annealing, and surface passivation protocols to obtain bright monodispersed nanophosphors. We will also functionalize them with required ligand and test their application as *in situ* X-ray excited light sources for sensing and actuating *in vivo*.

SERMACS 85

Polyaniline modified biochar to remove nitrate from aqueous system

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Helpful characteristics of biochar include the ability to increase soil fertility in dry environments and the ability to absorb and preserve nutrients in soil. Both aspects of use are available for low cost of production. The adoption of these uses of biochar have increased popularity of this product recently. Biochar has been proven to help improve the environment by decreasing the number of pollutants through its adsorptive properties. Douglas Fir biochar (DFBC) synthesized by fast pyrolysis method was modified with aniline to alter some of its properties. The modified biochar was then characterized by point of zero charge, BET surface area, thermogravimetric analysis and Scanning electron microscopy. Nitrates can potentially have a negative effect on the environment when an excess amount is present. The significance of this experiment is to investigate to see if polyaniline modified biochar works better than DFBC to absorb the nitrate pollutant from aqueous systems. The adsorption studies of nitrate were conducted using Liquid Chromatography with a UV detector at 210 nm for DFBC and PANI-BC. The kinetic studies were carried out at pH 6 with three different concentrations of nitrate. Batch sorption studies for nitrate were performed by varying the concentration of nitrate at three different temperatures and the data was fitted to different adsorption isotherm models for both types of biochar. PANI-BC exhibited a higher adsorption capacity for nitrate compared to the pristine DFBC.

SERMACS 86

Tuning the surface plasmon resonance by patterning plasmonic nanoparticles using metal grid/stamp, glucose crystal deposition and mechanical deformation

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Plasmonic nanoparticles have interesting optical properties which depend on their size, shape, and local environment including: optical absorption, optical scattering, surface enhanced spectroscopies, photocatalysis. Applications range from bioanalytical sensors to light guiding and enhanced photovoltaic light harvesting. Controlling particle shape and location is important for studying these optical phenomena and developing devices. Here, we describe a simple technique to change the shape of gold (72 nm) and silver nanoparticles (94 nm) by mechanically compressing them using a glass rolling pin. The resulting shape-change induces a red-shift in the unpolarized light scattering spectrum. We also patterned the silver nanoparticles and tuned their optical properties by mechanically pressing metal grids (TEM and VACCO grids) and depositing glucose crystals onto the nanoparticles to deform them. Patterning with TEM grid resulted in uniformly deformed area in shape of TEM grid with very sharp boundaries (for particles on the line, only portion of the individual nanoparticle is deformed). Additionally, the surface roughness of a stamp (VACCO grid) can also be transformed onto nanoparticle(s). Tape can be used to remove undeformed particles leaving only the pattern of deformed particles. In addition, glucose can be deposited on a surface covered with particles to create a protected region of nanoparticles around the deposited glucose crystal. Nanoparticles located further away from the glucose deposit showed change in shape leading to a red shift in the localized surface plasmon resonance (LSPR) scattering spectrum (Figure 1). In summery our approach provides a simple method to selectively change the shape and LSPR of nanoparticles and pattern the deformation either as a stamp, or with a gradient.

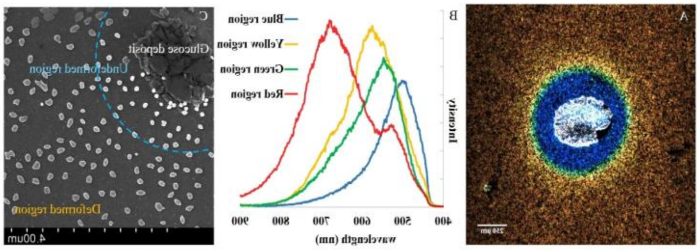

Figure 1: (A) Hyperspectral dark field image showing protected region of Ag NPs around the glucose deposit and deformed region away from the deposit. (B) Dark field single nanoparticle scattering spectra of undeformed (blue region), partially deformed (green and yellow regions) and deformed (red region) NPs corresponding to image (A). (C) Scanning electron microscopic image of patterned Ag NPs.

SERMACS 87

Aminooxy-functionalized metal monolayer-protected custers (MPCS) for catalysis applications

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Aminooxy (-ONH$_2$) groups are most commonly known for their chemo-selective reaction with carbonyl compounds (aldehydes/ketones). Aminooxy-based click chemistry has proven to be a versatile means of ligation, as evidenced by broad application in the fields of material science, biology, biochemistry, analytical chemistry, and nanoscience. Such versatility is proven to be the most attractive feature of this organic moiety, driving many researchers into this field. Our work seeks to exploit the facile reactions of aminooxy functionality, presented on the surface of gold nanoparticles, with aldehydes via oximation reactions to form the robust oxime ether adducts. We describe here the functionalization of gold monolayer protected clusters (Au MPCs) with a new trifunctional amine-containing aminooxy alkane-thiol ligand for the selective capture of various aldehyde-containing molecules on the Au MPC surface. Specifically, diethanolamine is transformed into organic soluble aminooxy thiol ligand using short synthetic pathways that feature Mitsunobu-like transformations for the incorporation of protected aminooxy groups. The thiol ligands were coated on 1.6 nm average diameter hexanethiol (C$_6$S)- Au MPCs using the well-known thiol place-exchange reactions. Subsequent ligand place-exchange of Au MPCs with aminooxy thiol ligands afforded gold mixed monolayer protected clusters (Au MMPCs). These MMPCs are used to prepare catalysts with improved selectivity, turnover, and recyclability in organic transformations. Results of caged catalysts prepared using aldehyde-functionalized polystyrene (PS) beads or agarose cross-linked aldehyde activated amino-link resin for use as catalysts for Suzuki-coupling reactions will be presented.

SERMACS 88

Nitrogen-Doped Screen-Printed Carbon Electrodes (N-SPCEs) and Carbon Ultramicroelectrodes (N-CUMEs) as platforms for electrocatalysis and immobilization of metal nanoparticles

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Nitrogen-doped carbon materials have garnered much interest due to their electrocatalytic behavior towards the oxygen reduction reaction as well as their ability to promote deposition of highly active metal nanoparticles. Here, nitrogen-doped screen-printed carbon electrodes (N-SPCEs) and carbon ultramicroelectrodes (N-CUMEs) were prepared through a simple soft nitriding technique similar to one recently reported for introducing nitrogen groups on carbon blacks and activated carbons. While the production of N-doped carbon materials often involves cumbersome processing steps and/or expensive materials or equipment, the simple, low-cost N-doping strategy employed here enables direct fabrication of N-doped carbon electrodes as platforms for electrocatalytic studies and applications. N-SPCEs and N-CUMEs show promise for electrochemical biosensing as they display good electrocatalytic activity towards hydrogen peroxide reduction. Amperometric detection of H$_2$O$_2$ using N-SPCEs with an applied potential of -0.4 V (vs. Ag/AgCl) exhibited good reproducibility and stability as well as a reasonable limit of detection and wide linear range even without the use of nanomaterials. Metal nanoparticles can also be deposited on N-SPCEs and N-CUMEs for improved performance and electrocatalytic behavior towards other important reactions like methanol oxidation. Overall, N-SPCEs and N-CUMEs are versatile, cost-effective tools for electrocatalysis and immobilization of metal nanoparticles.

SERMACS 89

Corrosion resistance of a tetrafunctional epoxy-amine resin coating

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Epoxy resins are one of the most widely used thermosetting materials in industrial and practical applications because they possess outstanding mechanical, thermal, and dielectric properties. In particular, multifunctional epoxies – dense and cross-linked structured resins, are used as molding compounds, sealants, and protective coatings for many barrier-related applications. In this work, we used a tetrafunctional epoxy-amine resin as a coating for mild steel and used electrochemical impedance spectroscopy (EIS) to investigate its corrosion resistance to a 3.5 wt% NaCl solution. The results indicate that the coating was able to resist corrosion and maintain a very high impedance modulus for more than 30 days of continuous exposure to the NaCl solution. Different resistance behaviors, as indicated by EIS, were observed for the coatings with artificially introduced damage. The coating also showed high thermal resistance and good adhesion to mild steel surfaces. This tetrafunctional epoxy-amine resin could effectively function as a high performance and corrosion resistant coating material for semiconductor, aeronautic, and marine applications.

SERMACS 90

High-temperature fast-flow reactor for the study of radical-radical reactions

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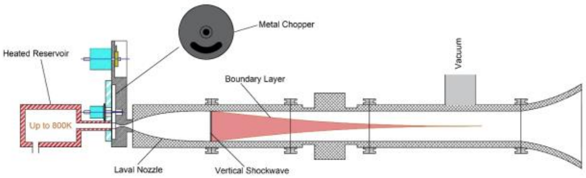
A novel pulsed fast-flow reactor was designed to allow for the measurement of free radical reaction rate coefficients at high-temperature using laser induced fluorescence (Figure 1). The 10-Hz pulsed fast-flow reactor delivers a uniform subsonic flow of gas at temperatures up to 800K that allows for wall-free kinetic investigations. The gas is heated and then isentropically expanded through a Laval nozzle to supersonic speeds. A vertical shockwave is formed at the exit of the nozzle by controlling the post-nozzle pressure in order to recover the reservoir temperature. The result is a laminar flow with homogeneous temperature, pressure, and number density for over 1 meter, corresponding to a hydrodynamic time of up to 1 ms. Gas pulsing is made possible by a rotating metal disk prior to the nozzle throat with an opening for the gas to travel. The design of this flow reactor allows for a reduced cost of gas volume and heating power and eliminates the need to heat near sensitive optical equipment.

Temperature measurements were conducted by measuring the rovibrational spectra of the CN radical and fitting the line intensities to a Maxwell-Boltzmann distribution. Velocity profiles were also taken at different temperatures via pitot tube to study the conditions inside of the flow. The velocity measurements within the nozzle corresponds well with the predicted velocity of the flow after the shockwave.

The fast–flow reactor will be used to measure the rate coefficients of selected radical–radical reactions at high temperatures. The radicals of interest which include the propargyl, allyl, and benzyl radical are resonantly stabilized radicals. These molecules are stable and relatively unreactive with molecular oxygen (Miller et al. 2005) and play a significant chemical role in high-temperature combustion environments (Sinha et al. 2016). The reactions of these radicals with the OH radical will be measured by LIF.



High-Temperature Fast Flow Reactor

SERMACS 91

Using the society for science & the public advocate grant to encourage Project SEED students to enter science competitions

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The Project SEED program at The University of Southern Mississippi (USM) has leveraged the Society for Science & The Public Advocate Grant to encourage ACS Project SEED students to further develop their SEED projects into science fair and other competitions. This talk will introduce the audience to the Advocate Grant program, illustrate how how USM utilized the grant funds to benefit the Project SEED students, and discuss the success of the Project SEED students in the science competitions. Information on how to apply for an Advocate Grant will be provided.

SERMACS 92

Growing a Project SEED site at Boise State University

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For the past several years, Boise State University and the Snake River Local Section have sponsored a small Project SEED program with 2-5 participants. This year, we increased the size of our program to 10 students and reached out to nearby institutions in order to expand the program's reach. This presentation will describe the program elements, aspects of the research conducted by SEED students, challenges encountered as a result of the expansion, and the impact of SEED on some of the participants. The SEED research projects include organic synthesis, bioinorganic chemistry, electrochemical analysis of manufactured stainless steel, and preparation and design of nanomaterials, among several other topics. Students also actively participate in a "summer research community" where they interact with undergraduates conducting research in several disciplines across campus. The summer research community provides opportunities for professional development, an introduction to interdisciplinary research, and social events. We strive to create a research environment where students begin to develop as STEM professionals. Lessons we've learned will be discussed in order to help others who would like to develop strong Project SEED programs.

SERMACS 93

ACS Project SEED at Clark Atlanta University

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The Department of Chemistry at Clark Atlanta University has been an ACS project SEED site since the summer of 2011. As an ACS Project SEED site we are now tapping into the vast group of talented, determined and gifted young men and women in the greater Atlanta area. The Department's goal is engaging high school students from low-income settings in cutting-edge materials research. The 2019 participants are carrying out the preparation of the MoS_2 (nanosheets)/polymer nanocomposites by solution processing. Characterization studies of the nanocomposites include NMR spectroscopy, FT-IR, SEM, DSC and light microscopy. The participants also meet weekly with other scholars (undergraduate students), graduate students, the mentors, and interested researchers to discuss topics of special interest in nanoscience/material science. Our goal is that the SEED participants will eventually pursue advanced degree in chemistry related areas.

SERMACS 94

ACS Project SEED student participation in molecular materials research at UNC Charlotte

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The Walter Research Group at UNC Charlotte has been studying the photophysical and electronic characteristics of porphyrin and thiazolothiazole materials for applications such as organic light-emitting diodes, organic solar cells, and electrochromic materials. Each summer, ACS Project SEED students have played an important role in this research. Specifically, students have participated in helping to understand the important role of exciton diffusion in thin films of porphyrin chromophores. The work has resulted in the development of a computational technique that uses the fluorescence quenching efficiency of electron acceptor materials to calculate exciton diffusion lengths. We have extended this work by further understanding how molecular orientation in single crystals impacts the exciton diffusion dynamics. Our group has also developed highly fluorescent thiazolo(5,4-d)thiazole (TTz) viologens, which exhibit reversal electrofluorochromism and unique photochemical properties. New structural TTz systems have now been developed to exploit their unique electrochemical properties. ACS Project SEED students took active roles in these projects and continue to contribute to the successes of our research program.

SERMACS 95

Polymer-protein biomaterial scaffolds for wound healing and cancer research

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Synthetic hydrogels are designed to mimic the extracellular matrix (ECM), which initiates cell differentiation in tissue regeneration and wound healing. Although synthetic hydrogel films are the gold standard for synthetic ECM materials, the material properties are exceedingly difficult to be engineered to match the native ECM. Poly-*n*-isopropylacrylamide (NIPAM) microgel particles are a reasonable alternative to existing synthetic ECM materials because they are soft polymer hydrogels in particulate form, which do not have a limited mesh size, and can therefore accommodate cell invasion through a dense suspension. Their elastic properties can also be tuned to properly strike the appropriate balance between cell-mediated degradation and cell adhesion by modifying the stiffness (crosslinking density) of the microgel particles. This SEED project focused on creating and characterizing fibroblast infiltration and migration through NIPAM microgel particle suspensions. The NIPAM microgel particles were surface-functionalized with collagen, via EDC/sulfo-NHS carboiimde chemistry, to allow for cell attachment and degradation. The material properties of the composites were tuned by modifying the crosslinking density of the microgel particles with molar concentrations ranging between 0% n,n'methylenebisacrylamide (BIS) and 2%. Cell morphology and migration will indicate the performance of the biomaterial as a scaffold for wound healing and cancer progression and will be characterized via fluorescence microscopy. The material properties of the microgel particles were analyzed via atomic force micrscopy (AFM). The results provide new alternative to hydrogels, to investigate and eventually control cell infiltration for future applications in cancer research.

SERMACS 96

Project SEED program at Georgia Gwinnett College: Successfully organizing Project SEED at a primarily undergraduate institution

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Project SEED program at Georgia Gwinnett College (GGC, a four year public institution) will be presented. From 2017-2019 GGC hosted 15 Project SEED fellows (5 SEED fellows/year). Selection of mentors, selection of SEED students, research topics as well as students experiences at GGC will be discussed.

SERMACS 97

Janus micromotors improve the catalytic efficiency of immobilized enzymes

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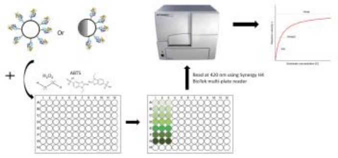
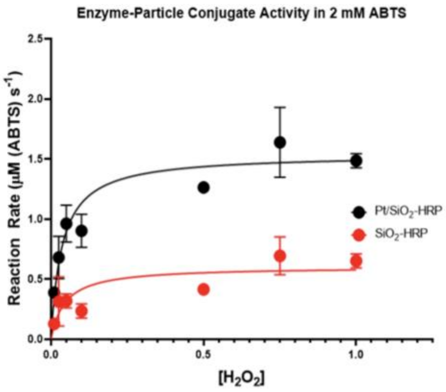
Enzymes have wide biological applications in biosensor technologies, bioremediation strategies, production of pharmaceuticals, or as therapeutics for disease treatment. Enzyme immobilization onto macro/micro surfaces is typically required for non-native applications. However, enzyme kinetics are negatively impeded when immobilized due to hampered mass transport and distortions of native protein configuration. We report herein a simple method of improving enzyme catalytic activity using a simple Janus micromotor. Janus particles are a special class of nano/microparticles with chemically heterogeneous surface chemistry which can be exploited to create particles with spatially confined functionalities. It has been demonstrated prior that Janus particles with enzymes spatially confined to one hemisphere can function as active swimmers in the presence of a compatible substrate through a phenomenon termed self-diffusiophoresis. We hypothesized that this self-actuation could serve to improve the mass transport of the system to promote enzyme-substrate collision. An SiO2/Pt Janus particle was created and then the enzyme horseradish peroxide was conjugated to the functionalized silica hemisphere using APTES-glutaraldehyde bioconjugation strategy. We used scanning electron microscopy to demonstrate successful creation of Janus particles and hemispherical segregation. A standard ABTS colorimetric kinetic assay was conducted and demonstrated remarkably improved kinetic activity of Janus particle-HRP conjugates compared to non-Janus particle-HRP controls. Janus micromotors may prove a promising strategy of improving immobilized enzyme catalytic activity and may have potential medical or industrial application.





SERMACS 98

Development of a fluorescence sensor for tracking heme insertion into proteins

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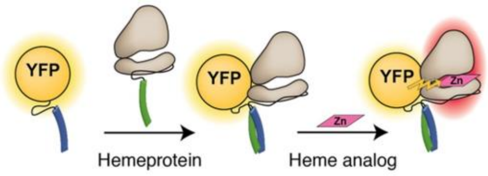
Hemeproteins, which use heme as a cofactor, serve diverse roles in metabolism, signaling pathways, catalysis, and transport of diatomic gases. Unbound heme is cytotoxic, however, and therefore requires careful trafficking to sites of hemeprotein synthesis, but the process of heme delivery is not well understood for most proteins. To address this, we are developing sensors which use Fluorescence Resonance Energy Transfer (FRET) to detect cofactor insertion into hemeproteins. The sensor consists of a fluorescent protein (FP) and an H-NOX hemeprotein domain. These components are either arranged as a fusion protein or on two distinct peptides that form a heterodimer. This design allows a FRET signal to be generated upon insertion of a fluorescent heme analog, zinc protoporphyrin IX (ZnPPIX), to the heme binding pocket of H-NOX.

The protein constructs were recombinantly expressed in *E. Coli* and purified by affinity and gel filtration chromatography. Sensor designs that require dimerization were assessed with pulldown assays, demonstrating tight binding interactions between the hemeprotein and FP partner. Additionally, fluorescence spectroscopy results show that our sensors are able to generate measurable FRET signal. Sensors with a ZnPPIX cofactor exhibit modest ZnPPIX fluorescence, as well as substantial FP quenching relative to the same sensor with a heme cofactor. We now explore the expression of the successfully validated heme sensors in bacterial cells to study heme trafficking dynamics in an *in vivo* context.



Fluorescent heme sensor scheme

SERMACS 99

Investigating Tat-SF1 interactions with HIV RNA

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Little is known about the human protein Tat-specific factor 1 (Tat-SF1) and its role in the production and regulation of the Human Immunodeficiency Virus (HIV). In human genes, Tat-SF1 is a factor during the transcriptional elongation process. This human protein is also involved with alternative splicing and possesses an RNA recognition motif typical of RNA binding proteins. Tat-SF1 also upregulates HIV infection and alters the relative levels of HIV-1 RNAs, but exactly how this occurs is unknown. The hypothesis for this study was that if Tat-SF1 helps stabilize, splice and/or export HIV-1 RNA, it must interact with the RNA physically. This work attempts to demonstrate if Tat-SF1 interacts with HIV-1 using *in vitro* RNA binding assays. Fragments of the HIV-1 genome were made using PCR, followed by DNA sequencing and *in vitro* transcription. HeLa nuclear extracts were prepared and confirmed by Western blotting to express Tat-SF1. These nuclear extracts, purified Tat protein, and the HIV-1 RNA fragments were used to perform Electrophoretic Mobility Shift Assays (EMSA) and Fluorescence Correlation Spectroscopy (FCS), two complementary binding techniques. Results showed that HIV-1 RNA at the 5' end of the genome was successfully made. Data supported our hypothesis that binding occurred between Tat-SF1 and HIV-1 RNA. Furthermore, this interaction occurred even in the absence of the viral cofactor Tat. Together, these results advance our knowledge of the molecular mechanism of Tat-SF1.

SERMACS 100

Kinetic isotope effect in the Kemp elimination catalyzed by heme systems

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The Kemp elimination is a reaction that has been used as a model for proton transfer from aromatic carbon and, more recently, as a benchmark for the computational design of enzymes. While often base-catalyzed, recent results have shown that heme proteins can catalyze the Kemp elimination via an internal redox mechanism. We found that the kinetic isotope effect (kie) of the base-catalyzed mechanism is around 6, while the kie of four different heme systems (hemoglobin, myoglobin, cytochrome c, and a water-soluble iron porphyrin) were noticeably reduced. This suggests a different rate-limiting step in the redox pathway, consistent with a different mechanism. The linear free energy relationship for cytochrome c and iron porphyrin were also determined by varying the substrate's substituents. These two systems had similar slopes, suggesting that they catalyze the reaction in similar ways. In contrast, these slopes were dissimilar to that of the hydroxide-catalyzed reaction, again consistent with a different mechanism.

SERMACS 101

Glyoxylate-based protometabolism serves as an analog of the citric acid cycle

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Transformations within the TCA cycle enable the net oxidation of an acetyl group into two molecules of carbon dioxide. This metabolic pathway serves critical roles in the storage of chemical potential as biological cofactors, as well as provides polymeric building blocks including amino acids. Genomic and metabolic analyses suggest that parts of the TCA cycle were active at the origins of metabolism, likely in an anabolic capacity. Simpler uncatalyzed analogs of the TCA cycle, with more limited functionality, may have emerged under prebiotic conditions and laid the foundation for the development of an increasingly sophisticated metabolism. Protometabolic reaction pathways have been demonstrated that convert glyoxylate into carbon dioxide through a series of intermediates that recapitulate portions of the citric acid (TCA) cycle. The reactions proceed from either pyruvate or oxaloacetate in the presence of glyoxylate under aqueous conditions at mild temperature.

SERMACS 102

Vitamin K2 analogs as anti-epilepsy therapeutics

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Epilepsy is a long-term, incapacitating disease. Current anti-epileptic drugs (AEDs) are therapeutically ineffective for thirty percent of epilepsy patients and target the symptoms of epilepsy instead of the cause of the disease. Mitochondrial dysfunction has been linked to epilepsy in patients with medication-resistant forms of the disease. Mitochondrial dysfunction leads to a shortage of ATP produced by the electron transport chain and can also create reactive oxygen species thus causing seizures. Previous studies have identified vitamin K2 (VK2) as neuroprotective *in vivo* and vitamin K3 (VK3) as reducing seizure activity in PTZ-induced convulsant zebrafish larvae. We synthesized a series of vitamin K2-analog naphthoquinone compounds to identify more effective, nontoxic AEDs. Our results indicate that several of these compounds restore mitochondrial health *in vitro*, mitigate seizure-like activity in PTZ-induced zebrafish at low concentrations, and are effective in mouse models of medication-resistant epilepsy with side-effects. In this presentation, we will discuss the types of synthetic VK analogs that show anti-seizure activity and their anti-seizure activity *in vivo*.

SERMACS 103

Study of 5-HT$_{1D}$ and 5-HT$_{1F}$ receptor interactions with mini G proteins via BRET analysis

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G protein-coupled receptors (GPCRs) are receptors involved in signal transduction, a process for converting extracellular signals into intracellular messages to elicit a cellular response. Signal transduction pathways involve activating various G protein subtypes (G_s, $G_{i/o}$, $G_{q/11}$ and $G_{12/13}$) which typically lead to second messenger production. Traditionally, second messenger concentration assays are used to identify GPCR coupling with G protein(s), but they are not efficient in profiling GPCRs since they compare the concentrations from different downstream signals. Instead, novel tools, such as Bioluminescence Resonance Energy Transfer (BRET) and mini G (mG) proteins, can be used to profile GPCRs. BRET is a technique that provides quantitative data when protein-protein interaction occurs and requires the proteins of interest to be fused with either a bioluminescent protein or fluorescent protein. In this study, we used mG proteins representing each G protein subtype to identify 5-hydroxytryptamine (5-HT; serotonin) receptor coupling upon serotonin stimulation. Through BRET assays, we determined that both the 5-HT$_{1D}$ and 5-HT$_{1F}$ receptors couple primarily with the mG_{si} and mG_o classes of mG proteins. This supports previous studies that these receptors couple to $G_{i/o}$ proteins and suggests that the use of mG proteins in BRET assays is an effective tool for GPCR profiling.

SERMACS 104

2-ethynylpyridine polymerization using His-tagged T4L, a variant of bacteriophage T4 lysozyme

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HEWL and T4L contribute to the hydrolysis of peptidoglycans and, recently, have been found to play a vital role in the catalysis of 2-ethynylpyridine (2-EP) polymerization. Both proteins have the ability to produce synthetic polymers derived from a reaction immersed in water; this deviates from the traditional method of polymerization that uses metals and other organic solvents. From our recent research, bacteriophage T4L contains two active site residues that influence both the lytic and catalytic abilities of the protein: E11 and D20. When manipulated, E11 hinders the protein's ability to lyse under standard conditions whereas D20 negates the polymerization of the 2-ethynylpyridine reaction.

In an attempt to facilitate faster, purified product, bacteriophage T4L was mutated into a His-tagged form. In doing this, it was presumed the protein would conform to the conditions of the previous protocol. This required a re-optimization of the expression and purification procedure involving a new protocol utilizing a nickel-charged His-column, size-exclusion chromatography, UV/Vis, and a fluorescence assay to produce a purified product. Preliminary comparisons of expression with this His-Tagged variant yields much higher amounts of protein that still needs more work to maintain solubility upon tag removal. Progress in this re-optimization process will be presented. With this new approach to T4L, this project will attempt to catalyze a 2-EP polymerization reaction as well as utilize HSQC to determine folding and protein-ligand interactions.

SERMACS 105

Toward an understanding of the relationship between sequence, acylation, and solution behavior in human ghrelin

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Ghrelin is a 28-residue growth hormone and neuropeptide whose activity is dependent on post-translational modification (PTM); ghrelin is modified with an *n*-octanoyl group on its third serine residue. The only known peptide hormone that is modified by a fatty acid, ghrelin has many functions, including glucose homeostasis and orexigenic regulation. Its notable modification, known to be crucial for activity, could also be integral to its inherent three-dimensional structure. Literature suggests that ghrelin's sequence is active down to small fragments, provided that the octanoyl chain is preserved. Our group is interested in the conformational and biophysical interplay between sequence length and this unique PTM. Our work thus far has consisted of the synthesis and purification of five-residue and ten-residue fragments of ghrelin and *des*-acyl ghrelin, optimizing conditions for acylation of Ser(3), and initial biophysical and NMR experiments to probe the relationship between peptide length, a fatty acid PTM, and solution behavior.

SERMACS 106

Bilayer interactions of the endogenous opioids

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The endogenous opioids are a class of neuropeptides which, in addition to their traditionally associated analgesic potential, have been implicated in the function of numerous other psychological and physiological functions including nociception, learning and memory, metabolism, and personality influences such as dysphoria, paranoia and depression. These peptides bind to the G protein-coupled opioid receptors: μ, δ, and κ, and common to all endogenous opioids is the N-terminal, four-residue message sequence, referred to as "YGGF" for its amino acid code; this message sequence is conserved across ligands of all 3 receptor subtypes. This study explores a range of YGGF-peptides, featuring structural and spectroscopic analyses of the δ-selective Enkephalins, μ/κ-selective adrenorphin, and κ-selective α-neoendorphin. We seek to evaluate the intrinsic biophysical programming role of the C-termini, investigating how they affect the structure of YGGF, perhaps pre-organizing the opioid message sequence for specific receptor binding. We also wonder if the address portions aid (or inhibit) membrane association relative to the YGGF. The opioids are studied under aqueous and bilayer-mimetic conditions. We establish critical concentrations and evaluate apparent conformational preferences utilizing 2D ^{1}H-^{1}H NMR experiments and establish to what extent lipid bilayer association is a general feature within the endogenous opioids using DOSY NMR experiments.

SERMACS 107

Molecular modeling of histone deacetylase complexes

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Histone Deacetylase 8 (HDAC8) decreases gene expression by coiling DNA on histone proteins. When overactive, HDAC8 can silence tumor suppressor genes and, therefore, aid in the development of certain cancers. This study investigates the depsipeptide class of HDAC inhibitors (HDACi), the most potent HDACi found to date, through computational methods. One such depsipeptide inhibitor, Romidepsin, has been approved for chemotherapy uses by the FDA and is a selective inhibitor of Class I HDACs which include HDACs 1, 2, 3, and 8. Understanding enzyme-inhibitor interactions provides insight for future design and synthesis of more potent and selective HDACi resulting in a more effective drug with less harsh side effects. Conformational sampling was performed with MODELLER to provide a flexibility component in the protein for docking. Using AutoDock4 supplemented with the AutoDock4Zn force field, the structures of the HDAC-Romidepsin complexes were determined. Interestingly, a large majority of the dockings showed Romidepsin “capping” the active site of the protein. This contradicts the generally accepted binding in which the thiol of Romidepsin binds to the catalytic zinc of HDAC8; there is no known crystal structures of Romidepsin in any HDAC, however. Preliminary computational studies have shown that certain modifications allow for better binding to the catalytic zinc of HDAC8, similar to other depsipeptide inhibitor.

SERMACS 108

Effects of cholesterol on amyloid beta aggregation in Alzheimer's disease

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Alzheimer’s disease, one of the most prevalent causes of dementia in the US, is a neurodegenerative disease caused in part by the aggregation of the peptide amyloid beta (Aβ). There is little known about the mechanism of amyloid beta aggregation, but in general, these monomeric peptides aggregate first into smaller, soluble oligomers, which ultimately fibrillize into insoluble plaques. One theory posed is that cholesterol interacts with oligomers to play a role in cell death, as both components have been implicated in the damage to the cell membrane of eukaryotic cells. Comparing amyloid beta samples with and without various levels of cholesterol can be used to determine the role it plays in the aggregation of the peptide, and whether cholesterol encourages oxidative stress and/or Aβ oligomer stabilization within the cell membrane. The amount of aggregation is determined through SDS-PAGE, Thioflavin T assays, and Bradford assays, which are used in combination to determine the amounts of amyloid beta found in both the oligomer and fibril form. Results from these tests indicate that the addition of cholesterol to samples of Aβ stabilizes the oligomeric form of the peptide. As the oligomeric form of Aβ is associated with the worsening of Alzheimer’s disease, it is hypothesized that higher levels of cholesterol may also be contributing to its pathogenesis. Further research is investigating the mechanism by which cholesterol stabilizes the oligomers, and whether cholesterol also chemically alters the Aβ chain or enhances oxidative stress within the cell.

SERMACS 109

Synthesis, structural characterization, and reactions of a new penta-coordinated cadmium(II) ion

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Neutral Penta-coordinated Cd (II) complex [$Cd(L)I_2$], where L is 2,6-diacetylpyridine, is prepared by reacting CdI_2 and 2,6-diacetylpyridine in acetone. Optical, electrochemical and spectroscopic analysis of all molecules will be presented. This complex crystallizes in two different forms and single-crystal structures of both polymorphs will be presented. Reactions of this new complex as a building block to synthesize hetero-nuclear metal clusters will be presented.

SERMACS 110

Synthesis and structural characterization of a new coordination polymer with nine-coordinated La(III) ions

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We have synthesized a new coordination polymer containing La (III) ions by reacting equimolar amount of Lanthanum (III) triflate and 2,6-diacetylpyridine in acetonitrile. Single crystal diffraction results of this new coordination polymer indicate that the La atom is nine-coordinate, bonded to one pyridine methyl ester ligand, two water molecules and four oxygen atoms of triflate anions. 1D chains are formed by the triflate anions bridging La centers, assisted by water-triflate hydrogen bonding. Another non-coordinated triflate anion links the chains into 2D sheets via more water-triflate hydrogen bonding. Spectroscopic analysis of this new coordination polymer and its analogs with other lanthanide ions will be presented.

SERMACS 111

Transformation of metal oxide nanoparticles in surface coatings: Hazards of inhalation and ingestion during application

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Surface coatings, including paints, stains, and sealants, have recently become a focus of “nano-enabled” consumer product engineering. Specifically, zinc oxide (ZnO) nanoparticles (NPs) have been introduced to surface coatings to increase UV resistance. As more products available for purchase are made with NPs, questions arise regarding the long term environmental and human health effects of these materials. Additionally, a lack of regulation and public awareness allows companies to provide little readily available information about the NP composition of their products. This study aims to understand the transformation of metal oxide NPs commonly included in surface coatings using ZnO as a test particle. Initial experiments were completed by incubating NPs in multiple synthetic biological fluids (SBFs) in order to model inhalation and ingestion that could occur during product application and use. Control samples consisted of manufactured ZnO NPs, while experimental samples incorporated ZnO NPs into commercially available stains. Subsequently, commercial products advertised as containing ZnO NPs additives were examined using identical methods. Subsamples were taken at various time points during incubation, sequentially filtered and analyzed via Atomic Absorption Spectroscopy to determine both the total and ionic zinc concentration. Zinc dissolution was found to be dependent on the pH of the SBF used in incubation regardless of product matrix. Smaller particles were more easily suspended than larger particles, and both suspended and ionic zinc concentrations were seen to decrease over time. Most noteworthy, the total zinc concentrations were found to be lower in purchased products than in model systems. However, dissolution of ZnO NPs into the ionic species still occurred at significant percentages in purchased products. Future analysis will focus on other relevant NPs used in commercial surface coatings including Ag, TiO_2, and CeO_2.

SERMACS 112

Lewis acid catalyzed formation of ligand-stabilized highly crystalline Cu_2O nanoparticles via a hot injection esterification method

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The properties of metal oxides nanocrystals are highly dependent on size, shape, or the introduction of metal dopants. Recent developments in the hot injection methodology has provided an efficient method for the controlled growth of metal oxide nanocrystals via an esterification reaction. However, the application of this method is limited by the formation of appropriate metal precursors. Here, we show that the addition of group 13 metals with known Lewis acid properties can effectively catalyze the formation of reactive metal precursors for nanoparticle formation and growth. This allows for the production of these materials under low temperature and with minimal time while allowing for the tunability originally provided by this synthetic method. Through the addition of a metal catalyst, we extend this synthesis to other metals oxides like copper(I) oxide, being previously unobtainable under similar reaction conditions. Additionally, the use of increasing amounts of catalyst or metals of differing Lewis acidities can effectively tune nanoparticle size and can contribute to the versatility of the synthetic method.

SERMACS 113

^{1}H-NMR investigation of displacement of oleate at PbS quantum dot surfaces using carboxylic acids, thiols, amines, and halides

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Lead sulfide quantum dots (PbS QDs) have shown great promise in recent years as photovoltaic cell sensitizers, heterogeneous photocatalysts, and thin-film field-effect transistors. The utility of PbS QDs for these applications relies on the ability to effectively tailor the QD surface chemistry through ligand exchange reactions. This presentation will discuss a series of ^{1}H-NMR experiments to compare the ligand exchange equilibria of colloidal, oleate-capped PbS QDs with a series of common exchange targets: carboxylic acids, thiols, amines, and halides. Carboxylic acids and thiols are observed to produce oleic acid as the final product whereas amines generate the conjugate base oleate. In general, compounds able to protonate the departing oleate are found to generate greater yields of displaced oleate at a given ligand:QD ratio. Halide exchange was performed with a variety of tetraalkylammonium and dialkylammonium salts; the halide-oleate equilibrium is sensitive to both the halide and the ammonium counterion used. Trends in exchange equilibria and exchange products are discussed in the context of an associative interchange mechanism. Implications of these findings on ligand exchange protocols for PbS QD-based devices will be discussed.

SERMACS 114

New synthetic route to heteroaromatic *N*-oxides bound to boron trifluoride: Synthesis, characterization and X-ray structural studies

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Previously reported heteroaromatic *N*-oxides bound to boron trifluoride have been reported using boron trifluoride etherate as a starting material. We have found quantitative yields of the product using tetrafluoroboric acid as a substitute in methanol. These compounds are readily synthesized and isolated in pure form. In this presentation we will discuss the synthesis and characterization of these complexes via various spectroscopic techniques. We will also report the X-ray structures of the pyridine *N*-oxide as well as a variety of substituted aromatic N-oxides.

SERMACS 115

X-ray study of the chemistry of haloaurates with heteroaromatic N-oxides

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We have examined the chemistry of haloaurate anions (AuX_4^-, where X = chloride, bromide and iodide) with a series of aromatic *N*-oxides. The chloride and bromide derivatives are formed by the reaction of tetrachloroauric and tetrabromoauric acid with two equivalents of the N-oxide. The complexes form hydrogen bonded bis-*N*-oxide cations with the corresponding aurate anion. Iodide derivatives are formed by the substitution of chloride in the tetrachloroauric acid using sodium iodide and the appropriate *N*-oxide to form a series of complexes with varying outcomes. This talk will present the results of the structural analysis and examine the similarities and differences in the structures.

SERMACS 116

Property and structure relationship of lanthanide paramagnetic ionic liquids

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Ionic liquids are molten organic salts with melting temperatures below 100 °C. They are also known for having a characteristically low vapor pressure, and other solvent and material properties that can be manipulated through various chemical synthesis techniques to be used for a broad range of applications. Paramagnetism, a less well-known property can be induced in ionic liquids to create magnetically susceptible paramagnetic ionic liquids (PILs). PILs are a relatively new class of magnetic fluids, differentiated from other magnetic fluids, such as ferrofluids, by the absence of magnetic particles and separate phases of carrier fluids. We have synthesized a series of lanthanide and alkyl-imidazolium based PILs by adding magnetically susceptible elements into the cation, anion, or both. There are many advantages and applications associated with PILs such as high thermal stability, high ionic conductivity, and variable magnetic susceptibility. We will present the physical properties of paramagnetic ionic liquids as they relate to the structure of the PIL as measured via FTIR, TGA, DSC, NMR, and density measurements.

SERMACS 117

Reductive removal of pertechnetate and chromium by zero valent iron under variable ionic strength conditions

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Tc is the main risk driver in the permanent disposal of low activity waste (LAW) by vitrification at Hanford due to its volatility and low incorporation into glass waste forms. Under current technology, volatilized Tc will be captured by an off-gas treatment system as a condensate and recycled back to the LAW glass melter feed. Off-gas recycle is effective at increasing Tc loading in the LAW glass but greatly increases concentrations of chromate and other salts hindering LAW processing. An alternative disposal route via reductive separation of Tc using zero-valent iron (ZVI) could enable effective separation of Tc from the off-gas condensate. However, the potential treatment of Tc with ZVI under LAW off-gas condensate conditions is not well understood due to the variability of the waste stream and presence of competitive redox-sensitive contaminants that could affect Tc reduction. The objective of this research is to investigate the suitability of ZVI as a separation technology to remove ^{99}Tc in the presence of chromate from LAW off-gas condensate under variable ionic strength conditions.

The competitive removal of Cr(VI) and Tc(VII) by ZVI (1.2 g/L, 297 µm, Ferox PRB, Hepure, Hillsborough, NJ) was studied in batch experiments over 30 days (25 mg/L Cr(VI), 1 mg/L Tc(VII), pH 10) under variable ionic strength conditions (NaCl 0.01, 0.1, 0.5, and 1 M). All samples were prepared in triplicate with parallel ZVI-free controls. Cr and Tc removal increased considerably with increasing in ionic strength and a second order removal rate best approximated results. Future work will consider the reductive removal of Tc(VII) and Cr(VI) in increasingly complex matrices representative of LAW off-gas condensate.

SERMACS 118

Mechanism and kinetics studies for the ruthenium-catalyzed oxidation of silyl ethers to silyl esters

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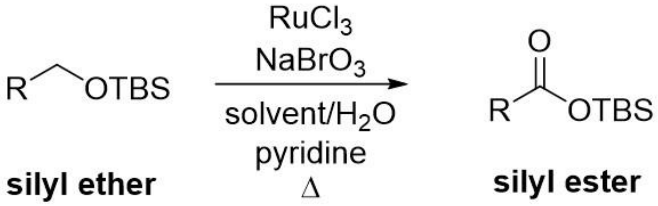
Various mechanistic probes were applied to the recently reported ruthenium-catalyzed oxidation of silyl ethers to silyl esters. Employing a biphasic system allows sufficient exposure to the water needed to activate the catalyst while still limiting hydrolysis of the silyl ester products residing in the organic layer. Removal of the water after catalyst activation but prior to TIPS octyl ether substrate addition led to 0% conversion with 10 mol% $RuCl_3$ and low conversions with stoichiometric $RuCl_3$, indicating that water is also essential to complete the catalytic cycle. Evidence for a previously suspected aldehyde intermediate for carboxylic acid side-product formation was observed in the aforementioned stochiometric oxidation and when TBS benzyl ethers were oxidized. Decreasing the water-to-solvent ratio for TBS octyl ether oxidations had no significant effect in the CCl_4/H_2O system but unexpectedly gave rise to more hydrolysis in the $EtOAc/H_2O$ system, leading to questions regarding the partitioning of the product mixtures within the two solvent systems. Upon further study, no carboxylic acid was found in the aqueous layer for non-polar TBS octyl ether but was observed for a substrate containing a more polar functional group. Preliminary kinetics studies with TBS octyl ether suggested a first-order reaction, and more studies are underway to measure the k_{obs} for the oxidation of a range of para-substituted benzyl silyl ether substrates.



SERMACS 119

Synthesis and characterization of thiosemicarbazones and its inhibition of topoisomerase II?

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Benzoylpyridine (BZP) has been previously studied as a thiosemicarbazone synthesized as the ligands and as a copper (II) complexes and tested to show its inhibition on Topoisomerase II*α,* an enzyme in cells that controls topology of DNA. These BZP complexes have being studied as anti-cancer agents because of its inhibition of Topoisomerase II*α*, which can result in inhibiting replication and transcription of DNA causing cell death. The interest of this study is to synthesize and characterize BZP with 4-tertbutyl-3-thiosemicarbazide (BZP-tBTSC) and Copper (II) in an undergraduate lab. Cu-BZP-tBTSC has been synthesized in the lab using a variety of lab techniques including the reflux method. The synthesized compound was characterized using ^{1}H-Nuclear Magnetic Resonance (NMR), Infrared Spectroscopy (IR), and Ultraviolet Visible Spectroscopy (UV-Vis). These tests were done to verify the structure and composition of each product throughout the project. The compound's stability in aqueous media is tested because enzyme assays are done in aqueous media. Furthermore, the data from crystallization of the compound, as well as determining crystal structure will be presented. Crystalline structures are unique, and it can represent as a means of identification for the BZP-tBTSC. To determine the effectiveness of the synthesized compound, enzyme assay data using DNA relaxation assays with the Topoisomerase II*α* enzyme are studied. The poster will discuss synthesis, characterization, crystallization and inhibition studies of the BZP-tBTSC in an undergraduate laboratory setting.

SERMACS 120

Computational studies of bis-phosphinimine NCN-pincer nickel(II) complexes

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Four analogs of bis-phosphinimine NCN-Pincer nickel(II) complexes are investigated to determine what effect changing the steric bulk of the ancillary phosphinimine hydrocarbon moieties had on ligation in the fourth coordination site of Ni(II) complexes and potential impacts on reactivity. Four analogs with varying numbers of cyclohexyl and phenyl ligands were characterized using density functional theory in order to investigate their ability to yield cationic isoindolium heterocyclic ligands via C-C and C-N bond forming reactions. Optimized geometries were computed for all analogs of the starting materials as well as the chlorinated and brominated isoindolium products using B3LYP theory with 6-31G+(d) and LANL2DZ basis sets with LANL2DZ effective core potentials and confirmed with harmonic vibrational frequencies. Further insight into electronic structure and bonding was achieved through utilization of natural bond orbital analysis. Preliminary results are in agreement with the proposed mechanism and suggest that the synthesis of the isoindolium products is most favorable with greater numbers of cyclohexyl ligands as their steric bulk destabilizes the pincer complexes and promotes the formation pathway of the more stable isoindolium product.

SERMACS 121

Formation and further application of silyl esters in one-pot reactions

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The silyl ester products of the recently reported ruthenium-catalyzed silyl ether oxidations are somewhat volatile causing their isolation to be challenging, thus we sought to test in-situ applications of the products without isolation. In one example, the product reaction mixture from the silyl ether oxidation in EtOAc could be mixed with TBAF and an alkyl halide leading to silyl ester deprotection and subsequent esterification. A range of alkyl halides were tested for this application, including bromide and chloride substrates as well as primary and secondary halide substrates. Several para- and meta-substituted benzyl halides containing electron-donating or -withdrawing groups were also tested. Alternatively, the reaction of the oxidation product reaction mixture with oxalyl chloride and DMF resulted in the formation of an acyl chloride that could then undergo further nucleophilic addition/elimination reactions. As alternatives to the initially employed carbon tetrachloride solvent, DCM and chloroform were tested as oxidation

reaction solvents and yielded comparable percent conversions and ester/acid ratios. The oxidation product reaction mixtures involving these solvents could then be used in both the TBAF deprotection/esterification and the oxalyl chloride chlorination applications.

SERMACS 122

Detection of TNT and other nitroaromatic explosives using porphyrin-doped silica sol-gels

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Development of a reproducible and reusable method for the detection of 2,4,6-trinitrotoluene (TNT) and other nitroaromatic explosive precursors in aqueous and vapor phase systems is of great significance in forensic science. Porphyrins and metal-porphyrin complexes immobilized within silica sol-gels were fabricated and used to study the binding of TNT to the porphyrin. Silica sol-gels were doped with free-base meso-tetrakis(4-carboxyphenyl)porphyrin, H_2TCPP, meso-tetrakis(4-hydroxyphenyl)-porphyrin, H_2THPP, and its zinc (II) derivative, ZnTHPP, during the polycondensation process. Absorption spectroscopy of the silica gel materials showed that the immobilized porphyrins maintained their intrinsic properties and no aggregation was observed. Sol-gel monoliths with and without entrapped porphyrins were crushed into powders and analyzed by ^{1}H MAS NMR, ^{13}C NMR and ^{29}Si CP MAS NMR as well as ^{13}C and ^{29}Si DP MAS NMR. Solid state NMR of the powders revealed that introduction of porphyrin moieties decreases the Q^1 intensities of the silica groups. The interaction of the porphyrin with nitroaromatics, the porphyrin functionality and the structural integrity of the doped sol-gel were examined using thermogravimetric analysis and fluorescence and UV-Vis spectroscopy. The results of the study including the binding of the TNT in aqueous phase with the pyrrole nitrogens in the porphyrin will be presented.

SERMACS 123

HPLC for separation and detection of organic gunshot residues extracted from silicone personal passive sampling devices

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Despite a decline in nonfatal firearm-related crimes, the fatality rate associated with firearms continues to climb. A challenge for criminal analysts has been the introduction of heavy-metal-free ammunition, which significantly reduces the effectiveness of Inorganic Gunshot Residue analysis techniques, such as Scanning Electron Microscopy. In an attempt to satisfy this protocol gap, studies are focusing on the quickest and most efficient method for Organic Gunshot Residue (OGSR) collection and analysis. Our research aims to determine the optimal extraction procedure for detection of OGSR collected from a silicone wristband used as a personal passive sampling device. High Performance Liquid Chromatography (HPLC) was used for separation and detection of OGSR. The HPLC method includes an isocratic separation with 50:50 acetonitrile:water using a Poroshell 120 EC-C18 column at 45°C. This HPLC procedure was effective in detecting each of seven common OGSR: akardite II (AKII), dimethylphthalate (DMP), diphenylamine (DPA), 2-nitrodiphenylamine (2-nDPA), 4-nitrodiphenylamine (4-nDPA), N,N-diphenylformamide (N,N-DPF), and ethylcentralite (EC). Using this analysis method, we focused on determining the most effective extraction solvent. These results will be presented along with figures of merit including resolution, retention factor, selectivity factor, and limit of detection.

SERMACS 124

Substrate scope of ruthenium-catalyzed oxidations of primary and secondary silyl ethers

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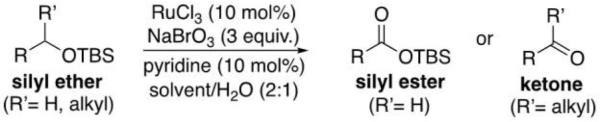
A previously optimized method for ruthenium-catalyzed oxidation of primary silyl ethers into silyl esters was applied to new primary substrates and one secondary substrate. Silyl ethers containing phenyl rings several carbons away from the oxidation site were observed to have poor reactivity. However, benzylic carbons attached directly to silyloxy groups oxidized readily to form silyl esters that were conjugated with the phenyl ring. A range of para-substituted benzyl silyl ether substrates containing various electron donating and withdrawing groups have been tested. A secondary substrate, cyclohexanol, was transformed into cyclohexanone under the same oxidation conditions, and a work-up method for the reaction was optimized.



SERMACS 125

Efforts towards the total synthesis of synoxazolidinone C

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Clinical resistance has been observed in all classes of antibiotics currently in use, making previously-treatable infections a significant threat to human health and thereby necessitating the development of new drugs. Synoxazolidinone C is a marine natural product that exhibits potent antimicrobial activity against both gram-positive and gram-negative bacteria, representing a novel platform for antimicrobial discovery.

Previously, our group has reported the synthesis of other oxazolidinone-containing natural products and analogs that act as potent antimicrobial agents; however, synoxazolidinone C has remained elusive due to the challenges set forth by the unprecedented bicyclic 4-oxazolidinone core. Herein, we report the rapid synthesis of a key bicyclic 4-oxazolidinone core from which an efficient, convergent sequence of chemical transformations would furnish the natural product.

SERMACS 126

Chemical determination of the efficacy of new and worn self-cleaning materials

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Certain self-cleaning materials slowly oxidize organic matter over time. Self-cleaning clothing and hygienic surfaces are increasingly being employed in spaces like hospitals and public restrooms. Replacement protocols for such materials are generally based on appearance, not on any demonstrated decrease in oxidative activity. We have developed a simple procedure, using organic dye solutions and visible spectroscopy, for determining oxidation rate constants of new and worn materials. Preliminary results show that the rate constants of tested materials initially drop off sharply (they get "broken in") but at moderate timescales become fairly constant.

SERMACS 127

Conformational flexibility in linear amino alcohols investigated by high-resolution Fourier-transform microwave spectroscopy and *ab initio* calculations

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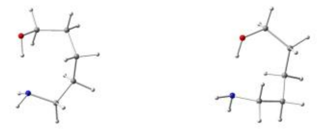
We have examined a series of linear amino alcohols of increasing backbone chain length. For shorter chain lengths (2-aminoethanol, 3-aminopropanol, and 4-aminobutanol) only one conformation has been observed at the 2 K temperature of the molecular beam. For the larger 5-aminopropanol, a second conformation has been detected under the same experimental conditions. We seek to understand the origin of the appearance of this conformational flexibiltiy as a function of backbone chain length in terms of the potential energy surface generated by rotations of the torsional angles that define the heavy atom backbone of the amino alcohol.



Two low energy conformers of 5-aminopentanol detected by Fourier-transform microwave spectroscopy

SERMACS 128

Purification and characterization of wild-type and modified small laccase from *Streptomyces coelicolor* in preparation for attachment to a surface

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The goal of most enzyme immobilization strategies is to achieve increased thermal, operational and storage stability while maintaining structural integrity and catalytic efficiency. Laccase is an enzyme that has been studied extensively, both free in solution and immobilized, for applications to bioremediation, biosensors and biofuel cells. The enzyme is an oxidoreductase that catalyzes the oxidation of a variety of substrates with concomitant reduction of oxygen to water. While a variety of immobilized, fungal laccases have been reported, few studies have utilized the small laccase from *Streptomyces coelicolor* (SLAC). This bacterial enzyme has a number of advantages when compared to its fungal homologues, including a homotrimeric quaternary structure, an increased stability and a much higher, broader pH optimum. Here, wild-type SLAC and modified SLAC are purified and characterized in preparation for attachment to a surface. Wild-type SLAC will be immobilized by amide bond formation between L-lysine residues and surface N-hydroxysuccinimide (NHS) esters. Modified SLAC incorporates a noncanonical amino acid (phenylalanine azide; E47AzF) that allows specific attachment to a surface alkyne using click chemistry. The enzymes were successfully overexpressed and purified from *E. coli* host cells. Enzyme activity was evaluated using a phenolic model-substrate (2,6-dimethoxyphenol (DMP) and a continuous assay where the oxidized product absorbs maximally at 470 nm (470 nm, = 14,800 M^{-1} cm^{-1}). Attachment strategies were verified using in-gel fluorescence.

SERMACS 129

Bioinspired polymers for sequestration of doxorubicin during chemotherapy treatment

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Liver cancer remains the third leading cause of cancer mortality in the United States. Liver cancer treatment often involves administering a chemotherapeutic agent, such as doxorubicin (DOX), during a transarterial chemoembolization (TACE) procedure. In this procedure DOX is released via a catheter in the tumor maximizing the amount of chemotherapy that reaches the tumor; however, DOX still enters systemic circulation, causing off target toxicity. We are developing polymers with pendant nucleobases to bind to DOX in the bloodstream before it leaves the liver and causes off-target side-effects. Nucleobase-containing polymers were prepared via free radical polymerization of acrylates with pendant adenine and thymine. The monomers and polymers were characterized by 1H NMR, 13C NMR, and size-exclusion chromatography. The binding efficiencies of the polymers and DOX were analyzed via DOX capture experiments. The nucleobase-containing polymers will also be attached to a polymer film for analysis of DOX capture. The polymers bound to surfaces will be tested in water, buffer solution, and human serum. After the analysis of thymine and adenine polymers, guanine and cytosine monomers will be synthesized and tested similarly. Finally, combinations of polymers will be tested.

SERMACS 130

Quantifying the connection between polymer architecture and metal chelation

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Rare-earth elements (REEs: La–Lu, Y, and Sc) are critical components in many technologies including magnets, hard drives, LEDs, catalytic converters, and green technologies (e.g., wind turbines, batteries, etc.). With advances in the electronics and clean energy industries, modern society relies heavily on REEs. Extracting REEs from non-traditional sources, such as coal ash, can dramatically increase the production of REEs and satisfy this ever-increasing demand. Polymers have several advantages as sequestration materials, including relatively low cost and high affinity for target compounds; however, little is known about the effect of polymer architecture itself on metal binding. As a result, we are investigating the application of polymers for selective heavy-metal-ion chelation. Specifically, we installed α-amino phosphonate chelating groups onto commercially available linear and branched polyethylenimine.

In addition to synthesizing these new materials, we investigated the application of polymers for the selective chelation of various heavy metal ions. Linear and branched polyethyleneimine polymers were functionalized with aminomethyl phosphonates, and the effect of polymer architecture on metal chelation was examined using isothermal titration calorimetry (ITC). Using ITC, we are able to gain insight into the thermodynamics of metal binding and elucidate the specific structure–metal binding relationships of these materials. ITC measures the binding affinity (K_a), enthalpy changes (ΔH), and stoichiometry of the interactions between these macromolecules and metal ions in solution. We found that the stoichiometry of the polymer-metal interaction is molecular weight dependent: Smaller polymers chelate more metal ions per polymer repeat unit than larger polymers. By elucidating the thermodynamic profile of each chelating material, we have gained insight into each polymer's properties as a metal chelator.

SERMACS 131

Isolation of calcium oxalate from fresh spinach

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Oxalic acid is a highly soluble and naturally occurring diprotic acid common to a variety of vegetables including spinach, rhubarb and parsley. The oxalate anion forms insoluble salts with metal cations such as magnesium and calcium, (K_{sp} Calcium Oxalate = 2.3×10^{-9}). The focus of our investigation is the isolation of calcium oxalate from fresh spinach. The results of the isolation and characterization of calcium oxalate on both a grams scale and milligram scale will be presented. A laboratory experiment for general chemistry students incorporating the principles of natural product isolation, acid-base chemistry and solubility is proposed based on the results of this investigation.

SERMACS 132

Chemoselective synthesis of *α,α′*-homodifunctional polymeric systems

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End-group functionalization of polymer chains is a commonly used technique for reversible-deactivation radical polymerizations (RDRP). These modifications can allow RDRP polymers to have a wide range of applications in both polymer and materials chemistry research. This research focuses on expanding current end-group functionalization techniques for the *α*-end of reversible addition-fragmentation chain transfer (RAFT) polymers by utilizing successive substitution reactions with 2,4,6-trichloro-1,3,5-triazine (TCT) to develop *α,α'*-functionalized polymeric systems. The increased stability of the TCT ring after each substitution ensures that previously attached groups will not be removed during successive reactions. This technique enables two unique functionalities to be attached to the *α*-end of the RAFT polymer chain. Because of this, the *α*-end exhibits di-telechelic behavior, allowing for further molecular additions and polymerizations to occur.

SERMACS 133

Calorimetric study of the adsorption of oxalate on hematite nanoparticle

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Many chemical and biological reactions in soils are impacted by the presence of natural organic matter (NOM) that often enhances the bioavailability of nutrient and overall soil fertility. In soils, NOM is strongly correlated with the Al and Fe-oxides content of soils. Therefore, it is important to study the surface interactions of organic molecules with Fe-oxides, particularly at various pH conditions that might control whether organic acids are retained in solid or released to nearby aquatic systems. To that end, this research aims to study the interaction of oxalate, a low molecular weight organic acid with hematite nanoparticles that are relatively abundant Fe-minerals. These studies were conducted using flow microcalorimetry as it allows for real time and in situ examination of the adsorption process. The heats (Q in mJ.mg-1) of oxalate adsorption were measured at pH values of 4.0 and 7.0, and ionic background concentrations of 1, 10, 100, and 1000 mM. Impeding results will be evaluated to ascertain if and how the pH and concentration of background electrolytes affect the heat measured for oxalate adsorption.

SERMACS 134

Antiproliferative structure-activity relationships of 5-substituted indoles and indole-based chalcones

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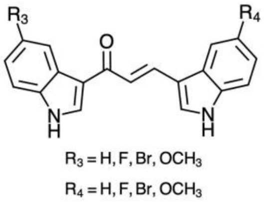
Indole-containing compounds and chalcones have proven useful as scaffolds for a variety of potent molecules with extensive medicinal applications. A series of substituted indoles and indole-based chalcones have been synthesized and evaluated against selected mammalian cancer cell lines and microorganisms. Substituents were chosen to give a range of electron density both on the aromatic ring and at the alpha-beta unsaturated ketone. Compounds with halogen substituents exhibited the highest potency against JEG-3 choriocarcinoma cells, MCF-7 breast cancer cells, and *Escherichia coli*.

5-substituted indole-3-carboxaldehyde and 3-acetylindole compounds



5,5'-substituted indole-based chalcones

SERMACS 135

Using multi-step synthesis for the production of hydrogels with adhesive properties

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Hydrogels behave as natural tissues due to its absorptivity and flexibility. Hydrogels are composed of networks of hydrophilic polymer chains, which make them extremely biocompatible. Today, hydrogels are being used for controlled drug delivery, fluid control, nerve regeneration and tissue engineering.[1] This presentation will demonstrate the experimental design and mule-step synthesis for the production of a remote activated, polyacrylamide hydrogels utilized for wound care. The first step is the synthesis of the DOPA derivative monomer, N-(3,4-Dihydroxyphenethyl) methacrylamide (DMA). This was achieved via free-radical polymerization using starting material dopamine hydrochloride reacted with sodium tetraborate decahydrate and sodium bicarbonate. The overall purpose is to successfully synthesize and characterize the copolymer, DMA.

SERMACS 136

Molecular docking binding activity of quinoline derivatives on Zika virus RNA-dependent RNA polymerase

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The outbreak of the Zika virus in 2015 was deemed a global health threat by the World Health organization in over eighty countries. The global distress of the epidemic of Zika virus initiated a rapid influx of investigation into inhibiting RNA-dependent RNA polymerase (RdRp) in the virus. RdRp of viruses has been a crucial component in drug designs because of its fundamental role in protein synthesis. Quinolines have previously been shown to display strong anti-bacterial and anti-viral properties. Eighteen quinoline derivatives were docked to the RdRp of Zika virus (PDB 5U04) to determine the relative strength of each ligand binding in the receptor site. The results will be used to identify promising targets for synthesis and testing as an inhibitor against Zika virus.

SERMACS 137

Sphingosine kinase inhibition using modified variants of a sphingosine kinase inhibitor

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The sphinogmyelin metabolic pathway is a popular target area of research due to the potential apoptosis in cancer cells. In the pathway, sphingomyelin may be converted to the final product of sphingosine-1-phosphate which is associated with cell proliferation in cancer cells. Inhibition of sphingosine kinase 1 would prevent proliferation and lead to the desired apoptotic outcome if a potent inhibitor can be identified. A successful inhibitor has been located; however, due to its hydrophobic properties, it remains inactive in the body. Derivatives of this inhibitor have been synthesized, analyzed and evaluated to assess whether these modifications effectively inhibit this enzymatic pathway.

SERMACS 138

Sulfamination of tethered aminoalkenes with *in situ* generated hypervalent iodine

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The pharmaceutical industry relies heavily on nitrogen heterocycles, which include substituted pyrrolidines and piperidines, and has a constant demand for economical and facile method. In recent decades, great advances have been made towards synthesis of these compounds with the use of hypervalent iodine, an economical and environment-friendly oxidant. Here we report a novel *endo*-sulfamination of tethered aminoalkenes yielding nitrogen heterocycle dimers bridged by a sulfate. This method produces 5-, 6-, and 7-membered rings in very good to excellent yields. This metal-free method relies on in situ-generated hypervalent iodine species. The reaction proceeds at room temperature and is air and water tolerant.

SERMACS 139

Characterization of the 3' untranslated region of *SAGA* mRNA from group A *Streptococcus*

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Streptococcus pyogenes is a Gram-positive bacterium known to cause necrotizing fasciitis, “flesh-eating disease”. Streptolysin S (SLS) is an exotoxin secreted by *S. pyogenes* associated with inhibition of the immune response during necrotizing fasciitis. SLS is the result of post-translational modifications to the SagA protein. The *sagA* gene is contained within the pleiotropic effect locus, *pel*, which has been identified as a small regulatory RNA (Pel) associated with the expression of virulence factors. The 3' untranslated region (UTR) of mRNA may regulate the expression of genes through post-transcriptional mechanisms. This research aims to identify RNA structural motifs within the 3' UTR of the *sagA/*Pel transcript that may regulate expression of *sagA* or other virulence factors. Patterns of mRNA interactions with the 3' UTR of *sagA*/Pel were predicted using TargetRNA. Secondary structures of the 3' UTR were predicted with the mfold web server. RNA constructs containing these regions were produced using linearized plasmid templates by *in vitro* transcription. In order to guide the interpretation of the data and the design of RNA-RNA binding studies, three-dimensional models of the 3' UTR were built using the FARFAR program in Rosetta. RNase T_1 digests combined with the sampling of various conditions using differential scanning fluorimetry were conducted to examine the stability of the RNA constructs. Crystallization of the 3' UTR will aid in determining the three-dimensional structure by X-ray diffraction. Characterization of this region will identify specific structural elements necessary for the expression of *sagA* and aid in the design of therapeutics that prevent the production of SLS.

SERMACS 140

Use of zinc-specific DNAzymes on nucleic acid functionalized nanocapsules for sensing applications

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Nucleic acid functionalized nanocapsules (NANs) are self-assembled micelles fortified with various crosslinkers and have been observed to be endocytosed. The NANs are crosslinked with either an ester crosslinker or a peptide crosslinker to be broken down by enzymes only within the cell, allowing the particles to be used for targeting intracellular functions. The design of the particle allows it to carry a hydrophobic cargo in its core, which would be released upon enzymatic cleavage of the crosslinker. The NANs can be functionalized with thiolated DNA by UV-assisted thiolyne chemistry. These strands can be functionalized with zinc specific DNAzymes, which in turn can be hybridized with an oligonucleotide substrate strand containing a fluorophore and quencher for sensing applications. Fluorescent kinetics studies upon the particle show functioning of the attached DNAzyme strands, the functioning of particle degradation in the presence of enzymes and its stability on the particle surface. Polymerase chain reaction studies confirm the attachment of the DNAzyme to the particle surface and help eliminate the concern of background fluorescence that may arise during fluorescence kinetics studies from free DNAzyme in solution.

SERMACS 141

Computational studies of the structures and electron-density topology of the group 14-substituted butatrienes $x{=}C{=}C{=}Ch_2$ ($x{=}Ch_2$, Cf_2, SiH_2, SiF_2, GeH_2, SnH_2, PbH_2)

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The nature of the C=X bond in group 14-substituted butatrienes $X{=}C{=}C{=}CH_2$ ($X{=}CH_2$, CF_2, SiH_2, SiF_2, GeH_2, SnH_2, PbH_2) was investigated by HF/6-311G(d,p), B3LYP/6-311G(d,p), and CCSD/cc-pVDZ structural optimizations of these molecules. The NBO populations reflect the changing nature of the hybridization at both C and X as the bond becomes more polar and the heteroatoms become pyramidalized. Quantum theory of atoms-in-molecules analyses suggest a lower electron density (ρ) at the C=X bond critical point and a smaller delocalization index (DI) for the bond as the electronegativity of X decreases down the group. Changes in the Laplacian of the electron density ($\nabla^2\rho$) and the electron kinetic energy density [$K(\rho)$] will also be discussed.

SERMACS 142

Design and application of green, solid-supported palladium catalysts for synthesis of important chemical targets in water

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Carbon–carbon coupling reactions are fundamental tools in organic synthesis, used in a variety of applications such as drug and natural product synthesis. Traditionally, homogeneous transition metal catalysts are used for these reactions, leaving behind trace amounts of metals in the final product and creating hazardous metal wastes. In pursuit of a heterogeneous catalyst to implement in aqueous coupling reactions, the unique reactivity of functionalized N-heterocyclic carbene rings (NHC) serves as the base for our solid-phase palladium catalysts. Synthesis and use of these catalysts offer several benefits when it comes to C–C coupling reactions. Bound to solid silica by thioether chains, the palladium–NHC catalyst is water stable and easily recoverable post-reaction, thereby reducing organic waste as well as allowing for full recyclability. As we implement these catalysts in Sonogashira reactions for the synthesis of resveratrol analogues in cancer research, we will be analyzing the effect on catalytic efficiency and recyclability by investigating several variable traits of the catalysts. Structural differences we are exploring include variations on the carbon chain length, counter ion used, functionalization of the NHC ligand, and alternate materials for the solid support feature, such as resins and magnetite. Aside from the applications within our lab, the functionality of this catalyst provides an exciting prospect for future utilization in many coupling reactions requiring a heterogeneous catalyst.

SERMACS 143

Investigation of the weathering of automotive clear-coat formulations using Fourier-transform infrared spectroscopy (FTIR) for forensic purposes

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Automotive paint analysis plays a vital role in solving hit and run crimes. In most hit and run accidents, automotive paint, as chips or smears, is the only evidence left at the crime scene. Using chemical information of the multilayered paint sample collected at the crime scene, a forensic analyst can narrow down the possible vehicles involved in the crime scene to a manufacturer, make, model, assembly plant and/or the year of the vehicle. The Royal Canadian Mounted Police (RCMP) maintains a database, which contains information on the automotive paint layers including the physical attributes, chemical compositions, and infrared (IR) spectra. In forensic analysis, IR spectra generated for an unknown sample is compared with the IR spectral database to narrow down the possible vehicles. A common sampling method in FTIR analysis, Attenuated Total Reflection (ATR), needs a minimal sample preparation and is therefore preferred by most forensic laboratories. This method scans the top surface of the sample hence, showing the spectral features of the weathered portion of the clearcoat. Vehicles that have been exposed to different environmental conditions will show significant spectral differences than their original clear-coat spectra. A forensic chemist would compare the collected weathered spectra with the library spectra that is unweathered; which, can lead to a misidentification of the sample. In this study, the top surface (weathered) and the bottom (unweathered) section of clearcoat layers of automotive clear coat samples from different automakers were analyzed using ATR-FTIR and compared. For all samples scanned, there was a significant difference between the weathered and unweathered portions of the clear coat samples. Comparison of the clearcoat spectra shows that there was a loss of the acrylic melamine, and self-condensation of -OH/-NH groups through hydrolysis that had occurred due to the weathering of the clear coat layers. Additionally, the samples contain acrylic melamine polymers show a higher degree of weathering compared to the samples contain acrylic urethane polymers. Inclusion of this information into a forensic analysis will facilitate the correct identification of the vehicle responsible for a hit and run accident.

SERMACS 144

Amino acids in soy sauces and alternatives: How do they affect the taste?

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Amino acids are major contributors to the taste of food. L-glutamic acid, for example, is a representative source of *umami* taste in its deprotonated form, and its sodium salt is marketed as a flavor enhancer monosodium glutamate (MSG). L-Aspartic acid also has *umami* and sour taste, though less potent than L-glutamate. Some amino acids possess sweet taste (L-alanine, glycine, L-serine, etc.) or bitter taste (L-phenylalanine, L-tryptophan, etc.). The taste of soy sauce is known to primarily come from its amino acid contents. There are many soy sauce alternatives as well, marketed for various reasons: as gluten-free or no-soy options (e.g. tamari), as a reduced sodium option, or simply as a cheaper substitute and/or as a diet supplement (coconut or liquid aminos). To understand the correlation between the amino acid contents and the tastes in these products, we have carried out high performance liquid chromatography (HPLC) analysis of 15 different soy sauces or alternative products to quantify 17 of essential amino acids in them per unit volume. We are finding that the difference in the ingredients (soy vs. coconut sap, soy with or without wheat, organic or not, sodium contents) and production methods (fermentation or acid-catalyzed hydrolysis) does have a correlation to the amino acid quantities and ratios, and to the characteristic tastes.

SERMACS 145

Identification of volatiles in tobacco products via thermogravimetric analysis

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The harmful effects of second hand smoke from tobacco products is widely understood to be a public health hazard. The exact temperature at which toxic chemicals like nicotine, formaldehyde, and acetone are vaporized during smoking and the volatilization of these toxic compounds in cigarettes do not always correspond directly to the vaporization temperatures of pure samples. To investigate the temperature that toxic chemicals in tobacco are released, raw tobacco, cigarettes, and cigarillos were analyzed using Thermogravimetric Analysis (TGA). Tobacco samples were heated at 30°C/min to 1000 °C and the emissions were collected in methanol. Analysis of the first derivative of the TGA curve indicated that each type of tobacco undergoes significant changes in mass over five major temperature ranges: 25-200°C, 200-300°C, 300-400°C,400-500°C, and 650-825°C. The TGA analysis of the tobacco products revealed that the Burley tobacco was most dissimilar from the others, with significant changes in TGA profiles at the 650-825°C temperature range. Analysis of the collected emissions have, to this point, been included to pinpoint the sources of the differences. Further work will focus on spiking of samples and optimization of collected emissions analysis to identify the potential source of these differences. In addition, statistical methods will be explored to move towards tobacco TGA "fingerprinting"-type analysis.

SERMACS 146

Design and synthesis of solid-supported palladium catalysts using N-heterocyclic carbenes for greener coupling reactions

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Electron rich N-Heterocyclic Carbenes (NHCs) are well known for their stability and as transition-metal ligands. Their role in the catalysis of carbon—carbon coupling reactions has been demonstrated in several popular synthesis routes including Suzuki—Miyaura, Heck, and Sonogashira. This research aims to reduce chemical waste by strategically designing and synthesizing recyclable solid-supported palladium catalysts using NHCs as building blocks. Not only are the catalysts green in the sense that they are recyclable, but they may also allow the use of water as a solvent in lieu of solvents that aren't environmentally friendly. First, an ionic liquid is synthesized using a simple SN2 reaction; current reactions combine N-methyl imidazole and haloalkenes with varying chain lengths. The ionic liquid is then "clicked" with (3-mercaptopropyl)trimethoxysilane forming a thioether, coordinated to palladium, and finally covalently bound to silica. After characterization, each catalyst will be tested for efficiency using a Sonogashira coupling reaction to synthesize resveratrol analogues. The ultimate goal of this research is to enable greener coupling reactions while maximizing catalytic efficiency.

SERMACS 147

Systematic study of the dependence of the quantum theory of atoms-in-molecules analysis of chemical bonding in first- and second-row chlorides (XCl, X-H, Li-F, Na-Cl)

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Previous work surveying the nature of chemical bonding in various kinds of molecules (ionic, covalent, *etc.*) using the quantum theory of atoms-in-molecules (QTAIM) has led us to consider the possible effects of the level of theory on these calculations. Thus, we have surveyed the complete set of first- and second-row chlorides (XCl, X=H, Li-F, Na-Cl) for the effects on ρ, $\nabla^2\rho$, DI, and $K(\rho)$. The numerical values changed insignificantly for most molecules comparing the B3LYP and M06-2X density functionals with large basis sets but showed some differences with CCSD wavefunctions and correlation-consistent basis sets.

SERMACS 148

Synthesis and characterization of l-asparaginase (l-asnase) encapsulated poly-l-lysine-graft-poly(ethylene) glycol (pll-g-peg) polymer nanoparticles for the efficient delivery of therapeutics

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L-asparaginase (L-ASNase) is a therapeutic enzyme that is widely used for the treatment of hematopoietic diseases such as acute lymphoblastic leukemia and lymphomas since 1970. But L-ASNase has intrinsic drawbacks such as low stability, short circulating lifetime, and low catalytic activity under physiological conditions. Research has suggested that the encapsulation of L-ASNase increases the efficiency and stability of the enzyme and provides efficient protection against enzymatic degradation. L-ASNase delivered by pegylated-L-ASNase (PEG-ASNase) form has been shown to improve clinical outcome of this therapy. Much research has gone into using red blood cells (RBCs) for drug delivery. Thus far, a variety of techniques have been developed to encapsulate proteins, drugs, and enzymes into RBCs. Most these techniques, however, require disruption of erythrocyte membrane to create large

pores for biomolecules to diffuse into the cell. The main disadvantage associated with these methods is the loss of RBC structural integrity and cellular components due to weakened cell membranes. Therefore, these modified RBCs are easily recognized by the host immune system. Hence, maintaining complete structural and functional integrity of RBCs is vital for achieving the benefits associated with using them as delivery vehicles for therapeutic biomolecules. Our long-term goal is to develop a nanoparticle system that is capable of entering red blood cells to extend therapeutic circulation time and therapeutic loading capacity. Current work is focused on synthesis and characterization of an enzyme encapsulated, maleimide functionalized poly-L-lysine-graft-poly(ethylene)glycol (PLL-g-PEG) co-polymer nanoparticle. ^{1}H NMR data shows successful polymerization between maleimide functionalized PEG and PLL. Nanoparticles synthesized by encapsulating a model enzyme: bovine serum albumin showed hydrodynamic particle size of 17 nm. Surface zeta potential data of these nanoparticles and catalytic activity of the encapsulated enzyme will be discussed.

SERMACS 149

Analysis of cannabinoid-infused consumer products

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Cannabis sativa has been a source of medicinal and recreational products for centuries. An agricultural variant, hemp, has been grown in over 30 countries and has a wide array of uses. Research into a class of chemicals found in hemp called cannabinoids has yielded a United States (US) Food and Drug Administration (FDA) approved medicine. Epidiolex®, approved by the US FDA for the treatment of Lennox-Gastaut syndrome and Dravet syndrome in patients two years of age and older, is based on cannabidiol (CBD). CBD, one of over 70 known cannabinoids, is being introduced to many consumer products including tinctures, vapes, edibles, drinks, and topical creams. However, the analytical testing of these products is still in its infancy. Without regulation or oversite, the industry lacks guidelines, and best practices aren’t readily available. This research focused on the development of a robust methodology for the analysis of consumer products that contain cannabinoids. The Association of Analytical Chemists (AOAC) Guidelines for Single Laboratory Validation of Chemical Methods for Dietary Supplements and Botanicals was used for method development and validation. The project also reports the potency results for 35 consumer products.

SERMACS 150

Analysis of the 5' untranslated region of *saga*/pel in *Streptococcus pyogenes*

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Streptococcus pyogenes is a human pathogen that is also known as group A *Streptococcus* (GAS), which is responsible for throat and skin infections as well as the more severe necrotizing fasciitis. The *sagA* gene codes for the protein streptolysin A (SagA) that is modified and exported as the cytotoxin streptolysin S (SLS). SLS is a virulence factor that seems to inhibit the response of neutrophils during necrotizing fasciitis. These studies target the 5' UTR of *sagA* in order to identify transient RNA structures affecting the transcription of *sagA* or the initiation of translation. RNA constructs containing predicted structured regions were produced by *in vitro* transcription. Secondary structures were predicted using the mfold and RNAfold servers. The predicted secondary structures were used to generate three-dimensional models using the program FARFAR through the ROSIE webserver. These models were used to interpret nuclease-protection assays of structured regions contained within the 5' UTR of *sagA*. Differential scanning fluorimetry was used to assess the stability of the RNA constructs and to screen a variety of conditions to be used in crystallization screens. Potential RNA targets were predicted using the TargetRNA webserver, and the predicted sites for recognition are being used to evaluate the predicted secondary structures in the 5' UTR of *sagA*. Characterization of the 5' UTR of *sagA* will identify structural motifs necessary for the regulation of gene expression at the post-transcriptional level and aid in the design of strategies to inhibit the production of the virulence factor SLS.

SERMACS 151

Analysis of cannabidolic acid (CBDA) and cannabidiol (CBD) ratios in consumer products

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Cannabis sativa plants naturally produce an acidic form of the cannabinoids that, when heated, form the decarboxylated cannabinoid. With the increase in consumer infused edibles, tinctures, and topicals, products derived from a cold-pressed hemp oil contain a high amount of CBDA and not the decarboxylated CBD. Since there are differences in biological activity between the acidic and decarboxylated forms, the analysis technique should be able to differentiate between them. In this study, HPLC was used to analyze consumer products to determine the CBDA to CBD ratio. This poster will discuss the decarboxylation kinetics, method to measure the ratio, and ratio of CBDA to CBD.

SERMACS 152

Finding functionality of enzyme 3H04 through computational analysis

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The purpose of our research was to identify the function of an enzyme, 3H04 from the protein databank (PDB) with known structure but unknown function. We used publicly accessible databases for protein analysis, such as Protein BLAST, Pfam, and DALI; macromolecule structure viewers such as PyMOL and ProMOL; and systems that model protein-ligand docking, such as AutoDock VINA, PyRx, and the Rosetta Online Server that Includes Everyone (ROSIE). With the cumulative data given from our resources, we were able to hypothesize that 3H04 is an Alpha-Beta Hydrolase that breaks apart triglycerides. Details of these results and structures of proposed protein-ligand interactions will be shared. The continuation of this research would be to test the protein in a *in vitro* lab setting and see if the lipids metabolized match the ones theorized by this study.

SERMACS 153

Development and validation of a differential FTIR method for the analysis of model prebiotic peptides

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A major goal of origins-of-life research is to determine how amino acids evolved into peptides, or small chunks of protein, in prebiotic times. The formation of a peptide bond between two amino acids requires the elimination of water; therefore, water is often heated to evaporation to drive this reaction forward. However, cyclic dipeptides known as diketopiperazines (DKPs) are typically the major products and hinder chain growth as they are thermodynamic sinks. Previous work has shown that mixing amino acids with hydroxy acids such as glycolic acid or lactic acid can circumvent this issue by forming copolymers known as depsipeptides. These oligomers begin to resemble biological peptides when subjected to repeated cycles of hydration and evaporation. The purpose of our research was to develop and optimize an attenuated total reflectance – Fourier transform infrared (ATR-FTIR) spectroscopy method to determine the relative amounts of amide and ester bonds in depsipeptide copolymers. Depsipeptides were formed by subjecting glycine and lactic acid mixtures to various cycles of hydration and evaporation. Both amide and ester functional groups were monitored as a function of cycling. FTIR spectra were compared to matrix-assisted laser desorption/ionization – time-of-flight mass spectrometry (MALDI-TOF MS), which is typically used to investigate oligomer lengths and amino acid compositions. Differential FTIR, in which monomer signals were subtracted from copolymer signals, was also used to identify both the amide and ester content within this model prebiotic reaction.

SERMACS 154

Vitamin K2 analogs in toxin-induced and genetic models of Parkinson's disease

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Parkinson's disease (PD) is a common neurodegenerative disorder caused by the degeneration of dopaminergic neurons. While the exact degradation mechanism remains poorly understood, evidence has shown that the progression of PD is linked to mitochondrial dysfunction. In particular, several familial forms of PD arise due to mutations in important genes for mitochondrial homeostasis. One such early-onset form of PD results from a mutation in PINK1, a protein involved in mitochondria quality control that is responsive to the mitochondrial membrane potential. Previous research, completed by Vos et.al, had shown that vitamin K2 (VK2) in *Drosophila* with a *Pink*1 mutation rescued flying ability, stimulated ATP production, and provided continual neuroprotection to the affected mutants. However, VK2 is unable to penetrate the blood brain barrier in humans. Our research pursues neuroprotective VK2 synthetic analogs. We have prepared a series of naphthoquinone derivatives and tested them ex vivo in rotenone-challenged mouse neuronal cells and in vivo in *Pink*1-mutant 76-hour post-fertilization zebrafish. Mild doses of the compounds resulted in increased viability and rescuing zebrafish behaviors. Future work would include optimizing ex-vivo cellular and the zebrafish assays that would provide rapid identification of VK lead candidates for further animal studies.

SERMACS 155

Molybdenum-catalyzed cycloisomerization of alkynyl anilines to indoles

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Indoles are widely produced in nature with significant biological activity including anti-inflammatory and anticancer properties. One synthetic route to indoles is through vinylidene complexes formed by reaction of alkynyl anilines with transitional metal catalysts. The goal of this research is to investigate the use of a molybdenum catalyst in the cycloisomerization of alkynyl anilines to produce substituted indoles.

SERMACS 156

GC-MS measurement of the intermediates of beta oxidation in the lipid bodies of *Brassica napus*

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Brassica napus is an agricultural crop used for the production of food oils. Fats are stored in lipid bodies in the seeds and during germination the fats are mobilized to support seedling growth. It is well known that this lipid metabolism occurs in plant peroxisomes, but there are indications that some lipid metabolism, including beta oxidation, may occur in the lipid bodies themselves. Lipid bodies were isolated from germinating *Brassica napus* and provided with the necessary cofactors to support beta oxidation. Lipids were then extracted from the samples, and methyl esters prepared from the extracted lipids. The fatty acid methyl ester products were analyzed by GC-MS.

SERMACS 157

Investigating the role of chirality in the formation and hydrolysis of model prebiotic peptides

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Proteinogenic amino acids are all L-stereochemistry, except for glycine which is achiral. The question as to why biology chose L over D chirality, or any chirality, is of interest to origins-of-life research. The majority of model prebiotic reactions and meteorites suggest early amino acid mixtures may have contained both L and D forms; therefore, it is unclear how L-stereochemistry emerged. Here, we heated mixtures of amino acids and hydroxy acids to form depsipeptides of varying chirality. Depsipeptides are peptides which contain both amide and ester backbone linkages. Amino acids and hydroxy acids were combined in different stereochemical ratios and all L-forms were 13C-labeled for purposes of differentiation. Post-cycle samples were analyzed by Fourier transform infrared (FT-IR) spectroscopy, matrix-assisted laser desorption/ionization – time-of-flight mass spectrometry (MALDI-TOF MS), and liquid chromatography - tandem MS (LC-MS/MS) to explore differences in depsipeptide polymerization or hydrolysis due to stereochemistry. Analyzing such differences in model primordial earth conditions may help to explain why this chirality preference remains today.

SERMACS 158

Microwave synthesis for materials chemistry labs

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The focus of this poster presentation is the use of microwave (MW) synthesis in the development of undergraduate materials and inorganic labs. Many traditional materials and inorganic lab experiments take a significant amount of time using traditional heating methods, which makes them inaccessible in these teaching labs. Microwave synthetic protocols are easier to perform, takes far less time, and are significantly safer than traditional thermal production methods. These qualities make MW synthesis an incredibly attractive synthetic method for undergraduate teaching labs, where students lack synthetic proficiency and time. By using MWs, students are able to get more out of their laboratory experience. In this research, traditional thermal and MW synthetic protocols are compared in terms of time, quality, and ease of synthesis. Materials with applications in the of fields biological imaging, lighting, and electronics (such as quantum dots, oxide spinels and magnetic particles) are investigated using both methods. The quality of the products are investigated using spectroscopy and microscopy techniques.

SERMACS 159

Synthesis and testing of selective ‘pyrrophen’ systems for visual uranyl (UO_2^{2+}) detection

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Demands for nuclear waste remediation warrant exploration for systems with the ability to selectively bind uranyl, while excluding potentially competing transition metal ions (Co^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, etc). Mixed-donor ligands such as salophen incorporate hard donors and have been studied extensively in this regard, yet soft-donor systems are less familiar. One exception is macrocyclic expanded porphyrins, but synthesis is challenging as they are costly, time-consuming, and less efficient. Coupling features from both expanded porphyrin-type and salen-type systems form a new category of hexadentate ligand that not only favors binding with uranyl over other cations but is also more easily synthesized. The modularity of the benzyl bis(pyrrol-2-yle)phenylenediamine ligand (or ‘pyrrophen’) offers opportunities for tuning steric and electronic features to maximize differentiation among metal complexes. Self-assembly of pyrrophen with UO_2^{2+}, Zn^{2+}, and Cu^{2+} yields a stable hexagonal bipyramidal uranyl complex (UO_2L) and dinuclear-helicate zinc and copper complexes (M_2L_2, M=Zn, Cu) respectively. With further exploration of steric and electronic contributions, a broader comparison of these pyrrophen derivatives can be made to determine which facets create the most effective and selective colorimetric sensor for uranyl detection.

SERMACS 160

Enzymatic dynamic kinetic resolution for the stereoselective synthesis of α-hydroxy ketones

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Thiamine diphosphate (ThDP)-dependent enzymes have been explored for their ability to produce α-hydroxy ketones through benzoin condensation reactions. Two of the most common enzymes for this application have been Benzaldehyde Lyase (BAL) from *Pseudomonas fluorescens* and Benzylformate decarboxylase (BFD) from *Pseudomonas putida*. These enzymes have been successfully employed in benzoin condensations to produce α-hydroxy ketones with high levels of chemo- and enantioselectivity. Less explored, however, is the ability of these enzymes to control the configuration about multiple chiral centers. Previously BAL has been used in kinetic resolutions of racemic substrates to produce α-hydroxy ketones with high levels of enantio- and diastereoselectivity. The limitation of this approach is that the maximum possible yield is 50%, as only one of the substrate enantiomers is accepted by the enzyme. Modifying the reactant so that substrate enantiomers can interconvert would allow for a theoretical yield of 100%, in a so-called dynamic kinetic resolution. This project focuses on developing an enzymatic dynamic kinetic resolution of racemic α-substituted aldoester substrates using the enzymes BAL and BFD. We have successfully synthesized the substrates and cloned the enzymes, with characterization of the enzymes in these reactions forthcoming. The successful completion of this project will result in an efficient and environmentally-friendly approach to producing synthetically valuable α-hydroxy ketone products.

SERMACS 161

Design and synthesis of self-complexing multi-substituted boronic acid derivatives as potential selective glucose sensors

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While large scientific institutions have access to high-tech and expensive instrumentation to determine sugar content in blood, the average diabetic person has only protein test strips to rely on as their measuring tool. The advantages of using an organomolecule rather than a protein are the increased shelf life due to a higher thermodynamic stability and the potential for a cheaper product. Our goal is to synthesize an organomolecule that will selectively interact with carbohydrates (glucose) to give a measurable response just like the test strips. The targeted multi-substituted boronic acid derivatives will give a ranged color changing response that will be visible to the naked eye rather than measured with an electric current through a niche device such as with the protein strips. The binding geometry of two boronic acid groups attacking the differently positioned hydroxyl groups on a single sugar molecule can be exploited to give selective sensing. To synthesize these sensors, a reaction of a bis-aldehyde derivative and a boronic acid amine can produce the targeted imine in very high yield. The synthesized reaction can be completed in a matter of hours using inexpensive and commercially available solvents and reagents.

SERMACS 162

Oxidative copper(II) catalyzed alcoholysis of 3-hydroxyflavone: Synthesis, characterization and structure of 3-hydroxy-2,3-dialkoxy-2-phenylchroman-4-ones and 3-dihydroxy-2-alkoxy-2-phenylchroman-4-ones

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Flavanols and quercetin have been implicated in several therapeutic applications due to their ability to release carbon monoxide upon irradiation with UV-light. Metals such as copper have been shown to catalyze this process. In an effort to produce a copper-flavonate complex to study the CO-releasing abilities of novel heteroleptic copper(II) complexes, 3-hydroxyflavone was reacted with $CuBr_2$ in methanol, ethanol, and isopropanol. Instead of isolating the desired coordination complex, a collection of coumarin-based acetals and hemiacetals were isolated. In most cases, the 3-hydroxy-2,3-dialkoxy-2-phenylchroman-4-ones (hemiacetals) were isolated in higher yield (dimethoxy 0.044 g, 27%; diethoxy 0.14 g, 86%; isopropoxy 0.087 g, 53%) than the 3,3-dihydroxy-2-alkoxy-2-phenylchroman-4-ones (acetals). Alcoholysis of the coumarin ring occurred through *anti*-addition to produce racemic mixtures of the dialkoxy coumarin hemiacetals. The monoalkoxy coumarins acetals were also isolated as a racemic mixture. While the synthesis of four of the six complexes have been previously reported, the isopropoxy derivatives are reported here for the first time, as well as the single crystal X-ray structure of five of the six derivatives (excluding the diisoproxy hemiacetal derivative).

SERMACS 163

Cellulose based edible film from soy hull

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Soy hull is an underutilized by-product of the soybean industry. The low cost of soy hull by-product makes it an attractive alternative source for a variety of commercial applications. The purpose of this research is to produce a cellulose based edible film with minimal introduction of chemical additives. Other major components of soy hull, pectin and lignin, also have valuable applications in food and chemical industry. However, we are focused primarily on cellulose. In order to produce the most cost-effective process, different extraction methods to isolate cellulose from soy hull were explored and modified according to outcome. Pectin and lignin were partially or completely removed from soy hull using acid and base extractions. The resulting cellulose rich products were evaluated for film formation. Based on this research, extraction of lignin using NaOH has a promising film forming product with the introduction of less than 5% additives. Pectin and residual water present in this product served as internal plasticizers promoting film formation. Further, as expected, addition of 1% glycerol improved film flexibility, while addition of 1% sodium silicate made the film brittle, indicating the nature of cellulose interaction in the film. Most of the commercially available cellulose films are based on chemically modified cellulose with external additives. Future directions include continued modification of the protocol to reduce waste and increase efficiency for commercial applications of soy hull.

SERMACS 164

Preparation and preliminary catalysis of a viable ruthenium-based olefin hydroarylation catalysis supported by bis(pyrazolyl)acetate

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Olefin hydroarylation–the net addition of the aryl C-H bonds across olefin C=C bonds– is an important process for the preparation of alkylbenzenes, which are utilized in the manufacture of commodity products such as resins, medicines, surfactants and plastics. Several transition metal-based systems have recently been developed to produce alkylbenzenes that operate on metal-mediated C-H activation, which are more atom economical and selective than contemporary methods. A ruthenium base catalyst,

$(BPA)RuPh[P(OCH_2)_3CEt](NCMe)_2$, supported by the facially coordinating tridentate bis(pyrazolyl)acetate (BPA) ligand has been developed by this laboratory that produces styrene and ethylbenzene. Preliminary catalysis studies suggest a stronger penchant for styrene production over ethylbenzene. While the best turnover number for styrene was 2.8 and 1.0 for ethylbenzene at 100 psi at 120°C for 40 hours, to our knowledge this is the first transition metal complex supported by bis(pyrazolyl)acetate to serve in this capacity.Herein we report the synthesis, characterization, and catalytic studies of $(BPA)RuPh[P(OCH_2)_3CEt](NCMe)_2$, as well as our future strategy to improve catalysis.

SERMACS 165

Synthesis of seedless latex emulsions for use in waterborne coatings

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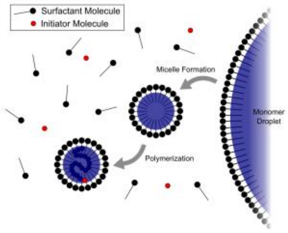
Emulsion polymers have a wide range of applications from waterborne coatings, thermoplastics and adhesives among many others. Emulsion polymerization reactions require one or more hydrophobic monomers stabilized with surfactant dispersed in an aqueous phase. Surfactant molecules play a critical role because at the correct concentrations micelles form and serve as the space where polymerization occurs. Once initiation takes place, and the monomer inside the micelle is consumed, more monomers will continue to enter the micelle allowing for the polymer to increase in size. The termination point of the polymerization reaction occurs when there are insufficient free radicals left in the system or when all monomer molecules have been reacted.

In industrial production environments, both seeded and unseeded latex emulsion polymerizations are common. Seeded emulsion polymerizations utilize smaller latex particles as nucleation points for the reaction. This process results in good control of particle size with low polydispersity. Production of the seed latex requires a separate reaction, which involves more reactor time and supply chain resources. An unseeded polymerization emulsion allows for the synthesis of latex particles without the need of seed latex. The goal of this research project was to create a reproducible seedless process that yields an aqueous emulsion with chemical and physical characteristics required for use in waterborne coatings.



SERMACS 166

Fluorescent responsive behavior of a soluble adenine-functionalized polythiophene synthesized via direct arylation polymerization

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Introducing functional groups at the terminus of the side chains of conjugated polymers is widely used to enhance their functionality or improve morphological or photophysical properties. Here, we incorporate adenine functionality, a nucleobase offering well-defined hydrogen bonding, into the side chains of an alkyl thiophene-based alternating copolymer that is synthesized via direct arylation polymerization (DArP). The synthetic methodology identifies and overcomes catalyst interference effects of adenine through Boc-protection of the adenine functionalized thiophene monomer and takes advantage of DArP being an atom efficient, environmentally-friendly synthesis method that runs under mild reaction conditions. In addition, solubility issues are surmounted by introducing additional side chain and backbone flexibility using the comonomer 3,3',3'',4'-tetrahexyl-2,2':5',2''-terthiophene (abbreviated as tT_{4h}). This design change makes the deprotected, alternating copolymer (T_{Ad}-tT_{4h}) soluble in common organic solvents. Relative to the non-functionalized homologue (T-tT_{4h}), thermal analysis show a ~57 °C increase in the glass transition temperature of the adenine-containing polymer, which is attributed to interchain hydrogen bonding interactions and an increase in main chain stiffness. This H-bonding-induced chain rigidity is also consistent with a smaller Stokes shift of T_{Ad}-tT_{4h} compared to T-tT_{4h}. Finally, fluorescence spectroscopy shows strong fluorescence quenching – as high as 91% – upon addition of Cu^{2+} ions, with nearly full recovery of the fluorescence emission upon washing with disodium EDTA solution. In total, DArP provides an effective route to nucleobase-functionalized polythiophenes, which may find utility in sensing and diagnostic applications, as well as in organic electronics.

SERMACS 167

Exploring multi-tiered conjugated oligomers as models for conjugated materials

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The electronic structure of semiconducting pi-conjugated materials continues to attract interest through both experimental and theoretical approaches. To explore the effect of intermolecular interactions between conjugated systems, we have embarked on an examination of the electronic structure of a series of molecules in which conjugated segments are held in a stacked manner. This arrangement mimics the packing of conjugated molecules in the solid state. Previous work in this area made use of [2.2]paracyclophane to scaffold pairs of either oligo(phenylene vinylene) or oligo(phenylene ethynylene) segments in a stacked arrangement. The compounds consisting of pairs of conjugated segments fluoresce at longer wavelengths than the isolated, unstacked oligomers. This emission indicates the presence of a low-energy excimer-like state in these compounds that arises from the interaction of the pi-systems of the two segments. An expansion of this work is underway to include compounds with three, four- and five-segments in a stacked architecture. These multi-tiered molecules provide better models for the extended nature of the excited states and charge carriers in conjugated materials. Pseudogeminal disubstituted [2.2]paracyclophanes and 1,8-disubstituted anthracenes have been prepared as scaffolds to hold conjugated segments in a stacked fashion and serve as building blocks for preparation of the multi-tiered structures.

SERMACS 168

Crystallization-driven self-assembly of cationic cobaltocenium-containing block copolymers

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Self-assembly of amphiphilic block copolymers is one of the most fascinating approaches to the creation of nanoscale micelles with core-corona architectures and a broad range of morphologies. Among self-assembly, Crystallization-Driven Self-Assembly (CDSA) of block copolymers has a unique ability to control 1D and 2D nano-objects. Metallopolymers, polymers containing metal centers in the main chain or pendant side chains, have also been featured in CDSA processes. I will present the CDSA behavior of a metallo-polyelectrolyte block copolymer, polycaprolactone-*b*-poly(cobaltocenium amidoethyl methacrylate) (PCL-*b*-PCoAEMA). Driven by the crystallization of PCL and the electrostatic interactions within charged polycobaltocenium segments, these block copolymers can self-assemble into various two-dimensional platelets from hexagons to diamonds in protic solvents.

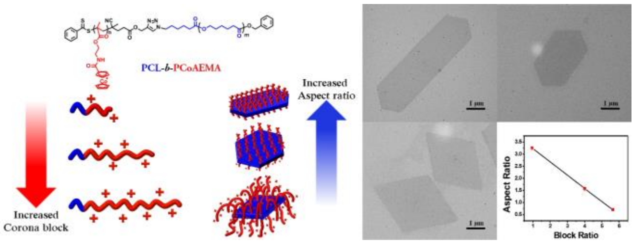

Figure 1. Two dimensional nanostructures from metallo-polyelectrolyte block copolymer by CDSA

SERMACS 169

Systematic exploration of structure–property relationship and thermotropic liquid crystallinity of branched side chain poly(3-alkylthiophene)s

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Semiconducting conjugated polymers bearing branched side chains have attracted significant attention as a result of their ability to increase the solubility and melt processability of a material. However, a systematic exploration of the effect of the structure of such side chains on the properties of the materials has not been conducted. In this study we sought to gain an understanding of the relationship between the length of the side chain and location of the branch on the properties of poly(3-alkylthiophene)s. The location of a branch point has dramatic effects on the assembly of polymer chains in the solid state, which in turn influences the charge transport of the material. Through this strategy we also expect to lower the melting point of the polymers to explore potential access to thermotropic liquid crystalline phases. In order to explore these relationships and the possibilities of thermotropic liquid crystalline phases, three different series of polymers were synthesized; methyl-branched poly(3-hexylthiophene) and poly(3-decylthiophene) analogs, and polythiophenes bearing semifluoroalkyl side chains.

SERMACS 170

Biomaterial-assisted delivery of lysostaphin to eliminate *Staphylococcus aureus* infection in non-union bone defects

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Nonunion bone defects are a common clinical scenario accounting for over 600,000 hospital cases per year totaling over 5 billion dollars in costs. The current standard of care includes surgical placement of bone grafts to facilitate healing. However, bacterial infection of bone grafts significantly increases implant failure rates, often leading to corrective surgery. Lysostaphin is an endopeptidase that has shown promising anti-staphylococcal activity. Yet, the lack of a delivery vehicle that would enable sustained, high dosing of lysostaphin at the injury site pose some limitation to its wide-spread use. Here we demonstrate a hydrogel-based implant prepared from four-armed poly(ethylene glycol) macromer for the delivery of lysostaphin to prevent (or cure) *S. aureus* infection at the site of bone injuries.

SERMACS 171

Mechanistic and kinetic studies of asustainable catalysis of a conjugated polymer by an enzyme

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We recently reported the observation that bacterial cell wall degrading enzymes are also capable of catalyzing the formation of "synthetic-type" polymers with potentially useful optical properties. This catalysis occurs in water under conditions that normally do not support efficient polymerization of acetylene substrates. Because these catalysts are derived from a sustainable source and the reaction takes place in water, it may represent a "green" chemical route to obtain conjugated polymers. This is in contrast to traditional synthetic-type polymerization reactions that often involve transition metals, organic solvents, and/or toxic radical generating substances.

We are specifically studying 2-ethynylpyridine polymerization by hen egg white and bacteriophage T4 lysozymes (HEWL and T4L) with three primary goals: 1) structural characterization of the polymer products, 2) optimization of the reactions for enhanced rate of synthesis, and 3) determination of catalytic mechanism. To address these aims, we have used liquid chromatography to separate and purify the polymer products and are investigating their structures using NMR and other methods. In addition, we are using modern X-ray crystallographic and multinuclear NMR techniques to determine the structures of enzyme-substrate, enzyme-product, and candidate enzyme-transition state complexes. Progress toward HEWL (via crystallography) and T4 lysozyme (via NMR) structures bound to product and product-analogs will be described as will other biophysical methods (CD, ITC, and UV/Vis) for analyzing theses complexes and studying the kinetics of polymerization. Our results indicate that conserved sidechains and substrate binding grooves important for natural peptidoglycan hydrolysis also utilized for these orthogonal carbon-carbon bond forming reactions. The implications of this convergence in SAR between these quite different chemistries will be discussed in terms of the potential for optimizing this reaction for commercial applications. This work integrates traditional structural biology/biochemistry with material science and thus affords unique opportunities for interdisciplinary training of undergraduate researchers.

SERMACS 172

Intimate and permanent ligating of photoresponsive and thermoresponsive polymers on plasmonic nanoparticles with switchable self-assemblies, optical properties, and catalytic activities

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The ability to dynamically organize functional nanoparticles (NPs) via the use of environmental triggers (temperature, pH, light, or solvent polarity) opens up important perspectives for rapid and convenient construction of a rich variety of complex assemblies and materials with new structures and functionalities. In this talk, I will present an unconventional strategy for crafting stable hairy NPs with light- as well as thermal-enabled reversible and reliable self-assembly and tunable optical and catalytic properties. The key to our strategy is to rationally design amphiphilic star-like diblock copolymers comprising inner hydrophilic blocks and outer hydrophobic stimuli-responsive blocks as nanoreactors to direct the synthesis of monodisperse plasmonic NPs *intimately* and *permanently* capped with stimuli-responsive polymers. The size and shape of hairy NPs can be precisely tailored by modulating the length of inner hydrophilic block of star-like diblock copolymers. The *perpetual* anchoring of stimuli-responsive polymers on the NP surface renders the attractive feature of self-assembly and disassembly of NPs on demand using stimuli of different wavelengths or temperature, as revealed by tunable surface-plasmon resonance absorption of NPs and the reversible transformation of NPs between their dispersed and aggregated states. By extension, the star-like block copolymer strategy enables the crafting of a family of stable stimuli-responsive NPs (e.g., pH-sensitive polymer-capped magnetic, ferroelectric, upconversion, or semiconducting NPs) and their assemblies for fundamental research in self-assembly and crystallization kinetics of NPs as well as potential applications in optics, optoelectronics, magnetic technologies, sensory materials and devices, catalysis, nanotechnology, and biotechnology.

SERMACS 173

RF plasma treatment of cellulose materials to fabricate paper-based analytical devices

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RF plasmas have been used extensively for thin film deposition and etching in the fabrication of microelectronic and photonic devices. These methods can be applied to cellulose (paper) and other porous substrates to alter surface and bulk properties and thereby create various analytical devices with applications in microfluidic devices and structures. For example, fluorocarbon plasma deposition converts the hydrophilic fiber surfaces on and in the paper into a hydrophobic network. Subsequent oxygen plasma exposure can remove the fluorocarbon film in specific regions, thereby forming channels in the bulk paper. This approach overcomes many of the limitations experienced with the current method to form paper-based devices, which involves stacking of paper sheets to generate channels in the bulk paper.

SERMACS 174

Electrospun polyelectrolyte fibers as nanoreactors

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Electrospun polyelectrolyte fibers (EPFs)have large surface area and rich functional groups (e.g. carboxylate and amine groups) that make them excellent candidate to produce various nanopartices in fibers. In this presentation, the fabrication of metal and metal oxide nanoparticles in EPFs and the applications in energy storage and catalyse are discussed.

SERMACS 175

Synthesis of phosphonium salts and their potential as cationic ligands

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We have synthesized a series of bis-heteroaryl phosphonium salts for use as cationic bidentate ligands. The challenges and insights into their synthesis are presented. Attempts to complex this ligand with a metal center have generated interesting salts, whose single crystals were studied by x-ray diffraction.

SERMACS 176

Chemistry of phosphaethynolato with early transition metals

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Is this presentation I will discuss the chemistry of the PCO and AsCO anion with various transition metals. Apart from its ability to be ambidentate, this class of ligand can undergo coupling, as well as deliver (in some case selectively) P and As atoms. We will discuss a series of early transition metals such as Sc, Ti, and V, and understand how such scaffolds can react with low and high-valent forms of these metal ions.

SERMACS 177

Bond activation reactions by boryl pincer complexes

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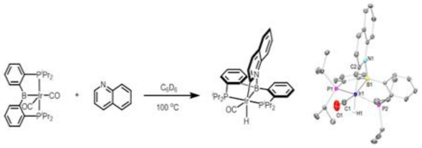
Pincer complexes of late transition metals have been widely used in studies of stoichiometric and catalytic activation of carbon-hydrogen and carbon-heteroatom bonds. Our group recently demonstrated the impressive potential of Ir pincer complexes in C-H bond borylation of terminal alkynes and arenes. Studies of transformations that involve metal-boryl intermediates where the boryl group originates from a reagent have led us to consider alternative approaches to bond activation that incorporate boryl donors into supporting pincer ligands. We have discovered that activation C-H and other bonds of heteroatom-containing substrates is possible with selectivity controlled by the coordination of the heteroatom to the metal-bound boryl donor. The presentation will focus on the stoichiometric reactions and on the current efforts to optimize this type of reactivity for catalytic applications.



SERMACS 178

Benzoxaphospholes as ligands for transition metals

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Benzoxaphospholes (**R-BOPs**) are exciting class of luminescent heterocylic conjugated compounds featuring phosphorus-carbon double bonds. During our efforts to produce higher analogues using late metal catalyzed coupling strategies, we have isolated and structurally characterized unusual dimetal complexes of R-BOPs with metals such as palladium and platinum. The reactions to produce these materials, as well as reactions to produce other types of complexes, will be presented. New routes to **R-BOPs** using the unique reagent Na[OCP] will also be discussed.

SERMACS 179

Lessons in phosphine ligand design: Best laid plans often go astray

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We designed and synthesized a binucleating tetraphosphine ligand to study dirhodium complexes for bimetallic cooperativity in hydroformylation catalysis. This turned out to be one of the best examples of bimetallic cooperativity in homogeneous catalysis (*Science*, 1993). Subsequent *in situ* pressure/temperature IR, NMR, and mechanistic studies on the dirhodium P4 catalyst revealed that the P4 ligand chelate effect was not strong enough, which led to loss of one of the rhodium centers and deactivation of the catalyst over time. The P4 ligand was redesigned with a much stronger chelate effect, which entailed about five years of synthetic efforts (*Inorg. Chem.*, 2014). The dirhodium catalyst based on this new P4 ligand appeared to have all the characteristics of a fantastic catalyst based on the initial *in situ* IR and NMR studies. Unfortunately, the actual hydroformylation results were quite variable and the catalyst suffered from what we believe are Rh-induced phosphine-ligand fragmentation reactions due to the presence of additional reactive P-aryl linkages in the P4 ligand. This would be a very sad story if not for testing one more catalyst based on the new stronger chelating P4 ligand. BINGO!

SERMACS 180

New catalysts and strategies for the enantioselective coupling of nucleophiles and unsaturated hydrocarbons

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The discovery of new chemical reactions that enable the intermolecular coupling of reagents for the rapid assembly of molecules with increased complexity, particularly those within new chemical space, is critically important. Especially valuable are catalytic enantioselective transformations that proceed with a high degree of atom economy. My group has developed a family of electron-deficient phosphino-oxazoline (PHOX) ligands for the Pd-catalyzed enantioselective addition of aliphatic amines (hydroamination) and pro-enolates (hydroalkylation) to acyclic 1,3-dienes and enynes. The unsaturated amines and carbonyls obtained through these hydrofunctionalizations are not easily attained through competing technologies and facilitate the construction of high-value downstream molecular targets.

SERMACS 181

Suzuki–Miyaura and Buchwald–Hartwig reactions utilizing a set of complementary imidazopyridine phosphine ligands

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Palladium-catalyzed cross-coupling reactions have become ubiquitous tools in the synthesis of otherwise inaccessible compounds because of the efficient, catalytic nature of these styles of reaction. The development of novel phosphine ligands to achieve the cross-coupling of substrates that are generally unreactive under standard conditions has developed into an extremely important area of research in the field of organometallic chemistry. Specific procedures have been previously developed to allow for many reactions to occur, but several challenges remain for both the Suzuki-Miyaura reaction as well as the Buchwald-Hartwig amination. Herein, we show the use of imidazopyridine phosphine ligands ("JagPhos I" and "JagPhos II") previously developed by our research group as a highly efficient solution to some of the challenges faced in these two reactions. Investigations into the synthesis of various bi(hetero)aryls and substituted amines utilizing these two ligands led to successful reactions proceeding in moderate to high yields.

SERMACS 182

Mechanistic studies and catalytic applications of conformationally flexible phosphine ligands

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Phosphorus ligands provide a highly flexible platform that can be used to modulate the course of metal-catalyzed reactions. Our group has a long-standing interest in developing an understanding of the role of steric and electronic properties of phosphines in catalyst performance. Phosphine ligands with conformationally flexible substituents, such as neopentyl or benzyl, afford catalysts with interesting synthetic applications. The highly flexible trineopentylphosphine ligand affords catalysts that are highly active for the C–C and C–N coupling of sterically demanding substrates. In contrast to sterically rigid ligands, such as di-*tert*-butylneopentylphosphine, trineopentylphosphine provides a highly active catalyst for coupling of sterically demanding aryl halides and aryl amines. The neopentylphosphine family of ligands provides for fine control of the product selectivity of Heck couplings of cyclic alkenes to afford either the kinetically or thermodynamically preferred olefin product. Neopentylphosphines readily form metallacyclic complexes by C–H activation of the neopentyl substituent. This process can serve as a catalyst deactivation pathway, but also can afford complexes with interesting catalytic applications. The $[Pd(\mu\text{-}\kappa^2\text{-}O,O\text{-OAc})(\kappa^2\text{-}C,P\text{-}(t\text{-Bu})_2PCH_2C(Me)_2CH_2)]_2$complex selectively affords *E*-5-aryl-2-en-4-yn-1-ol products in good yields under mild conditions with high chemo-, regio-, and stereoselectivity. Catalytic applications and mechanistic studies will be presented along with new adventures in phosphine synthesis.

SERMACS 183

Phosphine center stage: Profile of a leading and supporting actor in organometallic catalysis

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Organophosphorous compounds are arguably the most ubiquitous and well-studied ligand class in transition metal chemistry, being best known for their role as spectator ancillary ligands. Recent work in the Popp laboratory has revealed ways in which the phosphine moiety may become more intimately involved in catalysis. This presentation will focus on two late-transition-metal-catalyzed reactions: vinylphosphine hydroboration by rhodium and vinyl arene boracarboxylation by copper. The outcome of the former reaction is highly dependent on the phosphine substrate while the latter reaction can be modulated by exogenous phosphine ligand. Synthetic and mechanistic implications will be discussed.

SERMACS 184

Measuring pH in tumors with plain radiography by a hydrogel-based biosensor

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An injectable biosensor was developed to measure tumor pH using plain radiography to study cancers and effectiveness of treatments, *in vivo*. Plain radiography (X-ray imaging) is a rapid, noninvasive imaging technique which is widely used in diagnosis and monitoring of many diseases and conditions. However, plain radiography is blind to most local chemical concentrations that influence disease pathology. Here, we describe an approach to radiographically measure local tumor pH, in order to study cancer pathophysiology and monitor disease response to treatment. The pH in a tumor is heterogeneous with acidic regions typically in the range of 6.5 to 6.9, compared to ~ 7.2 to 7.5 in normal tissue. This acidosis results from a combination of anaerobic glycolysis in hypoxia environments, poor clearance of acidic metabolic products *e.g.* lactic acid, and inflammation. This local acidosis is believed to both be an indicator of dormant regions that are more resistant to therapies and a contributor to metastasis and influence immune response. We are designing a sensor that can be injected into tumors during needle biopsy procedures and or procedures to add markers for image-guided therapies and provide serial measurements at regions in the tumor used for initial diagnosis and grading. The sensor consists of a porous metal sleeve holding a pH-responsive hydrogel with an embedded radiodense tantalum (Ta) bead, all fitting within a breast cancer biopsy marker needle. Deswelling of the hydrogel at low pH causes the tantalum bead to move within the sleeve, and this motion can be measured with plain radiography. The sensor has a range of pH 4 – 8 with a precision of 0.065 pH units. Thus, the hydrogel-based biosensor provides a way to measure pH in tumors using plain radiography.

SERMACS 185

What's really in your e-cigarette? Analysis of psychoactive drugs found in over-the-counter vape products

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Due to the high number of serious and life-threatening side effects reported from use of an over-the-counter vape product called "Magic Puff Hemp Disposable", the authors wanted to determine the chemical composition of this product. Herein we report the active ingredient of "Magic Puff", later sold under the name "Butterfly CBD". The identified chemical is not CBD (cannabidiol), but is SGT-78, an illegal schedule 2 drug. Other over-the-counter products were analyzed and some were found to also contain illegal or potentially dangerous compounds.

SERMACS 186

Application of low-cost embedded computers and 3D-printing for automated titrimetric analysis

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In a drinking water treatment plant, alkalinity, hardness, and iodometric titrations are conducted daily to determine water quality parameters that inform how a superintendent will adjust the addition of treatment chemicals for that shift and that day. These three parameters are typically determined using potentiometric or colorimetric titration techniques. Liquid handling and end-point determination for titrimetric analytical methods are crucial for producing accurate and reproducible results. In alkalinity, hardness, and iodometric titrations, determination of the end point is one of the key factors in reproducibility between analysts. In short, different analysts visually detect different end points of the titrations. In a drinking water treatment plant, this can be a significant source of variability and thus cost the superintendent more in operating funds. In addition, titrations are core analytical procedures still used in quality control laboratories.

In this research, an automated potentiometric and colorimetric titrimetric analyzer has been developed using 3D printing and open-source, Raspberry Pi single-board computers. The automated titrator was developed as part of an automated pipetting system. The automated pipetting system can deliver 5 µL of the solution with an accuracy measured as 98 – 102 % mean percent recovery and precision measured as 5 % relative standard deviation. The accuracy and precision values mean that the automated pipet would also serve well as a titration system if a suitable detector and analysis algorithm could be developed. In this presentation, automated pipetting technology is adapted to build an automated titrator system for potentiometric and colorimetric titrations using commercial-off-the-shelf components. The results for the automated analysis of alkalinity, hardness, and iodometric titrations will be presented and include a statistical comparison to the standard manual titration methods in real-world water samples and bulk hypochlorite solution samples.

SERMACS 187

Redox-based fingerprinting method to sense antioxidants

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Redox processes are vital in living organisms, but they are also responsible for negative effects in the body. Oxidative stress has been proposed as a cause for multiple ailments, so antioxidants are in common use in many nutritional supplements. Oxidation is also a major pathway to product spoilage, so antioxidant preservatives are common in food technology as well. Detection of antioxidants is an interesting analytical challenge because of their extreme variety in chemical structure and properties, so the design of specific sensors is difficult to achieve. We approach this problem using multivariate analysis and pattern recognition methods. We constructed redox-based receptors using an organic redox-active dye, in water at neutral pH, to provide a reporter for the interaction of these reducing agents. 2,6-Dichloroindophenol, an organic dye that is bleached upon reduction, was used to develop an environment sensitive to substances with antioxidant properties. The process can be easily followed spectrophotometrically. Taken together, the extent and rate of dye bleaching associated carry information on the nature and concentration of the antioxidant. Measurements were carried out on 384-well microplates. The spectroscopic data obtained was interpreted using pattern recognition algorithms (principal component analysis and linear discriminant analysis) to detect and differentiate these reducing agents qualitatively at concentrations in the millimolar range.

SERMACS 188

Novel aptamers for serotonin and dopamine sensing on field-effect transistors

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The ability to sense serotonin, dopamine, and other important, small, neurochemical molecules *in vivo* will enable us to probe their complex influence on mood and behavior. Real-time, high-resolution *in vivo*neurochemical sensing is impeded by a lack of sensors capable of simultaneously measuring several physiological analytes and their interactions in the brain at relevant spatiotemporal scales. These measurements can give insight into neuronal interactions within chemical signaling pathways, but necessitate development of miniature, multiplexed, sensitive, and selective neuroprobes.

Eight novel aptamer sequences have been isolated by systematic evolution of ligands by exponential enrichment (SELEX) and demonstrated selectivity for the neurotransmitters serotonin and dopamine. We have characterized these sequences functionalized to FET biosensors as candidates for sensitive and selective neurotransmitter detection *in vivo*. Elucidating the aptamer structures on subsequent FET biosensor performance will inform the screening for aptamers selective to other small molecules found in the brain such as neuropeptides and steroid hormones.

SERMACS 189

Analysis of heavy metals and antioxidant capacity in Slippery Elm bark samples

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Slippery Elm (Ulmus rubra also known as “Indian Elm”) inner bark is used in herbal medicine (both in human and in veterinary medicine) and the concentrations of metals (particularly some heavy metals) in such herbal treatments are important because they may influence people and animals frequently using these treatments.

In this study, samples of Slippery Elm bark powder from four different suppliers were homogenized and fully digested/dissolved (by a simple wet acidic digestion procedure). The concentrations of several heavy metals in these samples were determined by graphite furnace atomic absorption spectrometry (GF-AAS) and inductively coupled plasma – optical emission spectrometry (ICP-OES). Additionally, the antioxidant capacity of Slippery Elm bark powders (extracts), total phenolic content and total flavonoids content were determined. The obtained analytical results will be presented and compared.

SERMACS 190

Implantable hydrogel-based synovial fluid ph sensor to detect hip infections using X-ray imaging readout

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We are developing a hydrogel-based sensor that attaches to prosthetic hips prior to implantation and measures pH in the joint fluid in order to detect, monitor, and study infection. Hip replacement surgeries are common procedures improving the mobility and lives of millions of people worldwide. Although the surgeries are generally successful, about 1% of prosthetic hips become infected (with higher rates for patients with traumatic injuries, immunosuppressed states, diabetes, and other risk factors). Bacteria colonizing the implant surface form biofilms that are resistant to antibiotics and the host’s immune system; if the infections are not detected and treated promptly with antibiotics and surgical debridement, device removal is almost always required to treat the infections. Thus, early detection is key to successful management. If infection is suspected, the joint is aspirated and the synovial fluid analyzed to find infection biomarkers (such as CRP, alpha-defensin, leucocyte counts, and low pH/high lactate concentrations). This analysis adds confidence to the diagnostic of infection (avoiding unnecessary surgeries), but this aspiration is painful, performed by a radiologist under fluoroscopy or ultrasound guidance, and is impractical for routine screening or serial monitoring during treatment. Here we describe a synovial fluid sensor for non-invasive early detection and monitoring of hip infections using plain radiography (X-ray imaging) which is already routinely acquired during patient follow up visits. The sensor consists of a pH responsive hydrogel made of polyacrylic acid and the change in length of the hydrogel was determined from the radiograph by measuring the position of a radio-dense tantalum bead embedded in the hydrogel. The hydrogel sensor could also be developed to detect C-reactive protein (CRP) levels for early detection of infection. Thus, the developed sensor could be used as a potential X-ray imaging functional chemical sensor.

SERMACS 191

Development of a low-cost liquid delivery system using Raspberry Pi and 3D-printing

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Liquid handling and standards preparation in analytical methods is crucial for producing accurate and reproducible results. Pipetting is one of the most common steps in liquid handling and good pipetting technique is required for minimization of variability. However, consider a case where people such as drinking water treatment plant (WTP) operators who may not have formal analytical training are running daily routine analytical tests. Differences in pipetting technique could be a major source of variability in test results. To address the issue of precision and accuracy in pipetting, automation of the technique might be an appropriate solution. Moreover, automation of the pipetting can reduce the effort and time in making standard solutions.

In this research, an automated pipet pump was developed using a Raspberry Pi single-board computer, low-cost stepper

motors/drivers, and 3D printed syringe pumps. The automated pipet can deliver 5 µL with an accuracy measured as 101% mean percent recovery and precision measured as < 5 % relative standard deviation. Different size syringes can be easily replaced to deliver the volumes needed and a Peltier based cooling system is implemented, which can cool the syringe to below 4°C to improve the stability of thermolabile compounds in the solution. The presentation outlines the development of simple, low-cost automated pipette – EZ-AutoPipete. The quality-control tests and statistical comparisons between different pipetting techniques will be presented.

SERMACS 192

X-ray Excited Luminescence Chemical Imaging (XELCI) of implant associated bacterial infection by a chromoionophore based pH sensor

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We describe a coating on implanted orthopedic implants that enables high spatial resolution, low background measurements of local pH for studying implant associated infections. The coating comprises a layer of Gd_2O_2S:Eu scintillators that generate 620 nm and 700 nm luminescence when irradiated by an X-ray beam, and a pH-sensitive film containing Chromionophore III which covers the scintillators and alters the luminescence spectrum. A focused X-ray beam irradiates one spot on the implant and the spectrum escaping through the tissue is measured to determine local pH; and image is formed by scanning the X-ray beam across the surface and measuring pH point-by-point. This provides a high-spatial resolution measurement, with low background and surface specificity from the pH indicator. The primary application is to study, detect, and monitor implant-associated infections. Detection and treatment of implant associated infections is challenging since the clinical symptoms are delayed or absent at early stages. At later stages, the bacteria form mature biofilms with dormant and low pH regions which are highly resistant to antibiotics and the host's immune system. Therefore, rapid, effective and in situ infection diagnosis will reduce the risk and costs from infection and surgical treatments.
In preparatory work, thin films of Chromoionophore III were prepared and pH sensitivity of the films was experimented between pH 3 and 9, controlled by the Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate additive amount in the cocktail mixture. These films were then imaged with XELCI to develop the calibration curve for pH imaging. A pH calibration curve can be obtained by taking into account the intensity ratios of 620nm and 700nm two emission peaks of the scintillator particles. We monitored pH sensitivity and reversibility by in vitro studies for our pH sensor. Later the orthopeadic plates will be coated with both scintillator layer and the pH sensitive film for imaging. A reference region can also be incorporated concerning spectral distortion from wavelength- dependent absorption and scattering in the tissue.
In conclusion, this sensor constructed based on lipophilic Chromoionophore III dye will be a promising method for monitoring implant associated infection and detect infections early by imaging pH. It is also a potential way of monitoring cations and anions of interest at the infection site by incorporating an ionophore to the cocktail mixture.

SERMACS 193

Sensing of penicillins and cephalosporins using a pamam–calcein complex in neutral buffered water

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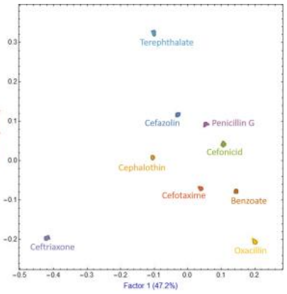
Antibiotics are used for human and animal diseases, and they are also added to animal feed to improve growth rates and feed efficiency. These contribute to the rising number of multi-resistant bacteria. Penicillins and cephalosporins are two of the most widely used antibiotic classes for both humans and animals. They are also structurally similar, with a β-lactam ring and at least one carboxylate group, similarities that make them hard to differentiate from each other. Thus, there is need in the detection of this family of antibiotics appearing in environmental fluids.
Our group has had success in using poly(amidoamine) (PAMAM) dendrimers as supramolecular hosts in carboxylate sensing applications. Such hosts can establish electrostatic and H-bonding interactions with a variety of anionic species, among which organic carboxylates, in addition to weaker hydrophobic interactions which may be relevant in binding antibiotics.
We became interested in exploiting these interactions for the detection of antibiotic analytes in water through optical spectroscopy. However, such interactions are hard to use analytically because neither the antibiotics nor the PAMAM receptors have detectable signals in the non-interfering visible region of the spectrum. We circumvented this problem by utilizing a dye-displacement assay based on PAMAM-calcein complexes. Analytical data was interpreted using pattern recognition algorithms to recover discriminatory power. In neutral aqueous HEPES buffer, we first formed a complex between a G5 PAMAM dendrimer and calcein, an organic dye. Then, an antibiotic was introduced, which caused dye displacement from its complex with PAMAM. The displacement was monitored through absorbance and fluorescence techniques. Linear discriminant analysis (LDA) was then used for data interpretation, to discriminate among these carboxylate analytes.



SERMACS 194

Implantable fluidic sensor for non-invasive measurement of tibial plate strain with plain radiography

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We describe a passive fluidic sensor for non-invasive measurement of tibial orthopedic plate strain, read using plain radiography. Bending of the tibial orthopedic plate, fixed on a fractured tibia with an unstable fracture under load presses an integrated lever upon a fluid reservoir which forces a radiopaque fluid (Cesium acetate 85% w/w%) through a micro channel. The degree of plate bending indicates by the change in fluid level within the channel. In early stages, the load is mostly supported by orthopedic plate and it will tend to bend more than later stages where load is mainly supported by the healing bone (fracture callus). As the healing progresses, bending of the plate decreases, therefore the fluid displacement.

There are around 2 million fracture fixation surgeries occur annually in United states, five to ten percent go on to non-unions. The risk factors include infection, mechanical instability, osteoporosis and etc. Among these, tibial fractures are the most frequent long-bone fractures and most common site of bony nonunion. Therefore, physicians need objective methods to evaluate when a fracture fixation is safe to resume weight- bearing. They routinely acquire plain radiographs to show the hardware and fracture callus as a method of diagnosis and evaluation. However, these grey scale images are ineffective in fully assessing the mechanical properties of the fracture callus. The fluidic sensor was experimented on a fractured Sawbones® tibia mimic and on a human cadaveric tibia with an unstable fracture by monitoring the fluid displacement (mm) vs the axial applied force (N). The experiment showed a fluid displacement of 1 mm for applied load of 100 N. Reproducibility of the fluidic sensor was examined by executing five loading and unloading cycles while fluid level within the channel was tracked with photographic images and plain radiography. The hydro-mechanical action amplifies the signal from the plate bending motion and the radiopaque fluid level is easily observed using plain radiography already employed in routine patient workups. This approach provides bio mechanical information by plain radiography. In addition, the approach is generalizable to detecting pressure from analyte-specific gel swelling for non-invasive *in vivo* chemical measurements using plain radiography.

SERMACS 195

Development of allosteric modulators of MC4R for the treatment of obesity

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The epidemic of obesity is an unparalleled health hazard, characterized by a Body Mass Index of 30 or higher. The accumulation of body fat causing obesity leads to various complications such as hypertension, diabetes, and increased risk of stroke and heart disease. Melanocortin Haploinsufficiency Syndrome, the most common monogenic cause of severe obesity, accounts for up to 5% of known cases. It is caused by a mutation of the melanocortin 4 receptor (MC$_4$R), a G-protein coupled receptor expressed primarily in the central nervous system with a dual function of regulating appetite and energy expenditure. In an attempt to find a therapeutic for obesity, efficacious MC$_4$R orthosteric agonists have been developed by various pharmaceutical companies; however, they cause adverse reactions such as hypertension and tachycardia. In an attempt to avoid adverse reactions, a high throughput screen was performed for allosteric modulators of MC$_4$R, yielding several promising synthetic series. Using the series with highest potential, and a multidimensional iterative parallel synthesis approach, libraries of compounds have been developed around the original lead series in an attempt to increase potency, solubility, and specificity. The compounds were evaluated for potency and selectivity by collaborators in Dr. Roger Cone's lab at Vanderbilt University. Gratifyingly, the first round of library development compounds showed both higher potency and solubility than the lead molecule. Guided by the information gleaned from the first round of libraries, additional libraries with modified cores were developed focusing on potency, solubility, and selectivity. Additional compounds were then synthesized using a mix-and-match approach by combining the best moieties from each library. Testing of the series with modified cores revealed a preference for the original core; however, the mix-and-match approach yielded compounds with improved potency that could be further optimized and developed into a possible therapeutic for the treatment of obesity.

SERMACS 196

Design of agonists of the GABAB receptor from β-amino difluoromethyl ketones

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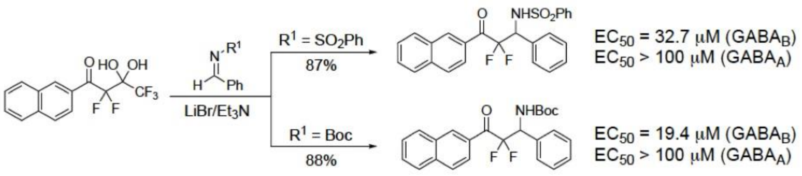
Many of the top selling pharmaceuticals display at least one fluorine atom which has driven the need for new synthetic methods to construct fluorinated organic molecules. Although there are many approaches to create fluorinated and trifluoromethylated structures, methods that produce difluorinated compounds are less developed. Our laboratory has pioneered a strategy to generate difluoroenolates for the synthesis of difluoromethyl ketones and this advancement has enabled the synthesis of many new types of difluorinated molecules. We have identified a new class of agonists of the GABA$_B$ receptor following the screening of difluoromethyl ketones at these neurotransmitter receptors. Subsequent characterization of structure-activity relationships has enabled the design of more potent agonists that display the β-amino difluoromethyl ketone. New synthetic methods to create β-amino difluoromethyl ketones from the addition difluoroenolates to activated and unactivated imines will be discussed. Also, additional structure-activity relationships for the design of potent agonists of the GABA$_B$ receptor will be presented.



SERMACS 197

Vial organic: Safer, cheaper pedagogy for organic chemistry labs

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Microscale organic methodologies have become the norm in the organic lab. While there is a decrease in the cost of chemicals and solvents, the micro glassware and equipment offset any savings.

The Vial Organic pedagogy replaces the higher priced equipment and glassware with inexpensive substitutes without sacrificing yield or safety.

Vial Organic labs usually take 1/2 the amount of time to complete. This allows more time for question, discussion or evaluation by the students.

Sample laboratory writeups will be distributed and or demostrated.

SERMACS 198

Spectroscopic analysis of medium-sized constrained rings for potential long-range hyperconjugation: Steric or donor-acceptor effects?

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Herein we report the $^1J_{CH}$ analyses, Natural Bond Orbital analyses, and X-Ray crystal structures of a number of C, O, and N constrained tricyclic cycles. These experiments provide access into the nature of the apparent Perlin Effect previously reported in constrained tricyclic cycles, as well as evidence suggesting both steric contraction and long-range hyperconjugation account for the observed $^1J_{CH}$ perturbations. We report a true Perlin Effect of 10.9 Hz in an azocane *and* large steric effect resulting in $\Delta^1J_{C\text{-}H}$ = 10.9 Hz in a cyclooctane.

SERMACS 199

Photosensitizers for molecular switching of single- and dual-component photo-electro flexors

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Azobenzenes and stilbenes are useful molecular 'flexors' based on their ability to reversibly transform between 'extended' thermodynamically favored *trans* and higher energy 'contracted' *cis* forms upon photo-stimulation. Photo- and thermo-isomerization and lifetimes have been studied for the amino derivatives whose contracted *cis* forms can be flexed open electrochemically. Target flexors include N-azobenzene-dianisylamine (**Ar$_2$N-AB**); N-stilbene-dianisylamine (**Ar$_2$N-ST**); N,N-*bis*(azobenzene)-anisidine (**AB-N(Ar)-AB**); and N-stilbene-N-azobenzene-anisidine (**ST-N(Ar)-AB**). The photostationary state (PSS) compositions of 'extended' and 'contracted' flexors and their rates of interchange have been measured by UV-vis and NMR spectroscopy. The 'contracted'-isomer lifetimes range from hours (**AB**) to years (**ST**) at ambient conditions, yielding a large temporal range of flexing dynamics for the dual systems. Organic cationic dyes have been employed as photosensitizers to stimulate light-mediated redox catalysis of 'contracted-to-extended' flexing (cis-to-trans isomerization) using red light. In this presentation the extent and dynamics of direct blue light mediated photo 'contraction' and red light mediated photo-electron-transfer catalyzed 'extension' of these flexors to complete the nanomechanical switching cycle will be reported. Stimulated cyclic flexing is thus demonstrated for these single and dual flexing systems using electronic excitation and electron transfer to trigger the shape changes.

SERMACS 200

Aurone as a fluorescent probe for the selective detection of H_2S in environmental and biological systems

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Hydrogen sulfide (H_2S) has been recognized as a third gaseous signaling molecule (gasotransmitter) following carbon monoxide (CO) and nitric oxide (NO). This endogenously generated H_2S, primarily from cysteine and homocysteine, has been identified to regulate a wide range of biological processes, while an abnormal level of H_2S has been implicated in various pathological conditions. As a result, the importance of understanding the biological role of H_2S has gained considerable attention. Currently available methods for the selective detection of H_2S are limited by their cellular incompatibility. In relevance to these limitations, fluorescence-based methods are emerging as a powerful tool for both qualitative and quantitative detection of H_2S as they are easy to use and afford real-time analysis without causing cell damage. In this context, despite their promising fluorescence characteristics, minor flavonoid aurones have not been explored well as a potential fluorophore scaffold. And particularly for H_2S detection, no fluorescent probe utilizing the aurone scaffold has been reported so far. Inspired by this gap, we envisioned and successfully utilized the aurone scaffold as a tunable fluorophore for the development of an azide reduction based fluorescent probe for the detection of H_2S in living as well as aqueous systems. In this research a rationally designed and synthesized turn-on fluorescent probe **(Z)-2-(4-azidobenzylidene)-5-fluorobenzofuran-3(2H)-one** is demonstrated to react effectively with NaHS in the presence of cationic surfactant cetyltrimethylammonium bromide (CTAB) resulting in the formation of the corresponding amine accompanied by both a color change and ~5-fold enhancement in the fluorescence intensity with a detection limit as low as 100 nM. The probe displayed excellent selectivity for hydrogen H_2S over cysteine, glutathione, and 2-mercaptoethanol revealing its applicability for quantitative detection of H_2S in both living systems and the environment.

SERMACS 201

Method for photocatalytic synthesis of diazo compounds

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A photocatalytic method has been developed to synthesize diazo compounds in high yields. Diazo compounds are widely used as pigments and dyes. More recently, diazo compounds are being explored as novel photoswitchable drugs. Traditionally, diazo compounds have been synthesized utilizing energy from increased temperatures as well as the addition of strong bases. This can result in large quantities of byproducts and excess waste. The photocatalytic method we have developed instead uses renewable energy from light to synthesize the product with water being our only byproduct. Employing this unique method, symmetrical and asymmetrical diazo compounds have been synthesized in yields up to 98%.

SERMACS 202

Theranostic nanoparticles for simultaneous detection and treatment of cancer cells

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Our research target is to synthesize the water-soluble, bio-absorbable theranostic nanoparticles (NPs) that will improve diagnostic and therapeutic efficacy for cancer. Such theranostic NPs are composed of carbon dots (CDs) conjugated with a targeting agent, folic acid (FA), and an anticancer drug Doxorubicin (Dox). Two series of CDs, FA-CDs and FA-CDs-Dox, was successfully prepared in the lab. The UV-vis, Fluorescence spectra, FTIR, DLS, TEM, and proton NMR of the samples was investigated and compared. The concentration of each part of the nanoparticles in the complex was also calculated. For the first series of FA-CDs-Dox, the final drug load content (DLC) and drug load efficiency (DLE) at pH of 7.4 was 9.48% and 75.8% respectively. The amount of Dox drug released from FA-CDs-Dox was 67.5% after 72 hours, conversely, at the pH of 5.0 the amount of drug released was 70%. The characterization of the diagnostic and therapeutic anti-cancer potential of the NPs are under investigation.

SERMACS 203

Synthesis of non-nucleoside SAM-competitive protein methyltransferase inhibitors

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Mixed lineage leukemia (MLL) is an incurable form of pediatric cancer. Disruptor of telomeric silencing 1-like (DOT1L), a protein lysine methyl transferase, is the only known enzyme associated with the initiation and progression of MLL-rearranged acute leukemias, and it has been identified as a potential therapeutic target.

In a collaborative effort, we designed and prepared a focused set of 14 potential non-nucleoside-based DOT1L inhibitors aided by advanced computational docking methods. Five of the prepared compounds demonstrated inhibition with IC_{50} values $< 25\ \mu M$ with the most potent exhibiting $IC_{50} = 1\ \mu M$. Post-assay modelling supports a binding mode comparable to that of EPZ004777, a high potency DOT1L chemical probe developed by Epizyme, Inc. that demonstrates high affinity for the SAM binding region and an inducible hydrophobic pocket. Inhibitor design, synthesis, and supported binding models will be highlighted.

SERMACS 204

Catalysis of the aza-Diels–Alder reaction by hydrogen and halogen bonds

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The combination of H_2C-NH and *cis*-1,3-butadiene to form a six-membered ring was examined by quantum calculations. The energy barrier for this reaction is substantially lowered by the introduction of an imidazolium catalyst with either a H or halogen (X) atom in the 2-position, which acts via a H or halogen bond to the N atom of the imine, respectively. X = I has the largest effect, and Cl the smallest; Br and H are roughly equivalent. The catalyst retards the formation of the incipient N–C bond from imine to diene while simultaneously accelerating the C–C bond formation. The energy of the π^* LUMO of the imine is lowered by the catalyst, which thereby enhances charge transfer from the diene to the imine. Assessment of free energies suggests catalytic rate acceleration by as much as 4–6 orders of magnitude.

SERMACS 205

Silver nitrate complexes as a potential cancer therapeutic

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Current therapeutics for cancer can be highly toxic to the body and can cause more damage than healing. From chemotherapy to radiation to surgery, patients universally suffer side effects from these methods of treatment. On the other hand, an ideal treatment would be one in which the therapeutic only affects, and eliminates, the targeted cells. This project centers on the synthesis of silver nitrate complexes containing N-heterocyclic thione (NHT) or selone (NHSe) ligands to generate compounds capable of limiting cancer cell viability. This presentation will describe the preparation of such compounds and their biological activity against three different cancer cell lines, namely cervical (HeLa), prostate (PC3), and breast (MDA-MB-231).

SERMACS 206

Qualitative identification of volatile organic compounds found in electronic-cigarette vapor and e-juice via GC/MS detection

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The rising popularity of electronic cigarettes and the congruent lack of regulations is cause for concern. Electronic cigarettes contain a heating mechanism which vaporizes a mixture of propylene glycol with flavoring compounds and nicotine. Electronic cigarette vapor is known to contain some of the same harmful compounds as traditional cigarettes, including volatile organic compounds. Additionally, the reported concentrations of nicotine in many e-cigarette liquid solutions vary greatly from the measured amounts. Environmental Tobacco Smoke (ETS) includes second-hand, side-stream, and third-hand smoke, which is when harmful chemicals from smoke or vapor are absorbed into cloth. Volatile organic compounds found in ETS are identified by analyzing cotton samples exposed to electronic cigarette vapor via gas chromatography/mass spectrometry (GC/MS). This presentation encapsulates the qualitative results and plans for future work.

SERMACS 207

Synthesis and characterization of porphyrin entrapped silica sol-gels for heavy metal detection

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Silica sol-gels were doped with free-base meso-tetrakis(4-hydroxyphenyl)-porphyrin (H_2THPP) during the polycondensation process. The application H_2THPP doped sol-gels as reusable colorimetric sensors for the presence of heavy metals in aqueous solutions were examined. Current heavy metal detection methods are destructive and nonreusable; consisting of color changing solutions, colorimetric paper, etc. For years, porphyrins have been used for a variety of colorimetric optical sensors with many different purposes because of their color changing properties. Absorption spectroscopy of the silica sol-gel materials showed that the immobilized porphyrins maintained their intrinsic properties and no aggregation was observed at the tested porphyrin concentrations. This poster presentation highlights the experimental design, synthesis, and functionality of the entrapped porphyrin observed during the project.

SERMACS 208

Utilizing sol-gel technology to create a portable detector of DNA

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Synthesis and functionality of a sol-gel with entrapped 4′,6-diamidino-2-phenylindole (DAPI), a fluorescent dye that binds to double-stranded DNA, was examined as a detector of DNA. Due to DAPI’s fluorescence and high binding affinity for DNA, the dynamic between DAPI and DNA can be used in tandem with sol-gel technology to develop a detector with good specificity for DNA. Silica sol-gel monoliths provide a protective, temperature and humidity resistant, robust material for encapsulated bio-molecules. Using fluorescence measurements, the entrapment of DAPI in tetramethyl orthosilicate (TMOS) sol-gels and binding with pBR 322 plasmid DNA were studied. pBR 322 is a commonly used bacterial cloning vector. Additional leaching and quenching experiments were conducted to better understand the interactions of the DAPI-TMOS monolith and pBR 322 DNA solutions, and to determine the

suitability of the monolith as a DNA detector. This poster presentation highlights the experimental design, synthesis, and the observed functionality of the sol-gel with the entrapped dye during the project.

SERMACS 209

Synthesis and characterization of a reusable pH sensor using silica sol-gels and ormosils

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The application of tetraethyl orthosilicate (TEOS) sol-gels and their manipulated porous structures were investigated as a reusable pH sensor using a variety of entrapped pH sensitive dyes including bromophenol blue, methyl orange and bromocresol green. Smaller porosity is proven to be beneficial in the prevention of leaching of the pH dyes but may restrict mobility and functionality when exposed to the analyte. To resolve this potential issue, mesoporous organically modified silica (ORMOSIL) structures were synthesized to grant the dye molecule the ability to move and function freely. Absorption measurements using ultraviolet/visible (UV/Vis) spectroscopy provided information about the functionality of the dye after entrapment. Additional comparison studies of TEOS sol-gels verses ORMOSILS were conducted. The synthesis, characterization, and pH testing results will be highlighted in this presentation.

SERMACS 210

Identification of volatile organic compounds on strawberries using gas chromatography/mass spectroscopy

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Shipped produce is frequently exposed to many different pesticides and fungicides which can leave behind extremely harmful residues often in the form of volatile organic compounds (VOCs). Proper washing of this produce is essential to avoid further consumption of these VOCs. This study examines the harmful residues found within strawberries after being soaked in distilled water for a set amount of time using gas chromatography/mass spectrometry (GC/MS). Analysis was done on the rinse water of whole and cut strawberries to compare the residues on the surface versus within the strawberries. Further analysis was done to compare the residues from the washings of organic and non-organic raised strawberries after a set number of washes. This presentation will highlight the experimental design and preliminary qualitative results.

SERMACS 211

Release of liquid hydrogen using perhydro dibenzyltoluene

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Purpose: While the United States is not currently in the Paris Climate Agreement, global warming is still a threat, it is imperative that we try to reduce carbon emissions for the health of the planet and humanity. Possible ways to reduce pollution would be to increase the usage of renewable energy sources such as solar and wind energy; a plausible problem that could occur is unpredictable outputs with limited ways to store the energy when conditions are not favorable. Solving this problem can be through the use of liquid hydrogen (H2(l)) as a fuel source and storing this fuel in the form of a liquid organic hydrogen carrier such as perhydro dibenzyltoluene (H-18 DBT). H-18 DBT releases H2(l) through the use of a rhodium on alumina catalyst, other factors that can affect the release of H2(l) include the temperature of the catalyst and H-18 DBT, dilution of the H-18 DBT with hexane to alter the ratio of H-18 DBT to catalyst, presence of a 365nm light, methods of making the rhodium on alumina catalyst, and the amount of time the catalyst reacts.

Methods: Two forms of the catalyst were created and tested for each set of experiments. Alumina was impregnated with rhodium to form a rhodium 2% by weight on alumina catalyst; the second form of the catalyst was prepared by creating rhodium spheres and mixing them with the alumina to create a rhodium sphere 2% by weight catalyst. The experiments on the H-18 DBT were split into non-dilute and dilute trials, the dilute solution was prepared by mixing equal parts H-18 DBT to hexane. All preparation methods were tested with 5mL of H-18 DBT, the dilute used 5mg of catalyst and the non-dilute used 10mg of catalyst; this was then allowed to react for 20 minutes at varying temperatures with a stirring rate of 500 RPM. The dilute was set to temperatures of 0C, 20C, and 40C; the non-dilute was heated to 0C, 20C, 40C, 60C, and 80C. 1mL of the diluted sample was diluted with 6.5mL of hexane, 300 µL of this was diluted with 2.7 mL of hexane. 500 µL of the non-diluted sample was diluted with 7.5 mL of hexane, 300 µL of this was also diluted with 2.7 mL of hexane. Both were tested in a UV-visible light spectrometer.

SERMACS 212

Development and characterization of azaleu-enkephalin analogs

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Leucine-enkephalin (H-Tyr-Gly-Gly-Phe-Leu-OH) is an endogenous opioid pentapeptide found in humans and other mammals. It is multifunctional and involved in numerous activities including pain reduction and neurotransmitter communications. Leu-enkephalin is conformationally labile; however, it is thought to adopt weak β-turn structures in its bioactive conformation. There has been a plethora of previous research on potential methods to make leu-enkephalin more potent, selective, and resistant to proteolysis. Aza-peptides are defined by the substitution of a single α-C atom for a nitrogen atom in an amino acid. The introduction of an aza-amino acid within a peptide has both conformational and electronic ramifications. Specifically, the C-to-N substitution can increase the propensity for turn-like geometry within peptides. Here, aza-amino acid substitutions in leu-enkephalin are being studied to further explore its impact on conformation. Analogs were synthesized using solid phase submonomer azapeptide synthesis on either rink-amide polystyrene resin or using a photolabile linker. The aza-peptides were analyzed by LC-MS to verify their mass and by circular dichroism to qualitatively assess their secondary structures. In view of making azapeptide combinatorial libraries, future studies will employ the aza-Leu-Enkephalin analogs as model peptides to study the impact of semicarbazide on Edman degradation sequencing procedure.

SERMACS 213

Hard and soft particle detection using machine learning

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The detection of hard versus soft particles is something that has yet to be used with machine learning which can hopefully tell the differences between the two types of collisions. To be able to find the differences between the two collision it first must have enough data of each collision inputted into its algorithm, which is why throughout this experiment roughly 300 runs of each collision were held. Each run roughly contained 35 collisions and with 300 runs this roughly rounds out close enough to 10,000 which was the goal. For the hard particle collisions, polystyrene beads were used to represent the hard particles and with the soft particles, a water and toluene emulsion was created to represent the soft particles.

Each collision was conducted in a solution of ferrocyanide containing 40μL of trihexyl phosphonium bis amide and 100μL of toluene for the soft particle collisions or 20μL of carboxyl polystyrene beads for the hard particle collisions. Each collision was extremely similar for both hard and soft particles and pretty much indistinguishable to the human eye as seen throughout this experiment which is the main reason the implementation of machine learning is wanted. As the advancement of this type of collision research continues to grow the ability to use this in the medical field grows as well. This would be done by training a machine learning model on things such as a viruses collision rather than a carboxyl polystyrene beads collision or a water and toluene emulsions collision.

SERMACS 214

Leucine-based copolymers for drug delivery vesicles: Effect of solvent and inclusion of a single valine on their self-assembly behavior

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Block copolymers have the ability to self-assemble into a rich variety of nanostructures, one being vesicles (polymersomes), whose versatility and amphiphilic characteristics make them appealing materials in the development of drug delivery systems. Recent work by Barnes and coworkers investigated the behavior of a peptide-based triblock copolymer, poly(ethylene-oxide-b-(leucine-*s*-valine)-b-lysine) or PEO-PLV-PK, found that interactions between a leucine zipper in the PLV midblock could be causing the formation of vesicles at only 6 wt.% hydrophobic content instead of the 50-70% hydrophobic content that is usually required. As an extension of that work, this study focused on investigating with dissipative particle dynamics simulations how the location of the single valine residue within the specific PLV 6-mer as well as different solvent compositions of water and trifluoroacetic acid (TFA) affect self-assembly dynamics and the likelihood of vesicle formation. Results of these experiments could provide some useful insight as to why the PLV block was able to form vesicular structures in the first place.

SERMACS 215

Design and synthesis of novel iridium N-heterocyclic carbene based complexes for application in magnetic resonance imaging

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The sensitivity of Magnetic Resonance Imaging (MRI) instruments commonly used to diagnose a variety of conditions is currently limited, which is why taking an MRI can take anywhere from around 30 minutes to several hours depending on the complexity of the scan. The large coil inside the MRI machine is tasked with detecting minuscule changes in the energy as the protons within the patient's body realign with the magnetic field. The purpose of my research is to investigate the design and synthesis of iridium N-Heterocyclic Carbenes(NHC) complexes used to drastically increase the sensitivity of MRI via a technique called SABRE. This approach has the potential to reduce the time necessary for an MRI as well as the overall cost of diagnosis. These complexes could also make MRI's safer for people with claustrophobia or people prone to panic attacks. There is also a potential to reduce the strength of the magnetic field produced by the MRI to make the technique compatible for people with medical implants and equipment such as pacemakers. The iridium-NHC complexes are known to somewhat improve the signal that is detected by the MRI machine, but further improvement is needed to provide a viable approach applicable to diagnosis. To do so, the goal of our research lies in the design and structural optimization of novel iridium complexes with improved SABRE activity, ultimately leading to more sensitive MRI techniques. Specifically, the synthesis of different electron-poor analogs is studied, as this property has previously been observed to improve SABRE activity.

SERMACS 216

Investigating the carrier protein CRM197 to shuttle molecules across the blood-brain barrier

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The blood-brain barrier (BBB) prevents most hydrophilic molecules from entering the brain and spinal column and thus hampers efforts to treat neurological diseases, such as Alzheimer's disease or tumors that have metathesized into the brain. Our research program is examining the potential of attaching molecules onto the carrier protein, cross-reactive material 197 (CRM197) in order to detect or treat these neurological diseases. CRM197 binds to the heparin-binding EGF-like growth factor (HB-EGF) receptor that is expressed on the surface of the endothelial cells that compose the BBB. Previous studies have demonstrated that CRM197 protein can shuttle attached molecules into the brain. This research would extend previous studies to include small molecule drugs that would normally not cross the BBB or are actively removed from the brain through efflux pumps on the BBB. Our research program is also engineering the CRM197 protein to bind to the mouse HB-EGF receptor in order to extend the use of this CRM197-based system to mouse models of diseases.

SERMACS 217

Anti-inflammatory activity of *Hypericum brachyphyllum*

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High blood pressure is often referred to as the "silent killer," as it can remain asymptomatic for many years, manifesting later in life as several other diseases. One of the root causes of hypertension is inflammation and the body's inflammatory response to external stimuli. In addition, inflammation can increase the incidence of other diseases, such as prostate cancer. Men with chronic inflammation in prostate tissue have nearly twice the risk of developing prostate cancer. Natural products remain an excellent first step in the discovery of molecules with the potential of treating these diseases. Plants in the *Hypericum* genus are of particular interest, as they produce several metabolites which have significant anti-inflammatory potential. In a preliminary investigation the crude extracts of *Hypericum brachyphyllum* displayed anti-inflammatory activity in vitro. We here-in describe the chromatography and evaluation of the medium polarity extracts of *H. brachyphyllum* against TNF-α production.

SERMACS 218

Lowering poly(vinyl chloride)'s glass transition temperature with urea and its derivatives

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Even though Di-2-Ethylhexyl Phthalate (DEHP) has been categorized as a probable human carcinogen by the EPA, it is still the primary plasticizer for the world's most plasticized polymer, Poly(vinyl chloride) (PVC). This project's goal was to find an alternative plasticizer that lowered PVC's glass transition temperature (Tg) and was not as harmful for the environment and our health as DEHP. Previous research at NC State found that urea could complex with amorphous polymers, such as poly(methyl methacrylate) (PMMA). PMMA's Tg increased when complexed with urea but decreased when combined with dimethylurea (DMU). Since PMMA's Tg varied based on the additive utilized, this sparked our interest to observe how urea and its derivatives interacted with PVC.Fourier-transform infrared spectroscopy (FTIR) showed that urea and its derivatives were complexing with PVC and Differential scanning calorimetry (DSC) illustrated we met our goal of lowering PVC's Tg.

SERMACS 219

Preparing for additive manufacturing using semi-conductive polymers

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PEDOT: PSS, at its most pristine, is soluble and an insulator. However, through the process of doping these properties can be manipulated to our needs in benefit of our goals. In the experiment, the ambition is to create and test a PEDOT: PSS formulation that is highly conductive, insoluble after annealing, and has appealing mechanical properties. Manipulating these allows for application into additive manufacturing.

To prepare for testing, a thin film of PEDOT: PSS formulation must coat the glass substrates. The formulation includes three additional additives, PEG, DBSA, and GOPS. In the solution, each additive is utilized for particular purposes, and with differentiating volumes.

A variety of methods were used to both create and test the samples. After cleaning the substrates, and creating the solution, a process called spin-coating on a spin-coater is used to create thin films. Now, with a final sample, the Van der Pauw and Collinear method of the 4-Point Probe is used to test the last samples and gather results.

If the experiment meets the goals, and there is preparing of a highly conductive, insoluble sample, then the implications of the products include utilization toward additive manufacturing. A highly conductive and insoluble material is vital for use in additive manufacturing. Insolubility gives it the properties to be more useful in 3-D printing.

SERMACS 220

Comprehending the molecular chemistry and chemical processing of high performance fibers

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High performance fibers are used in bullet proof vests, cut-resistant gloves, and flame resistant clothing. The purpose of this research topic is to investigate the mechanical properties of several high performance fibers and the process for manufacturing these fibers This is comprised of a literature review of fiber chemistries (based on two different polyaramids and an ultra-high molecular polyethylene), review of dry jet wet spinning, and a thorough analysis of fibers structurally by optical microscopy, measurement of linear density, and mechanical testing. Our research methodology included the tensile testing of commercial high performance yarns Artec, Kelvar, and Dyneema by American Standards of Testing Materials. In conclusion, fiber having very different chemical structures could all yield high mechanical strength and stiffness values.

SERMACS 221

Water quality chemical and microbial analysis of select water resources in Gwinnett County, GA

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According to the EPA, both phosphorous and nitrogen are vital nutrients for plants and animals in aquatic environments. However, the disruption of phosphorus and nitrogen cycles due to manmade activities may lead to excessive levels of nitrate and phosphorus in water and eutrophication. Therefore, this project focuses on the safety and quality analysis of water samples from Shoal Creek at upstream and downstream sites of the Lawrenceville City Lake, and two locations along the Yellow River. In this project, the total nitrate and phosphate concentrations were determined via colorimetric assays. Nitrate concentrations ranged from 0.08 ppm to 15.78 ppm, and the phosphate concentrations were negligible in the low ppb. Nonpurgeable organic carbon (NPOC) and total nitrogen concentrations in the water samples were measured using a Shimadzu TOC-L TOC analyzer. NPOC concentrations ranged from 1.12 ppm to 4.21 ppm, and the total nitrogen concentrations ranged from 0.21 ppm to 2.15 ppm. Additionally, investigated nitrate concentrations in the water samples via High-Performance Liquid Chromatography (HPLC). For the microbial analysis, the Most Probable Number (MPN) assay was performed to determine concentrations of viable microorganisms, most notably E. Coli

SERMACS 222

Synthesis and studies of N-(phenylalkyl)octadecanamides as low molecular mass gelators

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The properties of self-assembling low-molecular mass gelators (LMGs) are of high interest in pharmaceutics as they can be used for targeted drug delivery and release. We designed and synthesized a series of such gelators, derivatives of N-(phenylalkyl)octadecanamide, from stearic acid via an acyl chloride intermediate. The alkyl chain length of the amine was increased to observe effects on the resulting amides, or LMGs. The neat gelators were characterized using Nuclear Magnetic Resonance (NMR) and Infrared (IR) spectroscopy, and the thermal properties were investigated with a melting point apparatus and Differential Scanning Calorimetry (DSC). Gels were prepared using solvents of differing polarity for each LMG until critical gelator concentration (CGC) was found, and the melting temperature ranges of each gel were also noted with the inverse flow method. A direct relationship between the length of the alkyl chain and the solvents effectively gelled was determined in addition to one between gelator concentration and melting temperature. Mechanical properties and thixotropic studies of the silicone oil gels and hydrogels were investigated and will be presented.

We thank Prof. Richard Weiss (Georgetown University) for the use of rheometer and polarizing optical microscope.

SERMACS 223

Preparation and characterization of deep eutectic solvents based on amino acids

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Binary and ternary mixtures with various concentrations of naturally occurring amino acids (L-phenyl alanine, L-glutamic acid, L-tyrosine, L-aspartic acid, glycine), choline chloride and glycerol were prepared. Thermal properties of the mixtures (differential scanning calorimetry and melting point analysis) and spectroscopy studies (IR and NMR) will be presented.

SERMACS 224

Molecular docking of the interactions of fluorinated heterocyclic sulfonamides with human and plasmodium DHFR

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About half of the world's population lives in areas at high risk for malaria. This deadly scourge that results in 650,000 fatalities annually mainly targets children, pregnant women, and populations in tropical regions of the world. The folate pathway enzyme Dihydrofolate reductase-thymidylate synthase (DHFR-TS) is critical for producing key cellular components (amino acids and nucleic acids) required for the survival of the parasite Plasmodium falciparum, the causative agent of malaria. This, therefore, makes DHFR-TS a potential target receptor for antimalarial activity and the development of novel therapies. A number of antimalarial drug combinations have become ineffective due to parasitic resistance, as a result of point mutations of Plasmodium enzyme DHFR. In this study, we have used molecular docking, to calculate the binding energy of interactions between DHFR variants and heterocyclic sulfonamides. The affinities are benchmarked with common antimalarial drugs like artesunate, pyrimethamine, and chloroquine. The three-dimensional structures of human DHFR, wild type, double mutant, and quadruple mutant DHFR were acquired from the Protein Data Bank and the monomer structure was obtained using PyMOL. The monomer units of the DHFR variants were docked with seven heterocyclic sulfonamides and current antimalarial drugs using UCSF Chimera and Autodock Vina. Three sulfonamides showed greater interaction affinity with pfDHFR compared to current antimalarial drugs (chloroquine, pentamidine, pyrimethamine, and artesunate). A binding energy of -8.4 kcal/molecule was observed between Sulfonamide 7 and human DHFR compared to -9.7 kcal/mol and -10.1 kcal/mol for Plasmodium enzymes. The higher affinity of Sulfonamides 5-7 was due key hydrogen bond, electrostatic and van der Waals interactions. The sulfonamides in this study show stronger affinities than some current antimalarial drugs like primaquine and chloroquine.

SERMACS 225

Investigating the performance and stability of an enzyme inspired catalyst

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In order to store renewable energy as chemical fuels, hydrogenase-inspired catalysts have been developed to catalyze the reduction of protons to hydrogen. The performance of one such air stable bimetallic nickel-iron hydrogen evolution electrocatalyst, Ni(bdt)(dppf) (bdt = 1,2-benzenedithiolate, dppf = 1,1′-bis(diphenylphosphino)ferrocene), was evaluated under new conditions to determine if the catalyst would undergo aggregation or electrodeposition as has been previously observed for some bdt containing complexes. The activity of the catalyst was compared to a monometallic nickel complex, Ni(bdt)(dppe) (dppe = 1,2-bis(diphenylphosphino)ethane). Characterization by cyclic voltammetry (CV) in DCM identified a Ni(II/I) reduction couple at -1.59 V and an oxidative feature at 0.36 V vs Fc+/0 . Ni(bdt)(dppe) had a more negative reduction potential for the Ni(II/I) couple (-1.93 V vs Fc+/0). In the presence of benzoic acid, a weak acid, the onset of catalysis occurred at the Ni(II/I) couple for Ni(bdt)(dppf) and catalytic current continued to increase with additional acid up to 150 equivalents. The Ni(bdt)(dppf) catalyst was determined to be stable under the acidic conditions employed, as was confirmed via NMR.

SERMACS 226

Preparation of biodiesel using a DES

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To minimize the use of volatile organic solvents, a Deep Eutectic Solvent (DES) consisting of Choline Chloride and Glycerol (1:2) molar ratio was introduced as the co-solvent in the transesterification reaction of peanut oil to biodiesel catalyzed by sodium hydroxide. The DES used is an inexpensive, non-toxic, and biodegradable alternative when compared to the volatile and often toxic organic solvents. Through the evaluation of different oils and their effects as well as the repetition of the reaction to optimize results, biodiesel was eventually achieved. IR and NMR was done to examine the results of the reactions. These results indicate that a DES can be used as substitutes for the toxic and volatile organic solvents in the transesterification reaction of biodiesel.

SERMACS 227

Magnetic drug delivery of xanthohumol to adipocytes using ultrasmall superparamagnetic iron oxide nanoparticles (USPIO)

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According to the CDC’s National Center for Health Statistics, ~(39.8%) of U.S. adults are obese. Obesity has been linked to heart disease, type-2-diabetes, and certain types of cancer. Nutraceuticals such as xanthohumol (XN) have shown potential to inhibit adipogenesis, however, their bioavailability has remained controversial. Hence there is a need to develop targeted therapy, which will increase the concentration of xanthohumol in the adipose tissue. Currently, nanoparticles are used for drug delivery where conventional therapies have proven to be less effective. Among various types of nanoparticles, ultrasmall superpraramagnetic nanoparticles (USPIO) have found considerable attention in drug delivery as they are easy to synthesize, inert, and are biocompatible. Additionally, the use of magnetic nanoparticles as a drug delivering agent system under the influence of external magnetic field has received much attention. Thus our goal is to develop a XN loaded magnetic nanoparticles which when given *via*IV can be targeted to adipose tissues under the influence of external magnet.

However, to use them for drug delivery, the USPIO need to be surface functionalized by ligands such as 3-aminotripropyl ethoxysilane. The use of 3-aminotripropyl ethoxysilane provides an amine functional group on the surface of USPIO. Once amine functionalized, the USPIO-NH_2will be conjugated to XN *via*dicarboxylic PEG linker (HOOC-PEG-COOH) to yield USPIO-PEG-XN. These XN loaded magnetic nanoparticles can be targeted to the adipose tissue under the influence of magnet. USPIO were synthesized by reacting Fe(II) and Fe
(III) chloride salts in presence of NaOH. USPIO thus obtained were amine functionalized using 3-aminotripropyl ethoxysilane. TEM analysis revealed the presence of 20-25 nm particles for both USPIO and USPIO-amine.The presence of amine functional groups on the surface of nanoparticles was confirmed *via*FTIR and quantified using ninhydrin Assay. The ninhydrin assay revealed the presence of 4.5mM of amine groups per mg of the USPIO. Once synthesized the USPIO-PEG-XN will be evaluated for their specificity and toxicity both *in vivo*and *in vitro*.

SERMACS 228

Preprogrammed dynamic microstructured polymers

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The advancement of new-generation complex integrated responsive systems depends on the progress in the development of functional stimuli-responsive polymer components that could be combined and engineered to perform in concert as an ensemble. This presentation highlights recent results on the development of such soft-matter components capable of change according to preprogrammed scenarios. The components interact via interfaces that play a key role in the performance of the microstructured materials. The list of the most important properties that can be changed by altering the interfaces upon external stimuli includes gating, transport, release, wetting, adhesion, and self-regeneration (healing) realized in different architectures of soft stimuli-responsive materials.

SERMACS 229

Development of enzymosomes: Core-shell polmer particles with functional protein corona

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The investigation of protein-polymer or protein-nanoparticle interaction is critical for the development of novel biomaterials and hierarchically assembled nano-architectures. Among them, the polymer-protein core-shell nanoparticles (PPCS-NPs) are the most common structures which offer many advantages in the field of medicine and energy applications. Here we show that PPCS-NPs can be prepared based on synergistic interactions between proteins and synthetic polymers. This facile and versatile process can yield structural well-controlled core-shell structures, in which proteins stay as the corona and still maintain their original biological activities. In particular, using enzyme as the protein component, a series of enzymosomes can be constructed, which have application potentials in bioengineering and biotechnology applications.

SERMACS 230

Insights into intra-chain cross-linking

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Our group has largely focused on the topic of single-chain nanoparticle synthesis over the last several years. This talk will discuss several of the insights we've gathered related to desiging the intra-chain cross-linking reaction needed to facilitate the collapse of a single polymer chain into an architecturally defined nanoparticle.

This work has larger implications related to polymer modification and cross-linking and should be of interest to researchers in areas realated to smart polymers and coatings.

SERMACS 231

Development of smart polymer nanofiber mats for selective removal of PFAS from landfill leachate

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Innovative pretreatment technologies for PFAS in industrial wastewater are becoming more and more urgent after EPA tightens the regulation on PFAS. This presentation will update the progress in this field and introduce the technology our company is developing funded by the EPA SBIR Phase 1 award. The technology is using nanofiber mats fabricated by electrospun polymer nanofibers for the "smart" (selective) removal of per and polyfluoroalkyl substances (PFAS) from landfill leachate. The co-contaminants, low concentration, and complexity for PFAS in industrial wastewater are big hurdles for current technologies, this method overcomes the challenges and provide a unique approach for PFAS removal. The advantages of the nanofiber mats include:

1) A hybrid and synergistic PFAS removal with adsorption/membrane approach;
2) Smart and selective adsorption feature;
3) High loading flow rate;
4) Energy-efficient regenerable with PFAS recovery for further destruction.

The polymer nanofiber mats were fabricated by electrospinning. The target of this project is to reduce the combined PFAS concentration to below 70 ppt for wastewater treatment market, a fast-growing industry. The technology is compatible with other treatment processes.

SERMACS 232

Preparation and characterization of nanocomposites prepared from poly-3-hydroxybutyrate (PHB), lignin and cellulose nanocrystals by high torque melt mixing

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There is considerable interest in the use of biobased polymers and fillers to prepare fully biobased composites based on renewable starting materials that can be degraded to carbon dioxide and water. We have investigated the incorporation of cellulose nanocrystals (CNCs) and lignin prepared by the sulfuric acid hydrolysis of poplar (*Populus deltoids*) mesh in poly-3-hydroxybutyrate (PHB) by high torque melt mixing. We have prepared PHB nanocomposites incorporating 0.2 – 2 wt.% of varying ratios of CNCs and lignin and characterized them by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), tensile texting, thermal gravimetric analysis (TGA), wide angle X-Ray Diffraction. We have found that the intmiate mixtuire of lignin and CNCs leades to excellent dispersion and distribution of the nanomaterial in PHB and leads to improved thermomechanical properites, such as increased glass transition temperater T_g and modulus by DMA.

SERMACS 233

Biobased polymer coating and antimicrobials

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Polymer coatings have been heavily utilized in many industrial and civil applications where a protective thermoset material with enhanced properties such as chemical and physical resistance, thermal stability, and tailorable mechanical properties is desired. In this presentation, I will talk about our recent efforts in developing biobased emulsion polymers as high performance coatings. In addition, antimicrobial biomaterials and coating from natural products will be also covered.

SERMACS 234

Modification and characterization of polyol based polymers for ice recrystallization inhibition and thermal hysteresis activity

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Ice formation is a global issue that poses serious challenges for many applications. Certain species in colder regions of the world have adapted to that climate by producing antifreeze (glycol)proteins (AF(G)P) which exhibit ice recrystallization inhibition (IRI). Although several synthetic approaches for the exploitation of these proteins have been investigated, challenges remain in the synthetic design of biomimics. In addition, AF(G)P's have a complicated structure making it difficult to directly identify structure-property relationships relevant to the IRI mechanism. Poly(vinyl alcohol) (PVA) is by contrast a quite simple macromolecular structure and happens to be IRI active. Modifications of this PVA template have been reported, yet many fundamental relationships between structure and performance remain. Here, we were inspired by the active sites in anti-freeze proteins (AFP), such as the ice-facing beta-sheet in the AFP present in the desert beetle *Anatolica polita* (*Ap*AFP752) presenting threonines in an ordered array. Drawing comparison between the distance between hydrogen bonding sites in threonine, we describe our approach to position small organic molecules with known anti-freeze properties (such as ethylene glycol) pendent to a host polymer chain with consideration of their conformational freedom. In order to build systematic variations into both the backbone and side-chain structures, we have used poly(vinyl alcohol), poly(isopropenyl acetate), poly(acrylic acid), and poly(methacrylic acid) base polymers; behavior as small molecules in solution does not necessarily translate to solid-state performance. We have observed tremendous impact on IRI behavior of several (but not all) of our polymer scaffolds. FT-IR and NMR were used for confirmation of the functionalized polymer structures, where differential scanning calorimetry (DSC), XRD, and microscopy assays were used to observe the ice IRI behavior. Thermal hysteresis activity (THA), a depression of the freezing point without impact on the melting point (of water, here), as a function of the polymer modifications, is also characterized and corroborated with the IRI trends. The findings in this study will help pave the path for rational design of synthetic IRI polymers, useful for applications such as anti-icing coatings through to cryo-preservation methods for organ transport.

SERMACS 235

Reversible thermochromic alkali metal polydiacetylene microcrystals

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Polydiacetylenes (PDA) are highly conjugated, chromatic polymers. They change colors (usually blue to red) in response to a stimulus, such as heat, pH or mechanical stress. Some derivatives are able to respond to stimuli selectively and have therefore been investigated as sensors. In most cases, the colorimetric response is irreversible, however certain applications require a reversible sensor. We, and others, have found that alkali metal salts, made from base and 10,12-pentacosadiynoic (PDCA) acid can be irradiated to form microcrystalline PDAs that undergo reversible color transitions within particular temperature ranges. In this study, we present the results of a systematic analysis of the colorimetric response of salts from Li to Cs.

SERMACS 236

Effects of paraffinic oil on the mechanical behavior of the thermoplastic elastomer styrene-ethylene-butylene-styrene

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Soft and stretchable polymer composites are useful for many applications such as soft robotics and stretchable electronics. Creating composites by adding fillers to polymer matrices can increase the useful behavior of the host matrix by improving thermal and/or electrical properties. However, typically the overall rigidity of the composite is impacted, thus altering the desirable and soft properties of the polymer matrix. As the mechanical behavior of the polymer matrix is one critical factor in a polymer composite, the optimization of desirable composite properties requires understanding of polymer mechanical behavior to enable analysis of the impact of adding fillers. For example, the gallium-indium-tin alloy galinstan is a room temperature eutectic liquid metal that has the potential to act as dielectric material when dispersed in a polymer matrix. Current studies have found that utilizing galinstan in thermoset polymers can maintain the useful behavior of the added filler with a minimal impact on the soft and stretchable mechanical behavior of the polymer matrix. The use of thermosets is limited, however, due to a lengthy and intensive manufacturing process and the inability to reconfigure the composite once cured. Thermoplastic elastomers on the other hand, such as styrene-ethylene-butylene-styrene (SEBS), can be reused and reconfigured due to being solid at low temperatures and liquid at high temperatures, which results

in materials that are not only adaptable but cost-effective. The SEBS elastomer is composed of the SEBS solid polymer and the oil used to swell it. The mechanical behavior of the SEBS elastomer can be tuned by manipulating the oil used as the swelling agent, thus allowing the mechanical behavior of SEBS to be adaptable without changing the SEBS polymer chemistry. In this study, the paraffinic oil to SEBS solid polymer ratio and the viscosity of the oil used in the SEBS elastomer were manipulated resulting in the alteration of the mechanical behavior of the thermoplastic elastomer. It was found that through the manipulation of the paraffinic oil used in the swelling of the SEBS elastomer the material rigidity, elongation, and melting behavior can be tuned. A fundamental understanding of how the paraffinic oil used in the swelling of the SEBS polymer alters the mechanical behavior of the resulting elastomer will allow for the further analysis into polymer composite applications, such as galinstan dispersions for dielectric materials.

SERMACS 237

Free radical polymerization of alkyl-substituted stilbenes with maleic anhydride

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Substituted poly((*E*)-stilbene-*alt*-maleic anhydride) copolymers, a class of strictly alternating, semi-rigid copolymers, have polyelectrolyte properties when hydrolyzed. The controlled radical polymerization of several stilbene derivatives with maleic anhydride has been previously reported. This research focuses on the kinetics of conventional radical polymerization of a series of homologous alkyl substituted stilbenes with maleic anhydride. This research also seeks to measure how alkyl chain length affects the reactivity of substituted stilbenes in copolymerizations with maleic anhydride. Hydrolyses of anhydride copolymers give surfactants—poly((*E*)-3-alkylstilbene-*alt*-maleic acid) copolymers. Integration of ^{13}C NMR spectra is used to measure the ratio of monomers in the copolymer. Copolymers are further characterized by SEC, FTIR, and ^{1}H NMR.

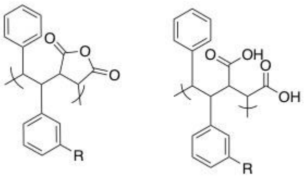

Figure 1. Chemical Structure of poly((*E*)-3-alkylstilbene-alt-maleic anhydride) and poly((*E*)-3-alkylstilbene-alt-maleic acid) Alternating Copolymers.

SERMACS 238

Increasing the functionality of electrospun polymer fibers through large particle inclusion

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Electrospinning is a valuable production method for nanoscale polymeric fibers, but has been limited by a requirement for high molecular weight polymers as the main component of the matrix. Many applications would benefit from a more expansive range in the materials able to be used for electrospinning including pharmaceuticals, diagnostics and wearable devices, active filtration, and precisely structured fibrous nanocomposites with particles much larger than the fibers. In order to develop these more advanced functional composites, a strong understanding of how particle inclusion affects the electrospinning process and fiber and mat properties is essential. In this work, we examine materials systems containing various polymers and active particles, focusing on how inclusion of particles affects electrospinnability and functionality of the fibrous mat. We demonstrate that, up to a 2 to 1 polymer to particle ratio by weight, particles are trapped within the individual fibers and that up to 10:1 particle:polymer mixtures may be spun for some systems. Unique morphologies, such as ‘bunches of grapes’ and web entrapment are also observed for certain mixtures of polymers and particles. We examine how particle inclusion affects the viscoelasticity of the solutions and tie this to the electrospinning process window; showing that a finite window of viscoelasticity yields optimal electrospinnability. These results provide a platform for product design for new electrospun materials with high loadings of functional particles.

SERMACS 239

Development of nitric oxide releasing polymers to improve biocompatibility of medical devices

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Blood-contacting devices, such as catheters and complex extracorporeal artificial organs, suffer from two major clinical problems: 1) platelet activation leading to thrombosis, and 2) infection. One approach to improving the hemocompatibility of blood-contacting devices is to develop materials that release nitric oxide (NO). Nitric oxide is an endogenous gas molecule produced by nitric oxide synthase (NOS) enzymes that has several key biological roles. Healthy endothelial cells exhibit a NO surface flux of 0.5 – 4.0 x10^{-10} mol cm^{-2} min^{-1} that inhibits platelet adhesion and activation. Macrophages also release NO that acts as a potent natural antimicrobial agent. Polymeric materials that mimic this NO release are expected to have similar antithrombotic and antimicrobial properties. In this presentation, examples of incorporating NO donor molecules such as diazeniumdiolates (NONOates) or *S*-nitrosothiols (RSNOs) in biomedical grade polymers will be discussed, including new methods to modify existing polymeric medical devices (e.g., catheters) with NO donor molecules via a solvent swelling technique. These new materials are used to fabricate “prototype” catheters and

extracorporeal circuits, and further evaluated for the hemocompatibility and antimicrobial activity via short-term (4 h) and long-term (1-2 weeks) *in vivo* experiments using clinically relevant animal models.

SERMACS 240

Polydiacetylene nanostructures as sensor platforms

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When assembled into arrays of the proper geometry, substituted 1,3-butadiynes (diacetylenes, DAs) are able to undergo an unusual topotactic polymerization reaction to give highly conjugated materials. When first formed, most pDAs are a deep blue color, but when the polymer chains are subjected to stress, they display an intense red color. The DAs can be polymerized in crystalline solids, liquid crystals, thin films, self-assembled monolayers, liposomes, and related structures, however not in solution. For example, the assembly of diacetylene-containing lipids into small, uni-lamellar vesicles of approximately 200 nm in diameter results in a polymerizable structure that can be derivatized to provide sensitivity towards biological species, including bacteria, viruses, DNA fragments, and others. The liposomes are remarkably robust. They may be incorporated into thin films, solution extruded into composite fibers, or deposited onto a substrate using inkjet printing, all without undergoing the blue-to-red color changes. The composite materials still display the chromism of the original liposomes, providing the host material is porous enough for the stimuli to reach the vesicle. This include sensitivity not only to temperature, pH, chemical, and biological stimuli, but also mechanical stresses such as impacts or tensile deformation. Selectivity can be imparted by chemical modification of the vesicle exterior, while reporting functions can be enhanced by incorporation of small (ca. 5 nm or less) nanoparticles into the bilayer. Encapsulation of species within the lumen allows for additional applications.

SERMACS 241

Crawford group: At the interface of sensors and soft materials

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Established in 2017 at the University of Central Florida in Orlando, the Crawford Group, known also as the Soft Functional Materials and Sensors Lab, seeks to cultivate the synergy found in working across disciplines such as materials science, bioengineering, nanotechnology, chemistry and medicine, to address overarching human-health and environmental challenges relevant to our 21st Century society. Specifically, the Crawford group develops soft functional materials that are designed for dynamic use at the biological interface. Research interests related to these efforts include: block copolymers, nanomaterials, interfacial interactions, soft matter synthesis and characterization, self-assembly, wearable sensors, and bionic materials. At the Polymers for Advanced Technologies Workshop, Dr. Crawford will introduce critical foundries from which she is building her independent research and share details of emerging projects in her group related to the interests of the polymer chemistry and bioelectronics community, to receive feedback from senior peers, and to actively engage in the symposium through discussion and participation throughout.

SERMACS 242

Structural transitions and encapsulation selectivity of thermoresponsive polyelectrolyte complex micelles

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Polyelectrolyte complex (PEC) micelles are formed by mixing a block copolymer composed of a neutral block and a charged block, with an oppositely charged polymer. The micelles formed have a PEC core, capable of encapsulating charged molecules like nucleic acids or proteins, while the neutral block(s) forms the corona, which protects cargo from being degraded under physiological conditions. This work explores using a thermosensitive polymer, poly(N-isopropyl acrylamide) (pNIPAM), as the primary corona-forming block and how that can be leveraged in the context of drug delivery. pNIPAM has a lower critical solubility temperature (LCST), above which a hydrophilic to hydrophobic transition occurs. We are characterizing micelles formed using a diblock copolymer of pNIPAM-poly(acrylic acid) with (1) poly(lysine) and (2) poly(ethylene glycol)-*b*-poly(lysine) using dynamic light scattering, small angle x-ray scattering, absorbance and fluorescence spectroscopy, and transmission electron microscopy. Our results indicate that mixing pNIPAM-poly(acrylic acid) and poly(lysine) creates worm-like micelles, while mixing the same diblock with poly(ethylene glycol)-b-poly(lysine) forms spherical micelles. At temperatures above 35ºC, the transition temperature of pNIPAM-poly(acrylic acid), the worm-like micelles lose their structure, while the spherical micelles retain their structure, but both aggregate into larger assemblies. Lastly, we evaluate the ability of these micelles to encapsulate and release model charged therapeutics, using a cationic monoion, methylene blue and a cationic polyion, polylysine conjugated rhodamine. We find that methylene blue is not encapsulated by the micelle, and instead exhibits counterion-like behaviour upon PEC formation. Conversely, fluorescence measurements of rhodamine-labeled polylysine show fluorescence quenching indicating that the polyion is encapsulated. By mixing labelled and unlabelled micelles, we identify molecular exchange between the single corona micelles, a phenomenon that was not observed with the double corona micelles and highlights an important distinction in the behavior of these two systems with their environment. Measurement of the micelle fluorescence above the LCST, decreases indicating no substantial release for either system. However, the increase in micelle quenching above the LCST and its persistence after cooling may offer an additional protective environment for cargo that can be triggered by temperature.

SERMACS 243

Charge photogeneration in water-soluble conjugated polymer solar cells

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Conjugated polymers and small molecules have been intensively studied due to their unique electronic and optical properties and have shown the potential for optoelectronic applications including solar cells Power conversion efficiency of about 14% has been achieved in these solar cells. However, maximizing the short circuit density and open circuit voltage is a critical issue to improve the performance of these solar cells. Here, we explored the limitations in charge generation efficiency of water soluble polymer solar cells based on PPDT2FBT-A polymer. We employed transient absorption Spectroscopy and Atomic Force Microscopy to study the charge carrier dynamics and morphology in these systems. We observed that largely aggregated and rough thin film morphology PPDT2FBT-A blend limits the exciton transfer and charge generation efficiency. Our results provide important guidelines for the design of aqueous soluble polymer solar cells.

SERMACS 244

Robust metallo-polyelectrolyte membranes towards energy storage applications

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Polyelectrolytes have been utilized in various applications ranging from coating to biomedical materials. Among them, polyelectrolyte membrane fuel cells (PEMFCs) have attracted much interest in recent years for their high energy efficiency and environmental friendliness. As a critical component for alkaline fuel cells, alkaline anion-exchange membranes (AEMs) with various polymer backbones and cationic functional groups have been investigated for better performance. Degradation of polymer backbones and cations under harsh alkaline conditions can result in reduction of mechanical properties and hydroxide conductivity. Herein, a comprehensive of study was conducted to elucidate the substituent effects on the alkaline and redox stabilities of a series of cobaltocenium cations, and a new design of metallo-polyelectrolyte membranes was conceptualized. (**Figure 1**) Compared to traditional organo-polyelectrolyte membranes, cobaltocenium AEMs exhibited excellent thermal, chemical and mechanical stability, as well as microphase-separated morphology, which are appealing for new-generation polyelectrolyte membranes for energy storage applications.

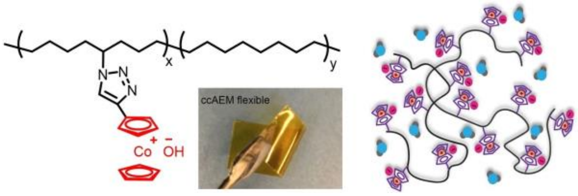

Figure 1. Metallo-polyelectrolyte membranes.

SERMACS 245

Soft material based analyte sensing device to noninvasively identify implant infection

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A novel radiographic chemical sensor was developed to measure pH on the surface of implanted medical devices to identify and study implant-associated infection. The sensor may be read using conventional radiography, a technique which is noninvasive, inexpensive, ubiquitously available, and routinely used in diagnosis and follow-up. The sensor comprises a radiopaque tungsten indicator dial embedded within a chemically responsive hydrogel film that exhibits pH-dependent swelling. An engineered stainless-steel device secures this hydrogel and attaches to an orthopedic plate. The pH on the implant surface is then determined radiographically from the extent of hydrogel swelling by measuring the indicator position or displacement. The sensor was calibrated in a series of standard pH buffers and tested in *Staph. aureus* culture. The sensor response was negligibly affected by changes in temperature, ionic strength within the normal physiological range, and long-term incubation with reactive oxygen species generated from hydrogen peroxide and copper ions. Pooled data from several sensors fabricated at different times and tested in different conditions had a root-mean-square deviation of 0.25 pH units from a pH electrode reading. Radiographic measurements were also performed in cadaveric tissue with the sensor attached to an implanted orthopedic plate fixed to a tibia. Dial position readings varied by 100 µm between observers surveying the same radiographs, corresponding to 0.065 pH units precision in the range pH 4 - 8. This passive pH sensor may be attached to almost any orthopedic implants and provides a simple readout using X-ray imaging that is routinely acquired for assessing bone healing or pathology. This hydrogel-swelling approach could be extended to many biomedical applications including noninvasive examinations of bacterial growth *in vivo*, the expansion and inflammatory response of tumors or other lesions, the diffusion and activity of neurotransmitters, and others.

SERMACS 246

Effects of hybrid additives on the thermomechanical properties of PMMA parts printed by fused filament fabrication

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Fused Filament Fabrication (FFF), a subset of Additive Manufacturing (AM), is attractive to a wide array of industries due to the design versatility and processability of polymer printed parts. However, FFF parts inherently have poor mechanical properties, which limits this manufacturing technology for certain applications. Herein we show that the incorporation of hybrid additives composed of poly(methyl-methacrylate-*random*-4-uriedo-(1H)-pyrimidinone) grafted nanoparticles (P(MMA-r-UPyMA)-g-NP) into PMMA resign drives a significant increase in thermomechanical properties of printed parts. The increases in thermomechanical properties are attributed to both the inorganic silica nanoparticle and by the UPyMA comonomer on the grafted chains which creates physical crosslinks through self-complementary, quadruple hydrogen bonding. Dynamic mechanical analysis (DMA) and tensile measurements, which were used to determine Young's modulus, elongation at break, ultimate tensile strength, and storage and loss moduli, show that the additives are active at low loading levels. Improvements in mechanical performance correlate with an increase in the concentration of the UPyMA comonomer in the random copolymer grafted chain, with an optimum seen at 5 mole percent. Moreover, the reversibility of hydrogen bonding maintains processability during melt extrusion (filament preparation) and printing. These specific additives provide a novel approach to address limitations of parts printed by FFF and highlight the importance of molecular design and functionality on performance and properties.

SERMACS 247

Aqueous romp and RCM, fast and furious

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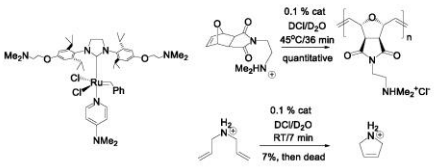
We have developed a novel Ru-based catalyst bearing an N-heterocyclic carbene (NHC) ligand with two pH-responsive NMe$_2$ groups bonded remotely to the aryl substituents. The complex was isolated as 4-dimethylaminopyridine (DMAP) 3rd generation Grubbs-type ruthenium complexes. Acidic aqueous conditions cause protonation of the amino groups and DMAP ligands, hence, the catalysts become water-soluble and perform aqueous metathesis at remarkable rates. Aqueous olefin metathesis still poses a challenge to the synthetic chemist. Water is a metathesis inhibitor and hence, catalysts operating under homogenous, aqueous conditions have been performing with low efficiency and low rates thus far. For example, a rate was accomplished up to 100 times faster than the fastest aqueous ring opening metathesis polymerization (ROMP) reaction known to date. Quantitative ROMP conversions have been accomplished using catalyst loadings as low as 0.1 %. Furthermore, the majority of polymerization reactions follow 1st order kinetics which suggest a good level of molecular weight control. We also investigated the aqueous ring closing metathesis RCM with these catalysts using various substrates. While extremely fast conversions were recorded, the catalytic activity for these complexes seized within minutes resulting in high turnover numbers compared to the literature but low overall conversion. We are currently investigating RCM protocols that allow for extended catalyst lifetimes and hence higher conversion rates.



Extremely fast ROMP and RCM in aqueous media using a pH-responsive 3rd generation Ru-alkylidene catalyst

SERMACS 248

Polyoxometalate oxidation catalysts in solar fuels and anticancer chemotherapy

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Polyoxometalates (POMs), including transition-metal-substituted POMs, are effective catalysts for the oxidation and/or hydrolysis of a range of organic compounds, and several of these processes have been commercialized in the last 25 years. More recently, transition-metal-substituted POMs have been shown to be highly effective water oxidation catalysts (WOCs), which is a core requirement to make solar fuel.

I will report new catalytic oxidations by Co-substituted POMs and polymers containing covalently-bound POMs as well as one polyvandate derivative (a POM of vanadium) that catalyzes the selective aerobic oxidative removal of protective antioxidants in cancer cells leading to their death.

SERMACS 249

Electrochemical water oxidation by a large pore, catalyst loaded, metal-organic framework

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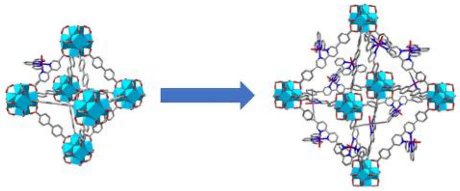
Due to the high kinetic and thermodynamic barriers associated with the water oxidation reaction, many artificial photosynthetic schemes are limited in their efficiency. Significant work has been done on development of water oxidation catalysts, but these catalysts often suffer from lack of reusability or unwanted side reactions that cause inactivity. To promote reusability and avoid use of sacrificial agents, molecular catalysts can be incorporated into heterogeneous supports such as Metal Organic Frameworks (MOFs).

MOFs are composed of metal ions or clusters connected by organic molecules to form 1, 2, or 3D structures with high porosity and internal surface area. Additionally, MOFs exhibit a high degree of tunability, allowing for a wide range of stability in different chemical environments and the ability to fine tune properties such as pore size and functionality. These characteristics, combined with their heterogeneous nature, have made MOFs an ideal target for incorporation of homogeneous catalysts. Previous work has shown that catalyst-incorporated MOFs retain the catalytic properties of the homogeneous catalyst, but small pore sizes limit catalyst incorporation. Here, the synthesis of a large pore, UiO-type MOF with $[Ru(tpy)(BPDB)OH_2]^{2+}$ (tpy = 2,2′:6′,2′′-terpyridine, BPDB = 2,2′-bipyridine-5,5’-dibenzoic acid) linkers is reported. The MOF was grown on a conductive surface and investigated for electrochemical water oxidation, compared to a similarly doped UiO-67. The large pore MOF retained the redox hopping pathway observed in other loaded MOFs and exhibited a faster diffusion rate and increased catalytic activity due to the decrease in intercatalyst distances and increase pore size.



SERMACS 250

Determination of optimal mild organic solvents for synthesis of PdNPs for carbon-carbon coupling reactions

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Interest in carbon-carbon (C-C) coupling reactions has been increasing since the Nobel Prize was awarded to Heck, Negishi and Suzuki in 2010. Current reaction conditions often employed for many C-C coupling reactions involve high temperatures and strong organic solvents, but the current climate of research is pushing towards replacing these conditions with milder alternatives. Pd nanoparticles have been widely studied as effective catalysts for such alternative systems. Pd nanoparticles synthesized using a biomimetic ligand have previously been shown to exhibit high activity in Stille and Suzuki coupling under aqueous and benign conditions. In these previous studies, small, monodisperse Pd nanoparticles were employed in aqueous conditions at room temperature and pressure with catalyst loadings ranging 0.0005 – 0.05 mol% Pd. While optimal for aqueous reactions, these materials do not translate into organic solvents. Since multiple relevant C-C coupling reactions occur in non-aqueous media, there exists a need to modify these nanocatalysts as such. In order to achieve this goal, hydrophobic domains were added to a Pd-binding ligand in order to increase the favorability for mild organic solvents. The domains were added either to one end or both ends of the Pd-binding ligand. The synthesis of Pd nanoparticles was then studied in ethanol, ethyl acetate and toluene. Following the synthesis, reactivity of these materials in Suzuki coupling reactions was explored, all in the same mild organic solvents as the synthesis. As anticipated, placement of the hydrophobic domain had a marked effect on both the synthesis of the Pd nanoparticles as well as the catalytic activity, depending upon which solvent was employed.

SERMACS 251

Study of photo-induced electron transfer from CdTe quantum dots to nickel molecular complexes in water

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Photocatalytic water splitting using solar energy for hydrogen production offers a promising alternative form of storable and clean energy for the future. Light driven proton reduction requires a three-component system with a photosensitizer that transfers electrons to a catalyst that reduces protons and a sacrificial donor. To make this process cost-effective, we need an inexpensive, durable and efficient catalyst that could reduce protons from water to produce hydrogen and we need to couple this catalyst to a photosensitizer that could supply the energy for water splitting. To develop a highly efficient photocatalytic system, the main challenge is the right and effective combination of the photosensitizer and the catalyst. Molecular approaches using quantum dots (QDs) as photosensitizers and enzymes or their functional mimics have been developed. Ni and its complexes are well known for their activities in in solar fuel production. The fundamental step for photocatalysis is to generate a charge separated state. To couple a catalyst for proton reduction to a photosensitizer, it is essential to understand the mechanism of charge transfer or photo-induced electron transfer from the photosensitizer to the catalyst. Therefore, we synthesized and characterized a variety of nickel complexes of tetradentate ligands with amine and pyridine functionalities (N2/Py2) and studied their interactions with Cadmium Telluride QDs stabilized by 3-mercaptopropionic acid (MPA-CdTe QDs). The studies performed include absorbance and emission spectroscopic behavior as well as lifetime measurements that will give us a direct insight into the photo-induced electron transfer process.

SERMACS 252

Visible light driven photocatalytic reduction of CO_2 to CO and CH4 with transition metal complexes

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Photocatalytic solar-to-fuel processes are of critical need to assist in providing growing energy needs. Molecular catalysts offer a relatively easily modified platform for the evaluation of structure-performance relationships. In this presentation, several systems being actively pursued for CO_2 reduction to CO and CH4 will be discussed. A focus will be on understanding the role of transition metal complexes as photosensitizers and as catalysts in photocatalytic reaction systems. Specifically, *N*-heterocyclic carbene complexes of nickel have shown remarkable reactivities for both CO_2 reduction to CH4 and CO2 reduction to CO in the presence of Ir(ppy)3 and water. The design, synthesis, performance, and mechanisms of this systems will be discussed in this presentation.

SERMACS 253

Aqueous CO_2 reduction catalyzed by Earth-abundant complexes bearing redox-active ligands

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The catalytic conversion of carbon dioxide (CO_2) and water (H_2O) into chemical fuels using solar energy or renewable electricity is an attractive strategy for long-term energy storage. In this process, H_2O oxidation at the anode provides the protons and electrons that are needed at the cathode for CO_2 reduction into energy-rich products. Water is therefore the ideal reaction medium, serving as a proton source and the ultimate reductant. However, many catalysts for CO_2 reduction are not stable in aqueous solutions and/or lack selectivity, catalyzing the reduction of protons to H_2 instead. As such, we have developed a series of robust molecular cobalt catalysts supported by tunable redox-active ligands that are capable of reducing CO_2 to CO with high Faradaic efficiencies in aqueous solutions. The results of metal ion substitution, mechanistic studies, and electron structure calculations will be discussed.

SERMACS 254

Carbon dioxide reduction catalysis with protic metal pincer complexes

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The first examples of a CNC pincer ligands with a central pyridinol derived ring were recently reported. The differences in catalytic reactivity between CNC ligands with a central pyridine ring vs. a pyridinol derived ring are substantial and highly active and robust catalysts have been synthesized and studied. In these pincer ligands, the 4-substituent can be OMe, OH, or O-, and these latter two options allow for altered catalyst properties as a function of proton concentration. Catalytic studies of carbon dioxide reduction have used ruthenium(II), nickel(II), and other transition metals. We have made metal complexes that can be protonated or deprotonated reversibly in situ to switch on or off the photocatalytic performance towards CO2 reduction. Furthermore, the methoxy group on the pyridine ring offers unique catalysis advantages not seen with the unsubstituted analog. Our best catalysts offer selective CO formation, >300 turnover cycles, and a 40h lifetime. Highly active self-sensitized catalysts have recently been developed. Steric and electronic ligand effects are being studied with these catalysts by experimental and computational methods. Recently, we have synthesized new pincer ligands with other functional groups to illustrate structure function relationships. These pincers and their ruthenium complexes have been used for both carbon dioxide reduction and other catalytic reactions in various solvents, including water.

SERMACS 255

Understanding cobalt oxide-promoted catalytic reduction of para-nitrophenol

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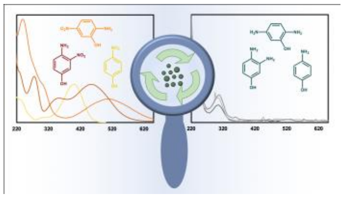
The reduction of para-nitrophenol (pNP) using heterogeneous catalysts is a well-established area of research due to its implications in environmental remediation/waste valorization. pNP is an organic, noxious pollutant produced from several industrial processes. When pNP is catalytically reduced in the presence of a hydrogen source, it forms aminophenol; this is considerably less hazardous and may be employed as a precursor for the synthesis of common pharmaceuticals such as paracetamol. From the academic perspective, this reduction is used as a benchmark for comparing the activity of heterogeneous catalysts, chiefly due to the ability to quantify catalytic rate using UV-Vis spectroscopy. A majority of the catalysts tested with this reaction are noble-metal catalysts (especially nanoparticles), and while these are capable at remediating pNP in the presence of a hydrogen source, the cost hinders any reasonably large scale environmental applications. To date, research has yielded a number of non-noble metal catalysts (ie. iron, cobalt, nickel) capable of this reaction. However, these are still typically accessed through more involved preparative routes. The catalyst synthesis explored in this study utilizes the green chemistry technique of vibratory ball-milling and annealing cobalt oxide-based particles at different temperatures, producing unique agglomerates with differing surface structures and catalytic properties.

Testing the reduction of pNP using these cobalt-oxide based particles shows positive results with complete conversion into aminophenol. Further analysis demonstrates that these catalysts are efficient for the reduction pNP in a flow process as well as the remediation of 4-amino-3-nitrophenol and 2-amino-5-nitrophenol with unique catalytic rates. While the heavily studied noble-metal catalytic reduction mechanisms are acceptably investigated and agreed upon, non-noble metal catalytic mechanisms are not well-studied or understood. The research presented elaborates on the development of a deeper mechanistic understanding for Earth-abundant oxides.



SERMACS 256

Conversion of methane, ethane and propane to form alkyl esters: Oxy-esterification as a strategy for selective partial oxidation

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The selective and low temperature conversion of light alkanes (methane, ethane and propane) to functionalized products has been a long-standing challenge. In protic media, the reaction of light alkanes with iodine oxides results in the conversion to mono-functionalized products with alkyl trifluoroacetates as the primary products. The transformations are effective over a broad range of temperatures (100 - 235 °C) and pressures (240-6900 kPa) in non-superacidic media. Alkane conversions between 15% and 40% with selectivity for mono-functionalized products between 85% and 95% have been achieved. The presentation will focus on mechanistic studies that incorporate selectivity patterns and kinetic isotope effects for conversion of light alkanes and model hydrocarbons (e.g., adamantane), spectroscopic identification of reaction intermediates, and computational modeling. In addition, preliminary efforts to extend the reaction to photo-mediated conversions as well as thermal processes with non-iodine based oxidants will be presented.

SERMACS 257

Heme sensor and inter-domain control of o_2-dependent globin coupled sensor signaling

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Globin coupled sensors are heme proteins that consist of a globin domain linked by a central domain to an output domain, such as diguanylate cyclase domains that synthesize c-di-GMP, a major regulator of biofilm formation. Previous studies have found that diguanylate cyclase activity is controlled by ligand binding to the heme within the globin domain, with oxygen binding resulting in the greatest increase in catalytic activity. Oxygen binding to the heme and c-di-GMP binding to an inhibitory site both control GCS oligomerization state, which regulates catalytic activity (tetrameric assemblies exhibit the highest activity). While oxygen binding must alter interactions between GCS monomers and between domains within GCS proteins to alter oligomerization, the lack of full-length structural information has hampered our understanding of this signal transduction event. The interactions and key residues required for signal transduction are being probed using chemical crosslinking, X-ray crystallography, FTIR, enzyme kinetic assays, and resonance Raman spectroscopy. Heme pocket residues involved in modulating O_2 affinity and redox potential of GCS proteins have been investigated, highlighting new regulatory interactions. In addition, we have identified O_2-dependent domain interactions that are likely involved in signal transduction and activation of the output domains. These studies provide insight into the molecular determinants of sensor globin ligand affinity and the mechanism by which heme ligand binding controls activity of globin coupled sensors, which will be important for develop methods to modulate GCS signaling and thereby regulate downstream phenotypes, including biofilm formation and virulence.

SERMACS 258

Modeling nitric oxide reductase utilizing Cu(II) centers and secondary sphere H-bonding functionalities: Intramolecular proton transfer facilitates $N_2O_{(g)}$ release

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Bacterial enzyme nitric oxide reductase (NOR) facilitates the reduction of nitric oxide (NO) to nitrous oxide (N_2O) within the enzymatically sophisticated denitrification process of geochemical nitrogen cycle. Such chemistry also holds pivotal significance in human pathology and environmental science. NOR possesses a heme/non-heme diiron active site, which is presumed to couple NO with the intermediacy of the key intermediate hyponitrite ($[O\text{-}N{=}N\text{-}O]^{2-}$). Heme/copper oxidases also mediate nitric oxide reduction, albeit with much lower efficiency. Modeling NOR activity with reduced metal centers is a challenging task due to the high tendency of NO to disproportionate (i.e., giving both NO_2^- and N_2O) in the presence of electrons. This study involves Cu(II) complexes with secondary sphere H-bonding functionalities, which readily couple NO to produce quantitative amounts of N_2O in MeOH under ambient conditions. Structural characterization of the final copper product reveals evidence for an intramolecular proton transfer event during NO reduction, with the protons originating from the acidic H-bonding group. Spectroscopic and computational studies strongly suggest the formation of a dicopper(II) hyponitrito intermediate initially upon Cu(I)/NO interaction, which then undergoes N–O bond cleavage upon intramolecular proton transfer from the ligand framework. This work sheds light on the crucial balance between the acidity and hydrogen bonding strength of active site components of nitric oxide coupling enzymes that leads to efficient reduction of NO in biology.

SERMACS 259

HNO trapping mechanisms with ferric heme proteins

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Many HNO scavenging pathways exist to regulate its in vivo and in vitro biological and pharmacological activities, including the involvement of numerous ferric heme proteins. Such reactions also build an important basis for HNO probe development. However, mechanisms of HNO reactions with ferric heme proteins are largely unknown. A computational investigation was performed to provide the first detailed pathways, using metmyoglobin and catalase as representative ferric heme proteins with neutral and negatively charged axial ligands. Results well reproduced experimental barriers with an average error of 0.11 kcal/mol. The rate-limiting step was found to be the dissociation of the resting ligand or HNO coordination where there is no resting ligand. Unlike the non-heme case, the reductive nitrosylation step for both heme proteins was found to be barrierless proton-coupled electron transfer, providing the major thermodynamic driving force for the overall reaction. Origin of experimental reactivity difference between metmyoglobin and catalase was revealed. Results will facilitate studies of other heme-based HNO scavenging systems and probe development.

SERMACS 260

Maturation and assembly of the key enzyme of methanogenesis

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Methyl-coenzyme M reductase (MCR) is the key enzyme in the biological formation of methane (methanogenesis), a potent greenhouse gas and biofuel. Homologs of MCR are also found in archaea that catalyze the anaerobic oxidation of methane (AOM) and other short-chain alkanes. The activity of MCR is critically dependent on the nickel-containing tetrapyrrole, coenzyme F430. In addition to housing F430, the active site of MCR contains several unprecedented post-translational modifications (PTMs), including 2-(*S*)-methylglutamine, 5-(*S*)-methylarginine, 3-methylhistidine, *S*-methylcysteine, and thioglycine residues. Because of its unique activity, MCR holds much promise for use in methane bioconversion strategies. However, a lack of genetic and biochemical information about the biosynthesis of coenzyme F430 and the PTMs of MCR have hampered metabolic engineering efforts utilizing this enzyme. Current progress in the understanding of MCR maturation and the production of *holo* MCR in a heterologous host will be presented.

SERMACS 261

Biological implications of amino acid coordination to Cu(II) and Fe(II)

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The three factors of metal ion availability, ligand availability, and thermodynamic stability of the resulting complexes control metal ion interactions with weakly coordinating amino acid ligands. These ligands may play an active role in mitigating biological metal-mediated oxidative damage, but stability of Fe(II) and Cu(II) complexes with the antioxidant sulfur- and selenium-containing amino acids is relatively unexplored. Cu(II) binds methionine, selenomethionine, methylcysteine, and methylselenocysteine with stability constants from 8.0-8.2 ($[CuL]^+$; L = amino acid); much weaker interactions are observed for $[Fe(II)L]^+$ complexes, with stability constants from 3.5-3.8 ($[FeL]^+$). The thiol penicillamine, used to chelate copper for treatment of Wilson’s disease, has a much higher $[FeL]^+$ stability constant of 7.5. Thio- and selenoether amino acid coordination to Cu(II) and Fe(II) occurs through the carboxylate and the amine groups, with no sulfur or selenium binding, as confirmed structurally for $Cu(SeMet)_2$. Thus, almost 100% of available copper is bound by these amino acids at pH 7, but very little Fe(II) is bound, consistent with their ability to prevent copper-mediated but not iron-mediated oxidative DNA damage.

SERMACS 262

Non-native redox processes by synthetic cytochrome *C* oxidase mimics

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Mitochondrial Cytochrome *c* Oxidase (CcO) utilizes a unique heme-copper binuclear active site to carry out the enzymatic four-electron four-proton reduction of dioxygen (O_2) to water; this reaction is coupled with the process of proton pumping and the biological ATP production. While O_2-reactivity at heme-copper centers is well studied, alternative redox reactions catalyzed by these systems have not been much explored. Our research goal is to contribute to a fundamental understanding of the non-native redox reactions (i.e., both reduction and oxidation) that can be catalyzed by heme-copper model systems. We previously described how synthetic heme-copper centers reduce nitrite ion to $NO_{(g)}$ or the reverse, oxidize $NO_{(g)}$ to nitrite. This redox interconversion of nitrite and $NO_{(g)}$ is believed to occur as part of CcO’s function, which is intimately tied to cellular O_2 balance. This presentation will focus on our recent studies on alternative redox reactions catalyzed by the related synthetic heme-copper systems, including the reductive coupling of $NO_{(g)}$ to nitrous oxide as well as new oxidative reactions.

SERMACS 263

Substrate tuning traps intermediates in radical SAM enzyme reactions

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Radical *S*-adenosyl-L-methionine (rSAM) enzymes employ a [4Fe–4S] cluster to reductively cleave SAM, yielding a putative 5'-deoxyadenosyl (5'dAdo$^\bullet$) primary carbon radical. This 5'dAdo$^\bullet$ radical can then abstract an H-atom from substrate to initiate its transformation to product. And while only 100 different products are known, genetic clues suggest more than 150 000 different rSAM enzymes may exist. We explore the influence of substrate analogs and enzyme variants on these transformations to decode the roles of individual amino acids and then use mutagenesis to reprogram enzymes to manufacture non-native products. Here we present a survey of our recent efforts on this front in which we employ EPR spectroscopy to identify paramagnetic intermediates in rSAM reactions and biochemical assays to monitor product outcomes.

SERMACS 264

Demystify the chemical logic of mononuclear iron enzyme catalyzed olefin and nitrile groups installation

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Mononuclear iron and 2-oxoglutarate (Fe/2OG) enzymes catalyze a broad array of oxidative transformations. In addition to those well-studied reactions, such as hydroxylation or halogenation, the possible reaction pathways and the chemical logic of other reaction types including C-C bond, C=C bond and C≡N bond installation have not been elucidated. Our recent discoveries in studying Fe/2OG enzyme catalyzed decarboxylation-assisted olefination and nitrile formation harness the power of the Fe(IV)-oxo species as versatile biological C-H activating agent and demonstrate the reaction outcome can be directed through neighboring group participation. It also sheds the light in utilizing Fe/2OG enzymes to catalyze other non-native reactions.

SERMACS 265

Synthesis of coumarin-derived hydrogen sulfide chemosensors

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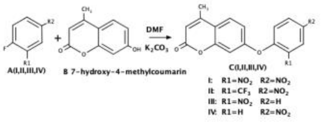
Hydrogen sulfide (H_2S), a toxic gas, is endogenously produced in the human brain and regulates synaptic transmission, inflammation, and transcription. Variant endogenous concentrations of H_2S are linked to Alzheimer's disease and diabetes mellitus, and regulation of H_2S serves as a pharmacological target for drug discovery. The focus of this project was to synthesize four coumarin-derived H_2S probes. 7-hydroxy-4-methylcoumarin (B), dimethylformamide, and potassium carbonate were combined with 1-fluoro-2,4-dinitrobenzene, 2-fluoro-5-nitrobenzotrifluoride, 1-fluoro-2-nitrobenzene, or 1-fluoro-4-nitrobenzene to produceC(I, II, III, or IV)respectively. Yields were 96%, 74%, 95%, and 46%, respectively. Structures were verified by ^{1}H NMR, HPLC, and mass spectrometry (MS).



One Step Synthesis of C(I, II, III, and IV)

SERMACS 266

Asymmetric synthesis of nitrogen heterocycles by electrophilic cyclization reactions

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Nitrogen containing heterocyclic compounds, which are bountiful in nature, are of great biochemical importance in the field of organic chemistry, particularly in pharmaceutical drug industry. Owing to this important socio-economic healthcare impact, the stereoselective synthesis of new heterocycles is vitally important. The purpose of this project is to synthesize heterocycles derived from acyclic homoallylic carbamates, thioureas and guanidines in order to difunctionalize the pendant alkene. Asymmetry is favorable in heterocyclic structures because enzymes are homochiral and single enantiomer prescription drugs are preferential. The thioureas used were synthesized in four chemical steps from commercially available benzaldehydes. The use of a stoichiometric chiral ammonia reagent (SCAR), namely the R-tert-butanesulfinamide or Ellman reagent, was utilized to create chiral imines. Indium mediated allylation of the imine afforded the homoallylic N-sulfinylamine in high yield and diastereoselectivity of greater than 20:1. Upon acid promoted deprotection of the N-sulfinyl group, the hydrochloride salts were isolated then further functionalized. For example, treatment with isothiocyanates such as phenyl isothiocyanate afforded the thiourea derivative. We hypothesized that the incipient C2 stereogenic carbon bearing the aromatic moiety would influence the nascent C4 stereocenter upon electrophile initiated cyclization. The cyclization process was initiated via electrophiles such as iodine, bromine, and *N*-bromosuccinimide. All crude reaction mixtures were analyzed by carbon and proton nuclear magnetic resonance spectroscopy to determine diastereoselectivity. We rationalize the formation of C2-C4-trans stereochemistry based upon minimization of allylic strain in the reactive conformation of the six-membered chair like transition state. Overall, this method is useful for the creation of 1,3-aminoalcohols and 1,3-aminothiols.

SERMACS 267

Towards a greener multidentate NacNac ligand

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Progress towards a greener synthesis of tri- and tetradentate NacNac ligands is presented. The modular approach presented allows for the generation of a wide variety of NacNac ligands with a wide tunability in both sterics and electronics. Our method of synthesis utilizes greener reagents than traditional syntheses, allowing for a wider application of these unique ligands.

SERMACS 268

Synthesis and analysis of primary amine functionalized silica sol-gels for catalyst extraction

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Primary amine functionalized silica sol-gels were prepared by a basic sol-gel process in water. The preparation was done by utilizing tetraethyl orthosilicate, or TEOS. They were then functionalized by (3-Aminopropyl)triethoxysilane, or APTS, which produced the primary amines on the surface of the sol-gel. In order to provide efficient functionalization of the silica sol-gels, there was a high ratio of TEOS/APTS. From this, the reactivity of these functionalized amine groups were tested by reacting them with carboxylic acid to form a covalently bonded amide. This was monitored by Fourier transformation infrared spectroscopy, or FTIR. Once the reactivity is confirmed, these sol-gels can be applied to immobilize the polymerization catalyst used in ring opening metathesis polymerization, or ROMP, aiding in the purification through simple filtration procedures.

SERMACS 269

Synthesis, characterization, analysis, and use of biofuel from campus dining operations waste oil and grease

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Biodiesel was synthesized from campus Chick-fil-A waste oil and grease and blended with commercial ultra-low sulfur diesel to produce fuel blends. Biodiesel and blends were characterized with GC-MS, ICP-MS, IR, NMR, and micro bomb calorimetry, along with temperature dependent density and viscosity measurements. Diesel and biodiesel:diesel fuel blends were used to power a diesel generator and generator exhaust gases were analyzed with IR and AFM. Results indicate fuel blends from Chick-fil-A waste oil and grease are suitable for use. Ongoing work includes pilot plant scale-up and synthesis using deep eutectic solvents.

SERMACS 270

Microwave-assisted oxidation of silyl ethers into silyl esters

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A microwave-assisted, biphasic, ruthenium-catalyzed oxidation of silyl ethers to silyl esters was optimized for high percent conversion and high selectivity of TBS octyl ester over a carboxylic acid hydrolysis product. Optimization variables included time, temperature, catalyst loading, solvent/water ratio, and pyridine additive equivalents. In a solvent screening, the percent conversion and ester/acid ratio were high for EtOAc and dichloromethane but low for chloroform. The microwave conditions were applied to a variety of silyl ethers containing different functional groups including nitriles, phenyl groups, ketones, chlorides, bromides, and epoxides. Substrates of varying chain-lengths whose carboxylic acid side products had the potential to form lactones via intramolecular nucleophilic attack were also explored.

SERMACS 271

Investigating novel nanocrystals as catalysts for heterogeneous cross-coupling reactions

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Catalysts used in cross-coupling reactions are extremely important in the fields of organic synthesis and medicinal chemistry. Heterogeneous variants of these catalysts are highly desirable to improve economy through catalyst recycling and to decrease purification needs to separate the toxic metals from the final pharmaceutical product. Palladium nanoparticles have been extensively investigated for heterogeneous cross-coupling catalysis, but compared to the scope of homogeneous catalysts, there is much room for improvement and optimization. We have tested different, novel nanocrystals as heterogeneous metal catalysts, including PdB_x and PdPS. The catalysts were tested under different reaction conditions for known cross-coupling reactions, such as the Suzuki reaction. Adjusting the solvent, aryl halide, temperature, and reaction duration allowed conditions to be optimized. The outcome of each reaction was analyzed via GC-MS. Solvent optimization brought yields up to 90%. Similar results and greater base stability were observed with the novel nanocrystals as compared to the standard palladium catalyst. Future work includes testing non-precious metals in cross-coupling reactions.

SERMACS 272

Mechanical properties of boron nitride nanoparticle reinforced aerogels

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Aerogels have been used in a wide array of commercial and technical applications, including as insulation, capacitors, and absorbents, and have many applications in aerospace technologies, yet silica aerogels are fragile and difficult to manipulate without damage. Boron nitride (BN) nanomaterials have been widely observed to have strengthening properties in composite materials. By studying the integration of boron nitride nanoparticles with silica aerogels, we hope to create a material that is hydrophobic, is ultralight and low density, and that can withstand high temperatures with an increase in durability and mechanical strength. Our group has developed a method to functionalize nanoscale BN to create a stable dispersion of BNNTs in a silica aerogel sol-gel. Once a stabile sol dispersion is formed, targeted covalent attachment can occur, and nanoscale BN can be well distributed and can be integrally linked in the aerogel matrix. Through these methods we overcome the poor dispersibility of h-BN in the aerogel composite and maximize property enhancement by the nanoparticle filler. Composite aerogel properties are tested using tensile strength tests, 3-point bending tests, and thermal conductivity measurements.

SERMACS 273

Sonochemical generated radical detection in fluorinated solvents

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Boron nitride nanotubes (BNNTs) and sheets are interesting analogues to carbon nanotubes and graphene that are wide band gap semiconductors and have been shown to be good radiation absorbers and have a high oxidation and thermal stability. Yet, due to their chemically inert surfaces, boron nitride BNNTs can be difficult to functionalize and integrate composite matrices which limits the translation of their properties to bulk materials. We have previously demonstrated a sonochemical technique to covalently attach alkoxy and fluoroalkoxy substituents to the surface of BN nanomaterials. We hypothesize that during ultrasonication, free radicals are generated which enable breakage and addition to the B-N chemical bonds. An easy method of radical detection in fluorinated solvents is needed. In this talk we present a method to detect the generation of these radicals in fluorinated solvent solutions. We use methyl viologen, a chemical compound that reacts with free radicals in solution to form a new compound which absorbs ultraviolet light and can be detected using UV-Vis spectroscopy. Methyl viologen dichloride is widely available, however, it is highly insoluble in fluorinated organic solvents. The structure of methyl viologen can be modified via metathesis of a larger, more complex ion, increasing solubility in perfluorinated organic solvents and allowing detection of radicals generated at different steps of our process.

SERMACS 274

Investigation of acid catalyzed Pictet-Spengler cyclization with suldonamides

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Piperidines are an important pharmacophore and essential in the field of drug discovery. Piperidine scaffolds are the building blocks for over 70 different types of commercial drugs, and have a wide range of therapeutic applications. The overarching goal of this project is to develop a robust catalytic, asymmetric synthesis of piperidine rings from feedstock chemicals. In one initial study of the Pictet-Spengler cyclization with *N*-para-toluenesulfonyl and *N*-tert-butanesulfonyl homoveratrylamine and 3-phenylpropanal, a screen of metal triflates was examined. Initial results indicated that scandium (III), stannous (II) and copper (II) triflates gave the fastest conversion to the *N*-sulfonyl piperidine, while triflates such as lanthanum (III), sodium (I) and magnesium (II) gave little to no conversion under the allotted time. However, the triflates that proved successful with *N*-Ts homoveratrylamine did not produce the same conversion when screened against *N*-Bus homoveratrylamine. Based upon accepted knowledge of the mechanism we propose that the cyclization proceed through an *N*-sulfonyliminium ion intermediate. In a second investigation, *N*-sulfonamides derived from tryptamine were examined with metal triflates. Future studies will focus on the use of chiral ligands to induce asymmetry in the cyclization event. These experiments will examine enantioselectivity of the Pictet-Spengler cyclization in comparison to earlier results with analysis by chiral HPLC.

SERMACS 275

Synthesis and application of a trifunctional small-molecule probe to study time-resolved protein-protein interactions

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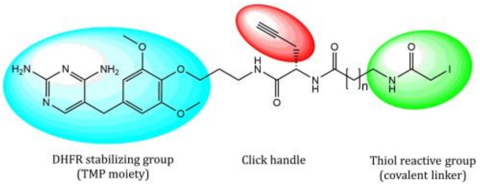
Dynamic protein-protein interactions drive most cellular processes and determining the precise timing of these interactions is crucial for elucidating molecular function. Here, we developed a trifunctional small-molecule probe to study protein-protein interactions in a time-resolved manner. We take advantage of a destabilized dihydrofolate reductase (DHFR) that can be fused to a protein of interest. Addition of the ligand trimethoprim (TMP) can stabilize the DHFR protein fusion, preventing proteasomal degradation, and can thereby initiate protein accumulation in cells. We synthesized analogs of TMP that maintained the trimethoprim moiety, thus stabilizing the complex, and appended a terminal alkyne which is amenable to Click chemistry. Furthermore, our probe design included different thiol reactive groups which can covalently react with a cysteine residue placed on the DHFR by site-directed mutagenesis.

We synthesized a panel of probe compounds with varying carbon linkers and thiol reactive groups and evaluated the stabilization and reactivity of DHFR-yellow fluorescence (YFP) protein in human cell lines. Furthermore, we tested locations of engineered cysteine residues on the DHFR protein to determine the most effective small molecule structure to stabilize and covalently engage the DHFR-YFP fusion protein. With this molecule initiating protein accumulation, the Click handle can be derivatized with biotin for streptavidin pulldowns enabling mass spectrometric identification of interacting partners over time. In the future, we plan to utilize this tool to elucidate the timing of host-pathogen protein-protein interactions.



Trifunctional probe design

SERMACS 276

Modification of thiols via nucleophilic aromatic substitution

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The IR stretching frequency of nitrile groups and the NMR chemical shifts of fluorinated compounds are very sensitive to the local electronic environment. Thus, introduction of nitrile groups and fluorine atoms into proteins can provide important information about the changes in the local electronic properties upon protein folding. We have previously modified various sulfur-containing molecules with several electrophiles, including 3,4,5-trifluorobenzonitrile (TFBN). Herein, we found that the UV-Vis spectrum of TFBN undergoes a significant change upon modification with thiols, with the appearance of a new peak with maximum at 290 nm. This peak can be used to monitor the reaction even in the presence of excess substrates, and its appearance allowed us to measure the kinetics of the modification and to determine the rate constant of the reaction. We have synthesized a mutant version of Mastoparan X, a peptide that binds calmodulin very tightly, and proceeded with the modification of this peptide using the same technique. Porcine hemoglobin, a protein with cysteine residues that are not involved in disulfide bonds, has also been modified. We have observed the peak at 290 nm in the UV-Vis spectrum and have confirmed this modification using MALDI-TOF mass spectrometry. Overall, our results suggest that TFBN can be used to inexpensively modify proteins to introduce NMR- and IR-active reporters.

SERMACS 277

Thermal shift assay development for finding novel antibiotics targeting a cystic fibrosis pathogen

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P. aeruginosa is a pathogen known to cause severe illness in humans, particularly patients who are immunocompromised. The bacterium is recognized for its ability to frequently develop multidrug resistance to antibiotics. This project will guide and develop original strategies to find novel antibiotics that are less likely to evolve resistance rapidly. Fragment-Based Drug Discovery is a strategy that screens for small molecules that bind selectively to a target protein; these could then be coupled to reactive warhead inhibitors to covalently inhibit the target protein. Thermal shift assay, using a targeted protein, has provided data for various conditions or fragments simultaneously. Previous aims for this project included finding appropriate dye and protein concentrations, optimizing buffer conditions to enhance protein thermodynamic stability, and screening of a library of small molecules for hits that covalently bind to and further increase protein stability. This assay uses the fluorescence of a hydrophobic dye to monitor the stability of the protein as it is subjected to increasing temperatures. This assay allowed for the screening of various drug fragments that bind the *P. aeruginosa*glutaredoxin protein, a factor that mitigates reactive oxygen species and is a model for biophysical studies. This factor also has a dithiolate active site that may be inhibited by known warhead chemistries.The use of this thermal shift FBDD assay has provided a fragment screen of hits that can be further analyzed by organic chemists as putative drug leads. Current project goals aim to validate fragment hits that showed a significant shift in the apparent melting temperature during the screening process, as well as attempt to obtain a $K_d$to help determine binding affinity of the ligand and protein by using nuclear magnetic resonance and isothermal titration calorimetry. Results to obtain these validated hits will be presented.

SERMACS 278

Utilization of organic contaminants as chemical tracers of elasmobranch ecology and physiology

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Elasmobranchs typically occupy higher trophic levels in food webs and, consequently, have a propensity to accumulate high organochlorine contaminant (OC) concentrations. However, not all sharks accumulate the same types of contaminants or at the same rate, making use of OCs a potential ecological tool. As test case, bioaccumulation with respect to ontogeny was examined among three species of pelagic sharks (Shortfin Mako *Isurus oxyrhincus*, Common Thresher *Alopias vulpinus*, and Blue Shark *Prionace glauca*) that have varying diets and life history characteristics. Using recently collected and archived tissue from sharks in an area known for high contaminant levels, organic contaminants (polychlorinated biphenyls and chlorinated pesticides) were measured in livers of both females and males from a range of size classes for all species. Significant differences were found in OC concentrations among species and by size. In addition, random forest analysis was able to distinguish species based on their contaminant signatures with a high degree of accuracy. Results suggest that foraging ecology and species-specific life history characteristics impact the accumulation of organic contaminants. Future work intends to build upon this information by examining how elasmobranchs may act as carriers and distributors of organic contaminants across geographical regions.

SERMACS 279

Controlled-PCO_2 aquaculture for long-term investigation of ocean acidification

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Ocean acidification has been actively studied for over 50 years, and while the environmental chemistry is well understood, the biological impacts in these systems are still unclear. Field studies offer little control on confounding variables; mesocosm studies are expensive to conduct and difficult to scientifically replicate; laboratory studies vary greatly in methodology. The sum of these research efforts create difficulty in interpreting the short- and long-term impacts on biota. We present the latest iteration of a system developed to simulate the slow, subtle impacts of ocean acidification by precisely controlling equilibrium pCO_2 in laboratory aquarium systems while holding all other key environmental factors constant. Early developmental systems were expensive, but recent improvements greatly reduce component costs, and operation only necessitates weekly replacement of reaction chemistry. Moreover, the latest development in automated control permits simulating natural diurnal to seasonal variation or a host of acclimation schemes, no longer is 'constant' control required. We present the results from a long-term acclimation study of the tropical coral *Montipora digitata* that we investigated the chronic and acute responses to a changing equilibrium pCO_2 environment. The chronic study observed the response of coral maintained at 400 μatm (nominally year 2015), slowly ramped down to 340 μatm to simulate year 1980, and slowly ramped up to 460 μatm to simulate year 2050. The acute study alternatively observed the response to rapidly increased pCO_2 simulating a sudden environmental impact that is ameliorated over 48h and maintained at pre-exposure levels for the duration of the 6-week experiment. This system's development was funded by the National Science Foundation, Natural Environmental Research Council (UK), and Sea of Change Foundation.

Coral *Montipora digitata* cultured during a long-term pCO_2-controlled ocean acidification study.

SERMACS 280

Experimental determination of flame retardant effects on aquatic communities of the Southeastern Coastal Plain

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Flame retardant chemicals are now pervasive in aquatic systems due to industrial use and discharge into municipal and industrial wastewater. Current information about the toxicity of organophosphorus flame retardants, such as tetrakis hydroxymethyl phosphonium chloride (THPC), is derived primarily from short-term laboratory tests on individual aquatic species. However, THPC degrades slowly and has the potential to not only persist in the environment with long-term effects on aquatic organisms, but also interact with other chemicals and abiotic stressors such as temperature. Thus to assess environmental effects of THPC, testing must include multiple interacting species under realistic conditions. The goal of these studies was to examine how THPC alone and in combination with other chemicals influences communities of pond and stream organisms in the southeastern coastal plain. First, we assessed THPC effects on communities in artificial streams. After two, two-week exposures to various THPC treatments, water quality and responses of algae, macroinvertebrates (insects, etc.), snails and crayfish were measured. Water chloride concentration, a THPC degradation product, indicated that THPC was still present. For all other measured variables, THPC effects were dependent on the presence of snails and crayfish, which appeared to obscure chemical effects. Furthermore, the environmental conditions (e.g. temperature, no other chemicals) were favorable during these experiments. Therefore, because THPC reaching freshwater systems likely becomes mixed with other chemicals, including excess nutrients from fertilizers and chemicals associated with the textile industry, we measured the influence of environmentally relevant concentrations of THPC and nutrients (ammonium) alone and in combination on freshwater plankton (microscopic plants and animals) abundance and species composition under field conditions. Miniature floating ponds received THPC and/or ammonium treatments for one month. Chemical treatments appeared to alter abundance of specific groups of plankton. For example, a group that provides essential food resources for fish averaged ~50% fewer individuals than the control treatment, indicting potential for reduced energy transfer in the community. These experiments are an important step toward addressing how flame retardant chemicals affect aquatic communities and illustrate the complexity associated with predicting chemical effects in aquatic environments.

SERMACS 281

Drivers and dynamics of change in Altamaha, Doboy, and Sapelo Sounds along the Georgia coast

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Changes in climate, weather, and population alter the biogeochemical dynamics of coastal environments. The Altamaha River Estuarine System provides a unique opportunity to assess how these dynamics are altered across three sounds (Altamaha, Doboy, and Sapelo) with unique freshwater inputs, hydrologic circulation, and physics. The dominant freshwater source to the system is the Altamaha River. The Altamaha watershed is the largest in Georgia and is comprised of five sub-watersheds covering roughly 35,500 km^2. Nutrient loads to the system were dominated by organic forms of nitrogen and phosphorous. Nutrient loading was strongly impacted by population, land and water use, and livestock, whereas retention within the system was affected by changes in climate and weather. The aim of this study was to elucidate the factors that impact biogeochemical dynamics in the Altamaha River Estuarine System. This was accomplished through integration of long-term chemical, climatological, and hydrological data collected through the Georgia Coastal Ecosystems – Long Term Ecological Research project (2000-2019), US Geological Survey discharge database, and the South Eastern Regional Climate Center. We project that the biogeochemical dynamics of the Altamaha River Estuarine System mirror the changes seen in the Altamaha River Watershed over this time period. These changes are likely exacerbated by changes in climate patterns.

SERMACS 282

Research framework for coupled hydrologic and biogeochemical systems in freshwater wetlands on Georgia coast barrier islands

***James B. Deemy**, jdeemy@ccga.edu, Kimberly Takagi. Department of Natural Sciences, College of Coastal Georgia, Brunswick, Georgia, United States*

Freshwater wetlands on barrier islands of the Georgia Coast are largely unstudied due to their relatively small footprint compared to nearby salt marshes. Small isolated and semi-isolated wetlands on barrier islands could act as biogeochemical hotspots embedded within terrestrial coastal ecosystems. Our objectives are to 1) generate a research framework for studying coupled hydrology and biogeochemistry in these systems; 2) establish a baseline dataset in a semi-isolated freshwater wetland on St. Simons Island; and 3) determine source waters through end-member mixing analysis.

Our focal wetland is a small semi-isolated wetland on St. Simons Island, Georgia near Oglethorpe Elementary School. Preliminary baseline data was collected from late Fall 2018 through early Spring 2019 (just before vegetation senescence to just after leaf-out). Focal parameters during this pilot study were turbidity, temperature, pH, dissolved oxygen, and specific conductivity measured at weekly intervals. Analysis of the baseline dataset indicates that the wetland is a well-mixed system suitable for end member mixing analysis.

Our pilot data serves as a baseline for the continuous monitoring of wetland stage and specific conductivity. Weekly measurements of current focal parameters will also continue with the addition of field measured NH_4^+, NO_3^-, and PO_4^{2-} using LaMotte colorimetric kits. Weekly samples will also be collected for cation and anion analysis.

Future analyses will focus on establishing distinct chemical signatures of hydrologic inputs for end member mixing models. Additionally, field measured chemical and physical parameters will be correlated with laboratory analyzed parameters to determine monitoring variables.

SERMACS 283

Detection and risk analysis of UV filter and paraben micropollutants in the tidal freshwater Potomac River

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Pharmaceutical chemicals and personal care products (PPCPs) are emerging pollutants of concern in human and ecological health.[1] The specific PPCPs targeted for analysis were UV filters and parabens. They are mild endocrine disrupting chemicals (EDC) and persistent, bioaccumulative, and toxic substances (PBTs). Objectives of this study were to (i) develop new methods for the analysis of UV-filters and parabens in sediments using the LC-MS/MS instrument, (ii) determine if UV filters and parabens in sediments are associated with wastewater treatment plant discharge, and (iii) establish whether the source profiles of UV-filters and parabens in sediments is unique geospatially. Through QuEChERS and dSPE extractions and LC MS/MS analysis the concentrations of butyl paraben, isobutyl paraben, octocrylene, and oxybenzone were determined. Results processing indicated the sources of the compounds were not associated with wastewater treatment plant discharge and they were not unique geospatially. Risk Index values to the fathead minnow (Ppimephales promelas) of each compound were calculated. The risk indexes of the sum of the compounds was above the threshold of toxicity. Further research in different environmental matrices, sampling locations, and quality assurance must be done to gain a better understanding of these compounds and their behaviors during sample processing.

SERMACS 284

Detoxification of waste water of Pb^{2+} and Cd^{2+} using agricultural waste of boiled groundnut (*Arachis hypogaea*) shells

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The adsorption capacity of boiled groundnut(*Arachis hypogaea*) shells for Pb^{2+} and Cd^{2+} ions from aqueous solution was investigated. Batch adsorption experiments were carried out as a function of pH, adsorbent dose, contact time and temperature with a constant concentration of 100mg/L and particle size of 500mm. The adsorption results showed that the pH of the aqueous solution affected the removal efficiency of both metal ions.The maximum adsorption for Pb^{2+} occured at a pH of 6.5 with adsorption effciency of 96%. while that of Cd^{2+} occured at a pH of 7.5 with adsorption efficiency of 94%. The effect of contact time on the adsorption capacity of both metal ions revealed that equilibrium adsorption for both metal ions were reached within 90 minutes. The effect of temperature on the adsorption capacity indicated that the adsorption process decresased with increasing temperature. The results from adsorption kinetics models showed that its kinetics fitted better into pseudo second order than the psuedo first order. The results generally showed thet the metal ions were considerably adsorbed by the boiled groundnut shells, this could be considered as an economic method for the removal of these metal ions from waste water before discharging into the environment.

SERMACS 285

Molecular dynamics simulations of micelle formation by surfactants and peptides

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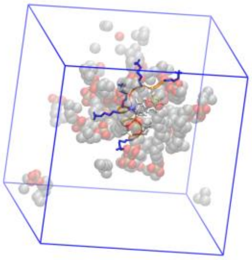
Interactions between proteins and micelle-forming amphiphiles (such as detergents, fatty acids, or bile salts) take place in a variety of settings – the research lab, the kitchen sink, and the digestive system. To model these interactions accurately requires force fields that can account for the thermodynamics of competing interactions among amphiphiles, proteins, and water. Using force fields parameterized to give correct alkane-water and alkane-alkane interaction thermodynamics, we have applied a new approach (the “PEACH” method) to characterize the self-assembly of simple phosphocholine surfactants into micelles from molecular dynamics simulation data, giving improved agreement with experiment. Simulations of octyl phosphocholine interactions with the CM15 antimicrobial peptide show that the presence of surfactant promotes folding into an alpha helix, in qualitative agreement with experiment. Statistical analysis using PEACH will allow the determination both of how the association of a peptide with a micelle influences the equilibrium number of surfactants in the micelle, and how the presence of surfactants influences the free energy of folding of the peptide.

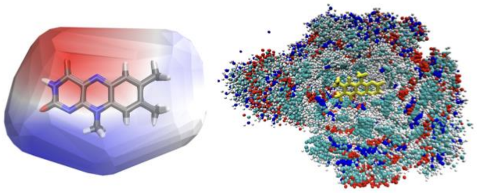


SERMACS 286

Electrostatic tuning maps and average protein configurations: Strategies to aid in studying flavoproteins

Yoelvis Orozco-Gonzalez, Mohammad Pabel Kabir, ***Samer Gozem***, *sgozem@gsu.edu. Department of Chemistry, Georgia State University, Atlanta, Georgia, United States*

Flavins are versatile molecules due to their ability to exist in multiple redox and protonation states at physiological conditions. Flavins also have a rich photochemistry, capable of photoredox, fluorescence, intersystem crossing, or photochemistry depending on the protein hosting the flavin. This rich chemistry and photophysics of flavin is in large part responsible for the wide array of biological processes performed by flavoproteins. However, we are still missing a fundamental understanding of how a protein exerts control over the the properties and behavior of flavin. As a first step towards such an understanding, our group is developing and applying tools to study these systems. In my talk, I will discuss two such computational approaches: Electrostatic tuning maps and average protein electrostatic configurations. I will also discuss their application to studying the spectral tuning of iLOV, a flavin-binding fluorescent protein.



SERMACS 287

Design of asymmetric catalysts through virtual screening

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Despite the widespread success of modern quantum chemistry in explaining the origin of activity and selectivity in asymmetric catalysis, the computational design of new catalyst is still far from routine. Ideally, one could identify new catalysts by screening virtual libraries of potential designs. In this way, only those designs predicted to be most highly active and selective would need to be synthesized and tested experimentally. We will discuss recent progress in the use of quantum chemistry to design new catalysts by screening potential catalyst designs. This is made possible by AARON (An Automated Reaction Optimizer for New catalysts), which is our tool-kit for the automated screening of potential catalysts designs. The application AARON will be discussed in the context of asymmetric organocatalysis and metal-based catalysis

SERMACS 288

Computational studies of 3-hydroxy-3-methyl-glutaryl-CoA (HMG-CoA) reductase complexes with steroid-based statin analogs

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Cholesterol is a biosynthesized steroid that is needed to help the body buid new cells, insulate nerves and produce hormones. However, elevated levels of cholesterol in blood constitute a primary risk factor for the development of coronary artery disease or atherosclerosis. 3-hydroxy-3-methyl-glutaryl-CoA (HMG-CoA) reductase is the rate-controlling enzyme in the cholesterol synthesis pathway and as such is the prime target the development of drugs, such as statins, that are effective in the reduction of cholesterol levels. In this studies, a combination of computational methods, including molecular docking and molecular dynamics simulations, are used to investigate the binding and dynamics of steroid-based statin analogs which could be promising HMG-CoA reductase inhibitors. The studies showed that the analogs successfully bound to the same binding site as the currently used drugs. The average binding energy of the current drugs in the binding site was found to be -6.737± 0.156 kCal/mol. The designed analogs showed slightly more favorable binding with average binding energy of -8.502 ± 0.101 kCal/mol. These results suggest that the designed compounds are potential inhibitors of HMG-CoA reductase and provide useful insights into the ligand binding and interactions involved.

SERMACS 289

Benchmarking G-protein coupled receptor homology model template selection in tandem with *de novo* loop generation

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G protein-coupled receptors (GPCR) are integral membrane proteins of considerable interest as targets for drug development. GPCR ligand interaction studies often use crystal structures and generated 3D models as a means of comparison. However, the underlying problem with GPCR are that many of their structures remain unresolved and are deemed “orphan” receptors without known endogenous or exogenous ligands. Traditionally, comparative model template selection is based on global sequence identity and such templates often poorly reflect the structure of the highly variable extracellular loop 2 (ECL2) region. Comparative modeling combined with de novo loop generation may produce models that better represent a biologically relevant receptor structure. This *in silico* benchmarking study uses 2 sets of 6 previously crystallized class A GPCR to test the accuracy of local template selection homology modeling in combination with de novo ECL2 loop modeling in order to further optimize GPCR modeling and ligand identification. For each receptor, homology models were generated and then loop modeled before being docked into using 3 ligand docking methods: MOE induced fit docking, MOE rigid receptor docking, and Rosetta. Comparisons between generated models and crystal structures were made based on calculated RMSD values. These comparisons were also used to assess the secondary aim of this study: docking method accuracy. Compared to previous studies, the local template-based loop-modeled homology models produced were just as if not more representative of the crystallized structure than models produced based solely on local template selection. Additionally, each receptor’s ECL2 region often possessed a lower RMSD value than a non-loop modeled receptor model. Ligand docking results showcased the ability of MOE induced fit docking to produce ligand poses close to crystallized ligand poses within homology models for each of the 12 receptors, with lower ligand RMSD values than ligand poses in non-loop modeled local template-based receptors. Overall, the findings produced by this study support the use of local template homology modeling in combination with de novo ECL2 modeling in the context of computational GPCR deorphanization methods.

SERMACS 290

Polymorphism and low-temperature data collection: Cautionary tale

William T. Pennington, *billp@clemson.edu, Khadijatul Kobra, Colin McMillen, Rakesh Sachdeva. Chemistry, Clemson University, Clemson, South Carolina, United States*

Polymorphism is the solid-state phenomenon of a given substance crystallizing in two or more different forms. Examples include: carbon (graphite, diamond), sulfur (rhombic, monoclinic),[1] $CaCO_3$ (calcite, aragonite, vaterite), TiO_2 (rutile, brookite, anatase), steroids (~67%), barbiturates (~63%), antihistamines, DNA, dyes, energetic materials, etc. With the current ubiquity of low temperature systems associated with single crystal X-ray diffraction systems, data collection at reduced temperature has become the default for most labs. Recently during a structural survey of various triiodide salts, we observed a new polymorph of methyltriphenylphosphonium triiodide ($[MePh_3P]I_3$), which at that point was known to be tetramorphic. Despite multiple and wide ranging attempts we were only successful in reproducing the crystallization of three of the four known forms, with all efforts for the forth giving only our new fifth form. Eventually it occurred to us that the forth form was reported at "room temperature," yet we collect essentially all of our data sets at reduced temperatures. This talk will describe the variable temperature polymorphism of $[MePh_3P]I_3$ and will compare the structures of the polymorphs of this compound with those of mixed trihalides (iodine and bromine) with the same cation.

SERMACS 291

Polymorphs, enantiomers, and intra/intermolecular interactions of D^8 transition metal complexes

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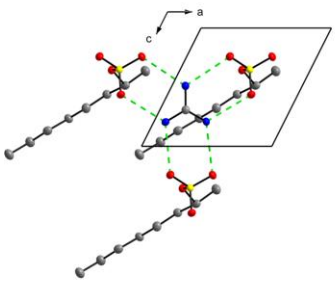
Intra- and intermolecular interactions play a strong role in the solid-state and solution electronic properties of d^8 transition metal complexes. This is in part due to the steric availability of the dz^2 orbital to interact with additional axial ligand donor/acceptor atoms or other d^8 metal centers. Persistent interactions of d^8 metals with atoms at distances and geometries that lie beyond covalent bonds but shorter than van der Waals radii can lead to interesting optical (both absorbance and luminescence), electrochemical, and NMR properties as well as unique reactivity. In our efforts to probe these types of weak interactions at d^8 metals, we have observed unexpected gold (III) templated ligand chemistry leading to spontaneous resolution of enantiomers, discovered multiple polymorphs in a platinum (II) system, each with unique photoluminescence properties, and studied a reversible temperature-induced single-crystal to single-crystal transformation in a palladium (II) complex accompanied by changes in color. The intra- and intermolecular structural features of these d^8 systems and their relationship to photophysical features will be discussed.

SERMACS 292

Organic sulfate crystallography: Versatile tool for chiral identification

***Colin McMillen**, cmcmill@clemson.edu, Beau Brummel, Kinsey Lee, Daniel C. Whitehead, Joseph W. Kolis. Chemistry, Clemson University, Clemson, South Carolina, United States*

Crystallography has always been a powerful tool for identifying the absolute stereochemistry of molecules. Not all materials are especially amenable to crystallization, however, which creates an obvious barrier to the crystallographic approach. In some instances, specialized techniques have been designed to identify and resolve enantiomers and diastereomers, with varying degrees of success and application. We present here a new approach to chiral identification blending principles of crystallography, crystal growth, and synthetic organic chemistry. Several classes of alcohols and amines are examined, which themselves resist crystallization. By converting these molecules to sulfates and crystallizing them as a salt using simple organic counterions, robust hydrogen bonding networks are established. These sulfate salts are excellent candidates for absolute structure determination by X-ray crystallography. We also extend the approach to include diastereomers where both the anion and cation of the salt contain stereocenters. Once all of the stereocenters have been identified, the original substrate can be recovered by routine hydrolysis. Careful control of the crystallization conditions may also be useful as a means to resolve enantiomers or diastereomers via bulk crystal growth.



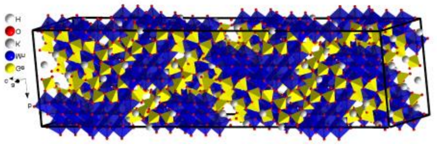
Hydrogen bonding interactions in $(C(NH_2)_3)(C_8H_{17}O_4S)$.

SERMACS 293

Similarities and dissimilarities between transition metal silicates and germanates

***Megan Smart**[1], meganmsmart@gmail.com, Tiffany Smith-Pellizzeri[1], Colin McMillen[1], Liurukara D. Sanjeewa[1], Joseph W. Kolis[2]. (1) Chemistry, Clemson University, Suwanee, Georgia, United States (2) Chem Dept, Clemson Univ, Clemson, South Carolina, United States*

Inorganic oxides, especially those of transition metals, have wide application in chemistry and material science. Silicate oxyanions are common tetrahedral building blocks in inorganic oxide materials, and can be useful to produce great structural variety by forming complex polysilicates from polymerized tetrahedra. Alternatively, germanate oxyanions are perhaps an even more versatile building block as they readily adopt 4-, 5-, and 6- coordinate geometries. This flexibility allows for the synthesis of otherwise inaccessible compounds and novel structures not found amongst the silicates. Our group synthesizes these materials with high temperature (>500 °C), high pressure (~ 2 kbar) hydrothermal techniques which mimic common mineral-forming conditions. Several transition metal germanates are presented and compared to structurally or synthetically analogous silicates, revealing new oxyanion structural chemistry. This includes unusually large unit cells, uncommon space group symmetry, potentially frustrated triangular systems, and complex chemical formulas.



The 76 angstrom crystallographic *c* axis of $K_{11}Mn_{21}Ge_{32}O_{86}(OH)_9(H_2O)$.

SERMACS 294

Computational and crystallographic studies of aromatic N-oxide oxygen-iodine halogen bonding

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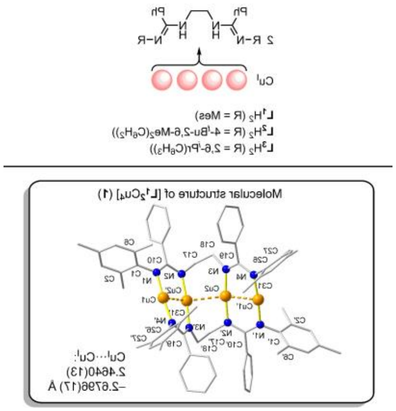
Various complexes of nitrogen heterocyclic and organic iodide compounds were synthesized and simulated computationally. Interaction energies and geometrical parameters were computed using the DFT method and SCXRD was used to measure the geometrical parameters. Computational results were compared to previous efforts for the non-oxide complexes and compared to experimental results. SCXRD results for several of these complex pairs will also be presented. Both experimental and computational results revealed strong halogen bonds within the structure, strongly supporting N-O-I bond formation. This talk will focus on several of our recent halogen bonding structures.

SERMACS 295

Multinuclear Cu^I bis(amidinates) as highly luminescent molecular strings

Michael Stollenz[1], *mstollen@kennesaw.edu, Janet Arras*[1], *Alvaro Calderon*[1], *Ethan T. Miller*[1], *Nattamai Bhuvanesh*[2], *Colin McMillen*[3]. *(1) Chemistry and Biochemistry, Kennesaw State University, Kennesaw, Georgia, United States (2) Department of Chemistry, Texas A&M University, College Station, Texas, United States (3) Department of Chemistry, Clemson University, Clemson, South Carolina, United States*

Although bis(amidine) and bis(amidinate) ligands have been well established in lanthanide and in Group 4 metal chemistry within the two recent decades, significantly less attention has been devoted to embed multiple metal ions into their polydentate binding pockets. This is in particular surprising for coinage metal ions as amidinates facilitate closed-shell metal $M^{I}\cdots M^{I}$ ($d^{10}\cdots d^{10}$) interactions (M = Cu, Ag, Au). The fascinating luminescence properties of these multinuclear complex assemblies lead to potential applications in nanoelectronics and as powerful building blocks for molecular/organic light-emitting devices/diodes (OLEDs). We have demonstrated that bis(amidinates) serve as convenient ligand scaffolds for fascinating multinuclear Cu^I string complexes. Herein, we report the most recent results related to synthetic strategies and photophysical properties.



SERMACS 296

Structure and reactivity relationship of mononuclear Cu(II) complexes with peroxides

Anusree Mukherjee, *anusree.mukherjee@uah.edu. Chemistry, University of Alabama in Huntsville, Madison, Alabama, United States*

The development of environmentally-friendly copper mediated oxidations with ecological oxidants has attracted considerable attention across many scientific disciplines. However, there is debate over which active oxygen species is responsible for chemical activity. In order to investigate the effects of ligand rigidity on coordination geometry and reactivity. In the present study, three tetradentate Cu(II) complexes, $[CuBPMEN](ClO_4)_2$, $[CuPDP](ClO_4)_2$, $[CuBPMCN](ClO_4)_2$, where the flexible ethyldiamine backbone of the tetradentate ligand BPMEN was substituted with more rigid cyclohexanyldiamine and bispyrrolidine substitutents to produce the ligands BPMCN and PDP, were synthesized. Increasing backbone rigidity reinforced square pyramidal coordination geometry around the copper center. The potential of these complexes to ward substrate oxidation were examined with hydrogen peroxide as an oxidant. Mechanism of the reaction were investigated using cumyl hydroperoxide. Both of the homolytic and heterolytic peroxide bond cleavage mechanisms produce different decomposition products that can be isolated and quantified via gas chromatography. Effects of ligand rigidity and denticity on the nature of peroxide bond cleavage products will be discussed.

SERMACS 297

Polydentate bis(amidines) as versatile ligand platforms for multinuclear coinage metal assemblies

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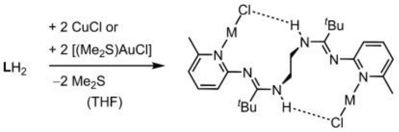
The versatile coordination chemistry of bis(amidines) and bis(amidinates) has essentially been limited to early transition metals and lanthanides to date. We have found that coinage metal halides (MCl, M = Cu, Ag, Au) undergo insertion into the two intramolecular NH···N' hydrogen bonds of **L**H_2 to form NH···Cl–M–N' hydrogen bridges. Herein, we present a series of new polydentate bis(amidine) ligands with sterically protected flexible backbones, their coordination behavior toward Group 11 metal halides, and reactivity with organometallic bases.



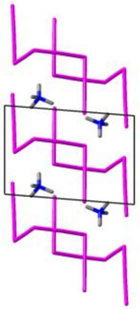
$[\mathbf{L}H_2(MCl)_2]$ (**1**: M = Cu, **2**: M = Au)

SERMACS 298

Exploring the continuum of halogen bonding and higher polyhalide anions

Colin McMillen, *cmcmill@clemson.edu, Khadijatul Kobra, Brad Hicks, Yuxuan Li, William T. Pennington. Chemistry, Clemson University, Clemson, South Carolina, United States*

Polyhalide salts were some of the first compounds to be studied by X-ray crystallography, and about a century of work has revealed a rich array of structural inorganic chemistry. However, there remain several open ends to this chemistry, not the least of which is the most basic question of how a polyhalide is best defined. Many times, the chemical formula of these polyhalides may not be particularly informative in terms of its structural chemistry. For example, what distinguishes the I_5^- anion from a structure consisting of the I_3^- anion with an I_2 molecule in close proximity? Or, is the I_9^- anion truly I_9^-, or should it be described as $I_2 + I_5^- + I_2$, or $I_2 + I_3^- + I_2 + I_2$, and so on? The construct of the halogen bond provides a useful lens through which the polyhalides may be viewed. Here we examine several new salts of polyiodides and polyiodides/polybromides having a wide range of stoichiometries and structural arrangements. We examine trends in halogen bonding that define the isolated anions as well as the extended structure, with potential applications to structural design and crystal engineering.



Structure of $(C_4H_{12}N)I_9$.

SERMACS 299

The Rigaku Oxford Diffraction *XtaLAB Synergy*: from powder analysis to electron density study and protein structure solution.

***Joseph D. Ferrara*[1]**, *joseph.ferrara@rigaku.com, Pierre Le Magueres[1], Mark DelCampo[1], Keisuke Saito[1], Jakub Wojciechowski[2], Mathias Meyer[3]. (1) Rigaku Americas Corp, The Woodlands, Texas, United States (2) Rigaku Europe, Neu-Isenburg, Germany (3) Rigaku Oxford Diffraction, Wroclaw, Poland*

Over the course of the last three years, the Rigaku Oxford Diffraction ***XtaLAB Synergy*** X-ray have been proven to be effective instruments for a wide range of diffraction experiments. The series include a dual wavelength microfocus sealed tube (the ***XtaLAB Synergy-S***), and a microfocus rotating anode (the single wavelength ***XtaLAB Synergy-R*** and dual wavelength ***XtaLAB Synergy-DW***).

The combination of a powerful microfocus X-ray beam (with a choice of Cu, Mo or Ag wavelength), whose divergence is user-tunable, to a versatile full 4-circles goniometer and the highly sensitive direct photon counting ***HyPix*** detectors allow powder, small molecule and protein crystallographers to cover a wide range of crystallography experiments.

In this work, we present results for the following experiments performed with the microfocus sealed tube Cu/Mo ***XtaLAB Synergy-S***:

1. Absolute structure of a tiny crystal of benzophenone

2. Analysis of a powder mixture in which a minor phase of 0.8% relative weight of rutile was successfully detected.
3. Electron density study of hexamine to 0.37 angstrom.
4. Structure solution of lysozyme by S-SAD phasing from a 1 hour data set collected on the 1st home laboratory curved photon counting detector, the HyPix-Arc150º.

SERMACS 300

Broadening the understanding of selective microwave heating on the 1,2-meisenheimer rearrangement

Alexander Ziegelmeier, *ziegelmeier005@gmail.com, Gregory B. Dudley, Michael Frasso. Chemistry, West Virginia University, Morgantown, West Virginia, United States*

Microwave reactors are common and safe devices that allow for the heating of reactions more rapidly and facilitate the use of solvents above their boiling points, in comparison with conventional heating. Some reactions carried out in microwave reactor give results that are not reproducible using conventional heating when conducted at the same apparent temperature. These results generally manifest as faster apparent reaction rate, and they are poorly understood. We hypothesize that in solutions containing a weakly microwave absorbing solvent and a strongly absorbing solute, that the microwave energy can selectively heat the solute. This selective heating of solutes can lead to an increased local temperature and thus a higher reaction rate. The 1,2-Meisenheimer rearrangement of an amine N-oxide to an N-alkoxy amine in nonpolar solvents was used to test the hypothesis. Preliminary results show that there is a rate enhancement when using microwave heating. Unexpected differences in solvent effects are presented as well.

SERMACS 301

Analysis of organic gunshot residues on activated charcoal passive sampling devices

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Gunshot residue analysis has historically relied on the presence of barium/antimony/lead particles for positive identification. The American Society for Testing and Materials (ASTM) method E1588-17 “Standard Practice for Gunshot Residue Analysis” relies on the confirmation of residue containing these elements. However, the advent of heavy metal and lead free ammuniton requires new forensic methods of analysis. To prevent the loss of gunshot residue as forensic evidence, techniques that analyze organic gunshot residue, OGSR, need to be developed. The purpose of this research is to determine if passive sampling, through the use of activated charcoal, and Gas Chromatography-Mass Spectroscopy (GC-MS) can replace active sampling methods, such as the swabbing or tape lift method, for OGSR. Complex mixtures of OSGR molecules were tested by GC-MS in order to calculate figures of merit. Detonation of OGSR was simulated in a bomb calorimeter. The activated charcoal was then exposed to residue from the detonation for a period of ten minutes in order to collect residue passively. The charcoal was then washed with acetone and the solution was subjected to GC-MS analysis. All analyses were performed using a Shimadzu GCMS-QP2010 Plus. From replicate analysis of the complex mixtures, all OGSR compounds used have resolved peaks over a period of seven minutes retention time.

SERMACS 302

Water purification efficiency using low-temperature atmospheric plasma jet under varying conditions

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Globally 2.5 billion people on Earth are not able to access clean drinking water and pollution is of growing concern. Traditional methods for water purification include filtration and advanced oxidation processes (AOP’s) that utilize oxidizing hydroxide radicals (OH) to break down organic molecules and kill bacteria, but many of these processes employ harsh chemicals and are costly to use. Low temperature, atmospheric pressure (LTAP) plasma processes present novel methods of creating advanced oxidation processes used in the purification of water. Plasma water purification using LTAP plasma provides a cheaper and environmentally friendly method of water purification because it creates plasma from ambient air and does not use chemical consumables such as ozone, oxygen, hydrogen peroxide, or chlorine that need continual replenishment. Thus the only cost associated with plasma water purification is the cost of the electricity to generate the plasma.

An LTAP plasma jet was created by pulsing a direct current through atmospheric pressure helium to ionize the gas. The research presented compared the effects of different voltages, pulse widths, frequencies, and stand-off distances (SOD, distance from the edge of the plasma tube to the surface of the water) on the purification of water. Solutions of methylene blue dye (a known pollutant and mutagen) with a concentration of 1.326E-5 M were run at standard conditions of a voltage of 10 kV, a frequency of 6 kHz, a helium flow rate of 2 slm (standard liter per minute), a pulse width of 1 microsecond, and an SOD of approximately 0.50 cm between the surface of the water and the tip of the plasma tube. Tests were then run at conditions above and below standard conditions for voltage, frequency, gas flow rate, pulse width, and SOD. Methods used to analyze results include: UV-visible spectrophotometry, total carbon content analysis, and comparison to spectrometer measurements taken of the plasma at these conditions. The results of this research are presented in this work as an examination of total carbon content and a comparison of reduced methylene blue concentration and spectrometer measurements as a function of different plasma jet parameters.

SERMACS 303

Inhibition of oxidation of cosmetic foundation

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A good skincare routine is beneficial to people's physical and mental health. A large aspect of many people's daily routines is cosmetics, including cosmetic foundations and bb creams. Cosmetic foundations contain three main pigments: titanium dioxide, iron oxides, and zinc oxides. Certain elements of skincare routine and natural factors (sunscreens containing titanium dioxides, facial sebum, exposure to air) can cause cosmetic foundation to oxidize once it is applied to the skin. This oxidation reaction is observed through color change when the hue of the foundation changes from the expected beige color to having an orange or pinkish tint. This color change can have a negative effect on a person's perception of the foundation and the foundation's producer.
In this experiment, we monitored changes in hue of seven foundations over the course of several hours. Previously, we have shown that oxidation is more significant in foundations containing SPF 35 or SPF 15 sunscreen, and that b-complex may inhibit this oxidative process. Here, we compare the ingredients of the different foundations to our data in order to identify if different compositions have an effect on color change.
Color change measurement was conducted using Adobe Photoshop, which had been programmed to assign numerical values to the hue, saturation, and brightness of colors. Our results show that there is an increase in foundation hue when an oxidizing agent is introduced, compared with the control. Conversely, following the introduction of an antioxidant, except for rose water, there was consistently a decrease in hue, compared with the control. The color change following rose water exposure was not as intense as that observed following oxidant exposure.

SERMACS 304

Aggregation patterns of insulin and amyloid-beta peptides

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Neurological diseases, such as Alzheimer's, have been correlated to the aggregation of peptides within the brain. Peptides, such as amyloid-beta (Aβ) and insulin (Ins), are very susceptible to aggregation. Whether Ins and Aβ are aggregated separately or together, both soluble oligomers and insoluble fibrils form, which have been shown to be toxic within the brain. With Aβ correlated to Alzheimer's disease (AD) and Ins to diabetes, the resulting aggregation patterns are used as evidence supporting the hypothesis that having diabetes increases the risk of developing AD later in life. To examine the aggregation patterns of these peptides, solutions of Ins and Aβ monomers were allowed to aggregate and the resulting solutions were analyzed using gel electrophoresis, Bradford assays, and Thioflavin T assays (ThT). For further analysis of the aggregation patterns, the insulin B chain (InsB) was used in place of normal Ins (covalently linked A and B chains) with Aβ. In addition, three mutated InsB chains (K29A, P28D, P28K/K29P), two of which are current diabetes treatments, were then to further establish modes of aggregation between peptide strands. The findings showed that when Aβ and a form of InsB were aggregated together, there was a larger presence of both oligomers and fibrils formed than when aggregated separately. The double mutant InsB was also observed to stabilize aggregation in the oligomeric form when in solution with Aβ. Further examination of peptide aggregation between both Ins and Aβ with α-lactalbumin have identified key components of the peptide chains that aid aggregation and helps link AD and diabetes.

SERMACS 305

HPLC analysis and evaluation of cephalexin for DPAL (Distributed Pharmaceutical Analysis Laboratory)

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This project describes our contribution to the DPAL project through the analysis and evaluation of Cepahalexin capsules. Our overall objective was to establish whether samples provided by the WHO meet product specifications or are suspected to be counterfeit or substandard. This presentation will describe the steps taken to ensure analytical validity in the analysis of Cephalexin by HPLC. First, the HPLC system was evaluated for suitability, then an adapted USP method was validated for analysis. Once the method was established an SOP (standard operating procedure) was put in place and control charts strictly maintained as the analysis of samples commenced.

SERMACS 306

Photocatalytic degradation of glutaraldehyde in simulated fracking wastewater

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Hydraulic fracturing, also known as "fracking", produces large amounts of contaminated water in addition to the extracted petroleum. A possible solution for degradation of these contaminants is photocatalysis. The focus of this study was using a photocatalytic method for degradation of glutaraldehyde, a biocide commonly used in fracking water. A compound parabolic array containing porous poly(methyl methacrylate)/TiO_2 composite materials was used to treat a 20 L aqueous solution of 120 ppm glutaraldehyde. After 26 h of solar exposure, the concentration of glutaraldehyde was reduced to 3.7 ppm. Additional experiments involved the photocatalytic degradation of glutaraldehyde in aqueous solutions that also included compounds commonly found in fracking water, such as ethylene glycol, sodium chloride, and 2-butoxyethanol. This photocatalytic system shows promise for the purification of fracking wastewater pending further experiments involving increasingly complex aqueous matrices.

SERMACS 307

Removal of organophosphorus compounds from water

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Growing environmental concerns have caused recent public demand for eco-friendly chemicals. There is a growing concern over several environmental contaminants. They are found in endocrine disrupting compounds, herbicides, cosmetics, pesticides, pharmaceuticals, plasticizers and flame retardants. Organophosphorus compounds have been used as flame retardant chemicals. Flame retardants are substances that are applied to fabric and other materials in order to make it more resistant to combustion. The process of applying flame retardants to textiles is water intensive, due to the numerous washing. The flame retardants this project explores are Tetrakis(hydroxymethyl)phosphonium chlorideand tris (1,3-dichloro-2-propyl) phosphate. Tetrakis(hydroxymethyl)phosphonium chloride (THPC) has been found to have a negative effect on the environment. Another flame retardant, tris (1,3-dichloro-2-propyl) phosphate (TDCPP), is used in the textile industry. Many of these compounds have been found in the water supply due to improper management. Organophosphorus compounds are found to be detrimental to the wildlife and inhabited species due to toxicity. Studies indicated health concerns among mammals when exposed to these organophosphorus compounds. Therefore, the removal of such harmful chemicals from water is imperative. Herein, the focus of this research is to investigate the potential elimination process of THPC and TDCPP from water using char as an adsorbent. Char is a carbonaceous material that is derived from inorganic substances, while biochar is a stabilized, carbon-rich by-product derived from pyrolysis of biomass. Char has many physical and chemical properties that allow it to have a high adsorption capacity such as high surface area, porous morphology, ash content, and various functional groups. Batch adsorption experiments will be performed in order to assess adsorption capacity of char. The experimental design will be tuned on the basis of temperature, contact time, and char dosage to optimize the adsorption capacity of the char. The preliminary results have shown that char can be used as a medium to adsorb THPC in aqueous conditions.

SERMACS 308

Systematic study of the effects of functionalization on the interaction between CO_2 and calixarenes

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High carbon emissions have shown a strong correlation with rising global temperatures as the world’s climate undergoes a dramatic shift. Work to mitigate the potential damage using materials such as metal-organic frameworks (MOFs), covalent-organic frameworks (COFs), and polymer membranes (PMs) have proven successful in small scale approaches; however, research is still being performed to enhance the capabilities of these materials for use at an industrial scale. One strategy for increasing performance is to embed these materials with CO2-philic molecules which enhance selective binding over other gases. Calixarenes are promising candidates due to their large chalice shape which allows for the possibility to bind multiple CO_2 molecules per site. In this study, a dataset of 40 functionalized calixarene structures was constructed with an automated, high-throughput structure generation through directed modifications to a molecular scaffold. This also allowed the faster determination of optimal binding energies for a vast array of chemical functional groups with less computational effort. Density functional theory (DFT) calculations were performed for the exploration of their interactions with CO_2. Conclusions from this study can aid synthetic efforts for the next generation of functional materials. Future work for this project will focus on studying the interaction between functionalized calixarenes and other molecules common in standard industrial gas emissions to gauge relative selectivity for CO_2.

SERMACS 309

Photophysical characterization of novel rhodamine B dimers

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Research on organic optoelectronic devices has experienced a surge in recent years in response to the demand for low cost and abundant materials. Furthermore, the performance of organic LEDs, lasing media, and dye sensitized solar cells depends on the ability of researchers to optimize the photophysical properties of organic materials. Leveraging these facts, we decided to synthesize and characterize four novel fluorescent dimers using rhodamine B to explore how linker stereochemistry influences fluorescent behavior. We utilized fluorescence correlation spectroscopy (FCS) to investigate the time-dependent photophysical processes of our dimers. By analyzing the dimers in solutions of varying ionic strength, we also explored how solvent environment influences photophysics and conformational flexibility. We found that the limitations and successes associated with different FCS fitting models provided insight into microsecond time scale processes that occur from fluorophore-fluorophore interactions within our dimers. Our discoveries from FCS, in tandem with molecular dynamic simulations and other optical analyses, could help guide the design of optically sensitive materials and heterodimers capable of fluorescence resonance energy transfer.

SERMACS 310

Complex synchronization patterns in small networks of chemical oscillators

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Synchronization plays an important role in the rhythmic behaviors of many biological, chemical, and physical systems. In biological systems, for example, a regular heartbeat is maintained by the synchronized behavior of pacemaker cells. The breakdown of synchrony can result in complex patterns, indicating the loss of rhythmic behavior or the onset of conditions such as heart arrhythmias. To gain insight into the emergence of complex patterns, we investigate the effect of time-delay coupling in small linear and triangular network structures of Belousov-Zhabotinsky (BZ) chemical oscillators. Experiments and simulations are carried out using a ferroin-catalyzed BZ system and a two-variable Oregonator model, respectively. In-phase, out-of-phase, and complex periodic behaviors are observed in both experiments and simulations. In-phase synchronization is frequently observed in triangular network structures in which oscillators experience short time-delays. Out-of-phase and complex periodic patterns mostly occur in linear network structures and systems with long time-delays.

SERMACS 311

Development of redox dopants for organic semiconductors and interface modification

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Organic semiconductors and hybrid/organic materials have attracted interest for electronic applications due to their potential for use in low-cost, large-area, flexible electronic devices. Here we will report on recent developments pertaining to both n- and p-dopants that could impact the charge injection/collection processes in organic light emitting diodes, organic field effect transistors, and organic photovoltaic and hybrid organic/inorganic perovskite devices, as well as on the bulk conductivity of doped semiconductors. We will consider the synthesis of new dopants and studies to illustrate the mechanisms by which the dopants react with organic semiconductors. We will discuss the development of organic and metallo-organic-based dimers as n-dopants. We will highlight the application of n-dopants for reactions with polymers that lead to exceptionally high conductivities for n-doped systems and may have interesting thermoelectric performance.

SERMACS 312

Synthesis of degradable polyacetals using enyne metathesis polymerization

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In this presentation, recent results will be described that highlight the utility of terminal alkynes to manipulate polymers though metathesis polymerization. Unlike olefins, terminal alkynes undergo rapid addition reactions with ruthenium alkylidenes and can be used to relay the intermediate carbenoid to a new site of metathesis. Following this general paradigm, the 1,6 enyne motif is used to prepare functional initiators in situ, effect stoichiometric polymer-polymer coupling, and generate new monomers for metathesis polymerization. Focus will be placed on a new enyne monomer family synthesized from furfuryl alcohol that leads to highly degradable polyacetal materials. A flexible synthetic strategy permits a range of functional groups to be incorporated, and structure-reactivity relationships reveal how the livingness of the polymerization depends on the steric environment and relative stereochemistry of the enyne monomer. Using this system, fully degradable diblock polymers can be prepared using metathesis polymerization for the first time, leading to opportunities in biomedical applications.

SERMACS 313

Silole-containing polymers for organic semiconducting materials

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Siloles (silacyclopentadienes) – have been shown to possess unique properties for applications in organic electronics. One of those properties is the electron mobility; silole-containing molecules show a two-orders of magnitude increased compared to the widely used electron transport material, tris(8-hydroxyquinolinato) aluminum (Alq_3).[1] Siloles have other properties that are essential for organic electronics such as, high quantum yield in the solid state and control of electronic properties by modifying the substituents at the 2,5-positions.[2] Due to these and other favorable properties of siloles, the Scott group has developed an interest in incorporating them into polymers as semiconducting materials for application in organic electronics.

In this presentation, we will discuss the design, synthesis, and properties of two series of silole-containing polymers based on the combination of siloles with diketopyrrolopyrrole (DPP),[3] and benzothiadiazole (BT).[4] In the silole DPP polymer series, 2,5-dithienylsilole, and 2,5-diphenylsilole were copolymerized with DPP, with and without an alkyne bridge. All the polymers had reduced bandgaps (Eg < 2 eV); however, the band gap is lower for the 2,5-dithienylsilole polymers compared to the 2,5-diphenylsilole polymers, highlighting the effect of thiophene - silole orbital overlap on the Eg. In the silole BT polymer series, the 2,5-dithienylsilole was co-polymerized with a series of difluorobenzodiimine-based electron acceptors; 5,6-difluoro-[2,1,3] benzothiadiazole (DFBT), 5,6-difluoro[2,1,3]benzoselenadiazole (DFBSe), and 5,6-difluoro[2,1,3] benzotriazole (DFBTA). Once again all the polymers possess reduced band gaps (< 2.0 eV), and the silole-DFBT polymer recorded hole mobility values in the range of 10^{-2} cm^2/Vs, which is superior to previously reported values for 2,5-dithienylsilole-containing polymers (10^{-4} – 10^{-6} cm^2/Vs) and comparable to dithienosilole-containing polymers. The silole-DFBSe polymer recorded hole mobility value in the 10^{-4} cm^2/Vs range, which is comparable to other 2,5-dithienylsilole polymers in the literature.

SERMACS 314

Development of C–H functionalization reactions for the incorporation of electron deficient building blocks in organic semiconducting materials

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C-H Functionalization has emerged as a powerful tool for the synthesis of complex molecules and functional materials. Herein we describe the development of reactions to functionalize electron deficient building blocks as components of organic semiconducting materials. C-H functionalization offers opportunities to circumvent complications of protodemetallation, reduction or the forcing conditions required to manipulate electron deficient aromatic molecules with classical reactions. The development of reactions to introduce versatile functional groups under mild conditions, as well as direct arylation reactions of electron deficient aromatic molecules will be discussed.

SERMACS 315

Advances in 3D printing functional nano-photonic devices by multi-photon lithography

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Multi-photon lithography (MPL) has emerged as a powerful technique for fabricating truly three-dimensional (3D) micro- and nano-scale structures. MPL is implemented by scanning the focal spot of an ultrashort-pulsed laser beam within a material. Multi-photon absorption occurring within the focal volume initiates a chemical or physical transformation, and translation of the focus within the 3D volume of the material enables point-by-point free-form patterning of arbitrary forms. Because the resolution achievable with MPL is connected to the wavelength of focused laser beam, the method can be used to create functional nanophotonic devices. The authors have used MPL in photopolymers and other materials to create a wide range of 3D periodic nanophotonic lattices that exhibit unique capabilities for controlling the propagation of light. Post-MPL processing has also been used to chemically functionalize structures and change their material and optical properties. Most recently, the team has used MPL to create aperiodic lattices that are spatially varied in one or more ways to force light to propagate along engineered paths, through an optical effect known as self-collimation. These devices provide unprecedented control over light and could open new routes to densely integrated 3D photonics and other applications.

SERMACS 316

Development of heterocyclic molecules for recognition of mixed DNA sequences with two G●C base pairs

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Small organic molecules with designed structures could specifically recognize DNA sequences. AT specific heterocyclic cations that bind in the DNA minor groove have had significant successes as cell and nuclear stains and as therapeutic agents which can effectively enter human cells. Expanding the DNA sequence recognition capability of the minor groove compounds could also broaden their therapeutic targets and have an impact in many areas, such as modulation of transcription factor (TF) biological activity. Success in the design of mixed sequence binding compounds has been achieved with *N*-X benzimidazole (*N*-XBI), pyridine, and azabenzimidazole. All three units can bind to a single G●C base pair (bp) DNA sequence strongly and selectively. The linear combination of two *N*-XBI modules with a -O-$(CH_2)_3$-O- linker gives the compounds the flexibility and appropriate length to match the curvature of two G●C bps DNA sequences minor groove and cover a full turn of DNA helix (-GAAAC-). Since -GTG- and -GGAA- occurs in regions of the PU.1 TF promoter sequence, a specific promoter sequence minor groove binder would be a significant contribution to the inhibition of PU.1 TF. Two different combination methods among single G●C bp modules were investigated to satisfy -GTG- and -GGAA- minor groove binding. 1) Linear combination and combined structure of reported azabenzimidazole and *N*-XBI module included single G binders to shorten the distance between two binding units for -GTG-. 2) Parallel linking through the proper length of flexible linker helps the stacking of two single G binders to realize two close G●C bps (-GGAA-) recognition. The compound / DNA interactions were evaluated with a powerful array of biophysical methods, and the results show that compounds with appropriate design can recognize mixed DNA sequences including two G●C bps with high affinity. These results indicate that abundant modification and combination manners among capable G●C bp recognition units can lead to new approaches for small molecules in biomolecular interactions and supply support to TF inhibition. Supported by NIH GM111749

SERMACS 317

Leveraging a FapR biosensor for malonyl-CoA and non-natural extender units

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Polyketides are clinically relevant natural products with a wide range of pharmaceutical activities including antimicrobial, antifungal, anticancer, and immunosuppressant. Polyketides are biosynthesized from their respective malonyl-CoA based building blocks by large enzyme complexes called polyketide synthases (PKSs). Accordingly, there is a need to assemble and optimize artificial pathways in heterologous hosts that can be used to access non-native and non-natural malonyl-CoA buildings blocks. Yet, designing and engineering such pathways is difficult and tedious. Subsequently, a genetically encoded biosensor for the *in vivo* detection of polyketide building blocks would enable the application of directed evolution and other high-throughput approaches to engineering novel metabolic pathways. Here efforts are described to alter the effector specificity of the transcription factor based biosensor, FapR. Herein, we have tailored the specificity of the biosensor for high-throughput detection of malonyl-CoA analogue biosynthesis *in situ* and other non-native extender units. This biosensor platform will be leveraged to engineer the activity and specificity of chemo-enzymatic routes to extender units. These advances will be coupled to PKSs for the development of novel approaches to polyketide biosynthesis and diversification.

SERMACS 318

Impact of acid insertions on packaging and damage of reconstituted arginine peptide-condensed DNA

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Spermatogenesis (sperm cell development) is a multi-step process beginning with mitotic and meiosis cell divisions that produce immature sperm cells known as spermatids. Maturation of the spermatids occur in the final stage of spermatogenesis referred to as spermiogenesis. During spermiogenesis, DNA packaging in the spermatid undergoes changes resulting in the replacement of the vast majority (>90%) of histones with arginine-rich peptides called protamines. Protamines undergo post translational modifications (PTMs) before binding to DNA. One such modification is phosphorylation/dephosphorylation. It is thought that the initial

phosphorylation of protamines facilitates the correct binding of protamine to DNA while dephosphorylation of protamines is necessary for correct sperm chromatin packaging. Alteration of the phosphorylation/dephosphorylation process of protamines is believed to impact DNA packaging in sperm cells negatively and thus, allows greater access to radical damaging species to accumulate and degrade sperm DNA. Across multiple species, a distinct feature of protamine primary structure is the presence of several arginine residue clusters. In this work, we have focused on hexa-arginine (R6) peptides as protamine mimics. Using reconstituted DNA, we have investigated the DNA-binding capacity and the free radical-damaging effects on various hexaarginine peptides bearing neutral and anionic amino acid insertions. Our results indicate that insertion of a phosphorylated amino acid residue greatly reduces packaging density while allowing an increased accumulation of radical damage to the DNA. Our findings are a preliminary view towards a better understanding of the impact of residual phosphorylation in protamines on DNA packaging in mature sperm cells.

SERMACS 319

Protein-RNA complex characterization using biolayer interferometry and isothermal titration calorimetry

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Long noncoding RNA (lncRNA) plays an important role in modifying and regulating the genome. However, it is the least characterized class of RNA and many of its functions are unknown. LncRNAs in Steroid Receptor Activator 1 RNA (SRA 1 RNA) family are thought to play a role in facilitating tumor cell growth. SHARP2 protein is known to bind to the STR7 region of SRA1 RNA. Biolayer interferometry can be used to create a sensorgram style graph for the association and dissociation of the SHARP2-STR7 complex. This curve can then be used to find the dissociation constant of the complex, indicating how long and how tightly the protein binds to the RNA. In addition, isothermal titration calorimetry can be used to measure enthalpy changes during SHARP2-STR7 binding. Together these experiments can be used to determine all thermodynamic and kinetic parameters including binding affinity. The results of these experiments will be compared to other studies including structure and function.

SERMACS 320

Elucidate possible reaction mechanism of cyclopropanation found in cycloclavine

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Cycloclavine isolated from plant such as seeds of the African morning glory shrub *Ipomoea hildebrandtii* has insecticidal and antiparasitic activities. From the structural point of view, cycloclavine contains a pyrrolidine-fused cyclopropane unit which is different from the other ergot alkaloids. Recently, the cycloclavine biosynthetic pathway along with the possible reaction mechanism accounting for cyclopropanation has been proposed. To investigate the chemical logics of this novel enzymatic pathway, mechanistic probes were synthesized and tested with the EasH. This research shed the light in reaction mechanism. It also inspires the biomimetic synthesis to prepare pyrrolidine-fused cyclopropane moiety

SERMACS 321

Elucidate the mechanism of key cyclization in the fumiquinazolines biosynthesis

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Fumiquinazolines, a class of peptidyl alkaloids, are found in terrestrial and marine fungi. The bioinformatics analysis and *in vivo* assay results suggest that two different class of enzymes are involved in the multi-cyclic quinazoline core installation. For example, flavin dependent proteins are involved in fumiquinazoline C and D formation. On the other hand, Fe(II)/2-oxoglutarate dependent enzymes are found to catalyze similar reactions in alanditrypinone and cottoquinazolines production. From mechanistic point of view, it is intriguing how these transformations are conducted. Herein, we demonstrate our recent discovery toward the understanding of fumiquinazoline core formation through mechanistic probe synthesis and *in vitro* assays.

SERMACS 322

Change in expression of host selenoproteins SePP1 and TR1 in cell lines due to Zika infection

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Zika (ZIKV) viral infection continues to be a growing concern for inhabitants of the southern United States, Puerto Rico, and the Caribbean. Infection in pregnant women can often lead to microcephaly in the gestating child, and with the expansion of the geographical range of the mosquito vector, the possibility of ZIKV being spread to the rest of the southern United States is a threat to many pregnant individuals and a concern for those looking to conceive. The need to understand how ZIKV causes microcephaly is therefore critical. Our group hypothesizes that regions of ZIKV RNA have an affinity for host cellular mRNAs that direct the cellular expression of selenoproteins, and that an interaction between the ZIKV RNA and these host cell mRNA strands is occurring through antisense complementation. Our group has demonstrated this knockdown occurs specifically with host cell selenoproteins selenoprotein P (SePP1) and thioredoxin reductase 1 (TR1). Various cell lines were infected with ZIKV. After infection, the mRNA and protein expression of these two proteins were measured via qPCR and western blot respectively. Our results show a knockdown of the expression of these proteins in the ZIKV infected cell lines. We predict these results could shed light as to why microcephaly is reported in cases where the mother was pregnant at the time of viral infection; since SePP1 is expressed highly in placental cells and essential to the transport of selenium into the brain for neuronal development.

SERMACS 323

Using choline kinase as a drug target leads to inhibition of *Steptococcus pnuemoniae* growth via dysregulation of lipoteichoic acid production

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New drugs against Gram-positives such as *Streptococcus pneumoniae* have to be continuously discovered as older lines of inhibitors lose their efficacy. Two promising new lead inhibitors against *S. pneumoniae* choline kinase (sChoK) have been identified. RSM-932A and MN58b have an IC_{50} of 0.5 µM and 150 µM, an MIC of 10 µM and 0.4 µM, and an MLC of 6.4 µM and 80 µM, respectively. Lipoteichoic acid production was differentially dysregulated in *S. pneumoniae* in the presence of these drugs. Both MN58b and RSM-932A were found to be bacteriostatic in nature. Steady state enzymatic analysis revealed that MN58b was antagonistic to both choline and ATP substrate binding, while RSM-932A was antagonistic to choline alone. Meanwhile cells cultured in the presence of MN58b but not RSM-932A became sensitized to autolytic induction. SEM revealed that MN58b distorted the cell wall, a result consistent with its dysregulation of lipoteichoic acid production, while RSM-928A maintained a cell wall similar to untreated cells, revealing the differential effects of these drugs on cellular metabolism. The sChoK enzyme can be used to screen for inhibitors of *S. pneumoniae* but the effects of these drugs can vary at a cellular level. Using sChoK as a target shows promise for the development of a novel family of antimicrobials for use as chemical therapies and food additives.

SERMACS 324

Identification of staphylococcal autoinducing peptides with ultrahigh performance liquid chromatography: High resolution mass spectrometry

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Virulence among gram-positive bacteria, such as the *staphylococci*species, is controlled by quorum sensing, a cell density dependent system that is activated by auto-inducing peptides (AIPs). AIPs are cell-to-cell signaling molecules that are produced in response to changes in cell-population and signal for the expression of virulence factors. Hence, identifying and elucidating AIPs unique structures is of great interest when studying pathogenesis among bacteria. In his study, the AIPS of four different s*taphylococcal* species were identified using an Ultrahigh Performance Liquid Chromatography System coupled to a High Resolution Mass Spectrometer (UPLC-HRMS). The ability to detect trace levels of peptides was facilitate by phase extraction and optimization of the UPLC-HRMS analysis.

SERMACS 325

Characterization of early steps from the biosynthetic pathway of the exomethylene β-branch in the polyketide difficidin from Bacillus velezensis FZB42

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The polyketide macrolactone, difficidin, is a secondary metabolite of Bacillus velezensis FZB42 with broad-spectrum antibacterial activity against both Gram-positive and Gram-negative bacteria. The difficidin structure contains an unusual exomethylene "β-branch," which is found in some other polyketide natural products such as pederin. While the majority of the biosynthetic pathway for difficidin likely follows canonical polyketide synthase chemistry, the biosynthetic steps for this type of β-branch is not well-understood. The goal of the work described in this poster was to characterize the hypothesized first step of this pathway, malonyl CoA-acyl carrier protein transacylase. We hypothesized that the enzyme encoded by baeC catalyzed the transfer of a malonyl acyl group from malonyl-CoA to the free thiol group of the phosphopantetheine arm on the holo form of the acyl carrier protein dfnX from the dfn difficidin biosynthetic gene cluster. To test this hypothesis we cloned and purified the baeC protein as well as holo-DfnX using a pET-Duet system that coexpressed dfnX and the 4'-phosphopantetheinyl transferase sfp gene from B. subtilis. Through the use of ESI-MS analysis on an LTQ-Orbitrap instrument, we observed a BaeC-dependent increase of 87 Da over the holo-DfnX, which is consistent with the addition of a malonyl substituent onto the holo-DfnX substrate. Further MS/MS experiments are ongoing to further characterize this step in the biosynthetic pathway.

SERMACS 326

Synthesis & mitochondrial analysis of sigma-1 selective ligands

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Sigma receptors were originally mistakenly identified as a subtype of opioid receptors but were later determined to be non-opioid and in a class of their own with two subtypes: sigma-1 and sigma-2. Sigma-1 receptors are endoplasmic reticular (ER) proteins consisting

of 223-amino acids with a molecular mass of 24-kDa, known to bind various drugs, including antipsychotics, neuroleptics and neuroactive steroids. Ligands that modulate the sigma-1 receptor have exhibited effects in several therapeutic areas related to the central nervous system (CNS), and could potentially slow down the adverse effects of Alzheimer's disease (AD). The purpose of this research is to synthesize 5,6-dimethoxy-3-methyl-*N*-phenyl-*N*-(3-(piperidin-1-yl)propyl)benzofuran-2-carboxamide KSCM-1, a highly selective sigma-1 ligand, to learn more about the progress of Alzheimer's disease. Our experimental methods include a series of reactions, encompassing the synthesis of 4-methyl-6,7-dimethoxycoumarin via methylation of 4-methylesculetin, followed by bromination and subsequent Perkins rearrangement to produce the corresponding benzofuran-2-carboxylic acid. In the presence of DCC/DMAP, the benzofuran-2-carboxylic acid is converted to the corresponding amide and then alkylated to produce the final target molecule KSCM-1. To assess the specificity of KSCM-1 to sigma-1 receptors, mitochondria associated membranes were isolated using neuroblastoma cell line followed by protein complex analysis. Our results indicate that in the presence of KSCM-1, expression of major mitochondria associated membrane proteins was changed significantly. Our results provide noteworthy evidence that carboxamides such as KSCM-1 have potential in the continued understanding of AD, as well as, for the development of pharmaceuticals in the treatment of AD.

SERMACS 327

Exploring allosterically induced enzyme dynamics in pyruvate kinase M2

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Pyruvate kinase (PYK) executes the terminal step of glycolysis by transferring a phosphate from phosphoenolpyruvate to ADP to produce the cellular energy currency ATP and pyruvate. Multiple isoforms of the enzyme exist throughout the body, including the allosterically regulated splice isoform PYK M2, found in fetal and proliferating tissues. Notably, PYKM2 is heavily associated with the successful anaerobic glycolysis of cancer cells. Also susceptible to regulation by other metabolites, this enzyme has been shown crystallographically to bind free amino acids such as phenylalanine, alanine, serine, and histidine. Each amino acid has been demonstrated to bind in the same pocket, removed from the canonical allosteric binding site for the requisite fructose-1,6-bisphosphate activator. Binding of phenylalanine in particular induces a conformational change that disrupts an interfacial interaction required for catalysis, a phenomenon also demonstrated *in vitro* by a loss of enzymatic activity. This isoform-selective allosteric inhibition of such a critical metabolic enzyme is an attractive strategy for cancer therapies.

To investigate the dynamic processes associated with the interconversion of active and inactivated states of the enzyme, native tryptophan residues may be used as non-perturbing fluorescence probes; the interfacial tryptophan residues W482 and W515 of each protomer are highly dynamic. Equilibrium fluorescence measurements from direct tryptophan excitation of *H. sapiens* PYKM2 complexes report on this change in interfacial assembly of the enzyme through the transition from uninhibited (T, -Phe) to inhibited (R, +Phe) states. In addition, Förster resonance energy transfer (FRET) can be observed from tryptophan donors to Tb^{3+} ions substituted in the active site for the native Mg^{2+}, offering additional structural information. Time resolved fluorescence measurements for the native Trp fluorescence and the FRET can provide the timescale of interconversion between states. Given the structural precedence and in vitro validation of other single amino acids as both inhibitors and activators of PYKM2 activity, this versatile fluorescence-based investigation offers insight as to how the effector binding and associated enzyme dynamics contribute to the enzyme's function, capable of informing inhibitor design for novel therapeutics.

SERMACS 328

Investigating 2-methylcitrate dehydratase (*mmgE*) in *Bacillus subtilis*: Victoria G. Meadows, Don A. Mora, and Jason J. Reddick

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Our laboratory has studied the methylcitric acid cycle encoded in the mother cell metabolic gene (*mmg*) operon of *Bacillus subtilis*. In this poster we report new results for the enzyme 2-methylcitrate dehydratase (*mmgE*), whose physiological function is to produce (Z)-2-methylaconitate from 2-methylcitrate. In this work we refined our structural characterization of the physiological activity of this enzyme and also sought to determine its tolerance for other substrates. First our published data showed that the enzyme will turn over components from a diastereomeric mixture of 2-methylcitrate to produce what we preliminarily assigned as (Z)- and (E)-2-methylcitrate. Here, we will report on NMR analysis to directly assign the structure of these enzyme products. We showed that the enzyme also has citrate dehydratase activity, converting citrate to *cis*-aconitate, but it does not have full aconitase activity in converting citrate to isocitrate. Enzyme kinetics of this citrate dehydratase activity were measured. The enzyme utilized citrate with a kcat = 0.077 ± 0.009 1/min and Km = 0.186 ± 0.075 mM. Since the *mmgE* enzyme can turn over different diastereomers of 2-methylcitrate as well as citrate, we explored its tolerance for other 3-hydroxyacids, because any promiscuity could enable biocatalytic applications of this enzyme in the synthesis of alkenes. We assayed for dehydratase activity with seven 3-hydroxyacids. Of these seven the enzyme could only turn over malate to produce fumarate. We also found that the enzyme catalyzed the surprising isomerization of *cis*-aconitate to *trans*-aconitate. Kinetics studies for these alternative activities are ongoing and the most updated results will be included in this poster. Although the enzyme was not as tolerant as hypothesized, the tolerance for substrate stereochemistry and product double bond geometries can lead to a better understanding of the mechanism of the enzyme.

SERMACS 329

Determination of mitochondrial metabolism using western blot protein analysis

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Mitochondria, a double-membrane subcellular organelle is responsible for the production of ATP and steroid hormones in all cells of animals, plants, and fungi. Mitochondria are very sensitive organelles and external factors like pH, temperature, drugs etc. can change the expression, folding and relative ratio of various mitochondrial proteins involved in steroid hormone biosynthesis. Any change in mitochondrial proteins expression can be detected using Western Blot analysis that gives a quicker result instead of further time-consuming tests.

Characterization and analysis of mitochondrial proteins may provide a useful tool to detections of metabolic disorders and diseases. Western blot analysis using gel electrophoresis is one of the most extensively used technique to check the expression of variety of proteins and effect of various drugs molecules on these proteins. This is a cost-efficient technique that have multiple use in protein analysis studies. Western blot analysis technique directly or indirectly can be used to detect the existence of substances such as peptides, proteins and hormones. It can also be used to detect the mitochondrial health and respiration to study various diseases. In this research, Western blot analysis using Gel electrophoresis was performed to test presence of a drug and its toxic effect on mitochondrial proteins.

SERMACS 330

Analysis of mitochondrial protein regulatory function in presence of synthetic compounds

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Mitochondria are bilayer sub-cellular organelles and are considered an integral part of normal cellular physiology in all cells of animals, plants, and fungi. They are responsible for the production of ATP, thus supplying energy for a variety of key cellular processes, especially in the brain. Although ATP production is a key function of mitochondria, its role extends far beyond ATP production to steroid hormone biosynthesis, cell signaling and epigenetic regulation–functions that contribute to cellular proliferation, differentiation, apoptosis, and migration. Mitochondria are very sensitive organelles and a change in mitochondrial proteins can be detected using a verity of techniques like ELISA. Use of a drug may change the expression and relative ratio of various mitochondrial proteins involved in steroid hormone biosynthesis. ELISA can be used as a screening test it gives a quicker result instead of further time-consuming tests. Also, western blot protein analysis along with ELISA can effectively provide an evidence of change or absence of targeted mitochondrial proteins.

Measurement of mitochondrial biogenesis is becoming a standard part of drug detection and drug safety characterization. ELISA (enzyme-linked immunosorbent assay) is a plate-based technique, it is one of the most extensively used assay test out the variety of immunoassay tests because it’s cost efficient, exceptionally accurate, and have multiple matrices. This assay is used to detect the existence of substances such as peptides, proteins, antibodies, and hormones. Recognition of these substances are proficient by calculating the conjugated enzyme activity by incubation with a substrate to yield a measurable product. In this research, ELISA is used to test presence of a drug and its effect on mitochondrial proteins.

SERMACS 331

Kinetic characterization of the rate-limiting C–H activation step of *M. oryzae* lipoxygenase and the effects of *N*-linked glycosylation

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Lipoxygenases, including those from pathogenic fungi, catalyze the C-H activation of polyunsaturated fatty acids to form a diverse set of cell-signaling hydroperoxides. While the lipoxygenase catalytic domains are structurally and functionally similar across species, fungal enzymes are uniquely decorated with multiple, heterogenous *N*-linked glycans. The effect of these *N*-linked glycans on the structure and function of these enzymes remains largely unknown. One standout lipoxygenase is MoLOX, from the fungus *M. oryzae*, that is emerging as an important target for the devastating rice blast disease. The ability to stably label C-H bonds with deuterium enables for the assessment of rate-limiting steps of catalysis based on the magnitude of the kinetic isotope effect on the transferred hydrogen. In this presentation, we will demonstrate that hydrogen transfer, associated with C-H cleavage of the substrate linoleic acid by MoLOX, is rate determining and occurs via a hydrogen tunneling mechanism. Using the differential enthalpic barrier for hydrogen and deuterium transfer, ΔE_a, as a kinetic reporter of tunneling efficiency, a disproportionate increase in the activation energy for deuterium transfer is observed upon treatment of MoLOX with a novel peptide:N-glycosidase. This glycosidase cleaves the *N*-linked carbohydrates from the protein proficiently at cool temperatures. The observed increase in ΔE_a after glycosidase treatment is consistent with an impairment of both the tunneling ready state and the ground state enzyme-substrate structure. These results provide a new insight into the functional consequences of *N*-linked glycosylation on lipoxygenase C-H activation. Current efforts to explore the effect of other surface functionalization will be presented.

SERMACS 332

Inclusion complex formation of synthetic AHL receptor antagonists and related compounds with β-cyclodextrin, a quorum sensing sequestration inhibitor

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Many bacteria display phenotypic switching as a function of population density. Common examples include motility and bioluminescence, as well as biofilm and virulence factor production. This phenomenon, known as quorum sensing, relies on the synthesis, transmission, and perception of low molecular weight signal molecules generically termed autoinducers. In Gram-negative bacteria, such as *Pseudomonas aeruginosa*, autoinducers are predominantly members of the *N*-acyl-L-homoserine lactone (AHL) family. Inhibition of these quorum sensing circuits or ‘quorum quenching’ have been shown to reduce virulence in pathogenic bacteria, providing an alternative to traditional antimicrobial strategies that often drive the evolution of resistance. AHL-receptor antagonism, through the use of synthetic AHL analogues (SAHLAs), has been particularly successful in this regard. However, many of these compounds are poorly soluble under biological conditions and require co-solvents (*e.g.*, DMSO) that can disrupt biological membranes. We hypothesized that, given the hydrophobic nature of these compounds, β-cyclodextrin (β-CD) could be used to enhance solubility, stability, and bioavailability. Here, we report on the inclusion complex formation of related compounds with β-CD as determined by fluorescence spectroscopy, indicating the potential use of β-CD as a delivery vehicle for SAHLAs.

SERMACS 333

Assessing the ability to predict drug-induced mitochondrial toxicity in mammalians

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Steroid hormones are essential for the survival of all vertebrates. The synthesis of these steroid synthesis takes place inside the mitochondria. Mitochondria are universally known for its synthesis of ATP (Adenosine Triphosphate), but the organelle is much more versatile. Many mitochondrial proteins, along with other nuclear gene products assist in the functionality of the organelle. Any change in the production of steroid hormone, may result in metabolic diseases such as child birth disorders and hypertension and is fatal for the survival of species. Our research focuses on detection of mitochondrial dysfunction and toxicity using western blot protein analysis method. Mammalian cells used for the experiments are grown in the lab using cell culture. Since, mitochondria are very sensitive organelles, a change in mitochondrial surroundings (i.e. salt concentration, temperature, pH) may change mitochondrial protein expression. Some harsh conditions may create mitochondrial dysfunctions that can be detected using western blot analysis. Various drug molecules are used to incubate with cells followed by mitochondrial isolation from the test cells. This analysis will include determining whether there is a change in mitochondrial viability and respiration due to presence of external factors like drug concentrations. The mitochondrial protein concentrations and relative proteins ratios are analyzed by conducting the protein gel electrophoresis experiments and western blot analysis.

SERMACS 334

Effects of chaperones on protein-protein interactions

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Mitochondria are well known for the synthesis of steroid hormones. The synthesis of steroid hormones is essential for the survival of all species. The process of steroid hormone synthesis is initiated with the movement of cholesterol from the outer to inner mitochondrial membrane. Most of the mitochondrial proteins are synthesized in ribosome and are transported to different compartment of mitochondria. During transportation of these mitochondrial proteins, a unique folding of proteins is required to enter mitochondrial import channels. Sometimes this unique folding pattern is also required for multiple activities of some mitochondrial proteins.

During the transportation to mitochondria, a specific and proper protein folding is a cumulative effect of chaperone and many other proteins expressed on the transportation pathway. The expression and concentrations of proteins residing in the surroundings of mitochondrial membrane regulates the folding of proteins, hence regulating the transport mechanism. Biochemical and biophysical approaches using statistical analysis are used to determine the effect of protein expression and concentrations on mitochondrial protein folding. Protein folding into mitochondria is a dynamically regulated process that varies in response to conditions such as oxidative stress, metabolic disorders and drug treatment. Misfolded species are prone to forming toxic aggregates, which can be linked with neurodegeneration in Alzheimer and Parkinson disease, and many other pathologies. So understanding effect of chaperones mitochondrial protein folding will add on to our current understanding of metabolic diseases.

SERMACS 335

Regulation of G-protein signaling: Interaction of RGS10 proteins with calmodulin and the G-alpha subunit

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Approximately 35% of all drugs currently in clinical use target a single family of proteins: G-Protein Coupled Receptors (GPCRs). Due to the therapeutic importance of this class of proteins, it should be no surprise that proteins involved in regulating signaling initiated by GPCRs are gathering attention as potential drug targets. One such family of proteins is known as the Regulators of G-protein Signaling (RGS). These proteins function as an “off-switch” for G-protein signaling by binding to the GTP-bound G-alpha subunit, accelerating the hydrolysis of GTP to GDP. In turn, RGS proteins are themselves regulated by direct interactions with other

biomolecules. For instance, RGS10, which is integral for neural and cardiovascular function, is differentially regulated by a sophisticated, poorly understood competitive binding to the membrane lipid phosphatidylinositol (3,4,5)-triphosphate (PIP3) and the ubiquitous calcium signaling protein calmodulin (CaM). Our current focus is on the interactions of RGS10 with CaM and PIP3 and how this competitive interaction affects the RGS binding to G-alpha. We have thus far produced recombinant full-length RGS10 and the RGS domain only (RGS10 lacking N- and C-terminal regions), as well as the G-alpha subunit, and purified them to homogeneity. Using intrinsic tryptophan fluorescence, we measured the affinities of the RGS10 proteins for CaM and their dependence on ionic strength. The full-length RGS10 binds much tighter to CaM than the RGS domain alone, suggesting a role for the terminal regions, and the affinities of both complexes decrease with increasing ionic strength. The results indicate 1:1 stoichiometry of the complexes. NMR spectra reveal the expected slow-exchange behavior when isotopically RGS proteins are titrated with unlabeled CaM, but the binding mode is complex. We are currently examining the interaction of the RGS10 proteins with the G-alpha subunit and how the addition of CaM affects this interaction.

SERMACS 336

Biochemical characterization of phosphoethanolamine methyltransferase from *Eimeria tenella*

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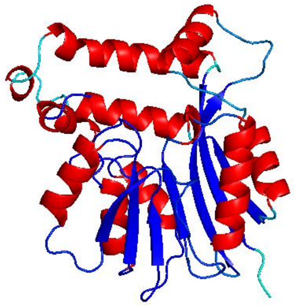
Eimeria tenella is an apicomplexan parasite that is a leading cause of coccidiosis, the haemorrhagic enteritis in chicken caeca which consequently restricts the ability to gain weight and occasionally causes death. Previous studies suggest that Eimeria tenella synthesizes phosphocholine via S- adenosylmethionine-dependent phosphoethanolamine methyltransferases (PMT). The PMT catalyzes the methylation phosphoethanolamine (pEA) to phosphocholine for membrane biogenesis. That specific pathway is also found in plants and nematodes but is not found in humans. Because of the essential nature of PMT in the survivability of the parasite it is considered an antiparasitic target. The new crystal structure of PMT from Eimeria tenella (EtPMT) provided detailed information of the three-dimentional active site. Examination of the biochemical activity of EtPMT and the role of active site residues that may determine substrate specificity. To determine the effect of changes in the substrate and cofactor binding sites, a series of point mutations were generated by QuikChange PCR mutagenesis and the resulting proteins expressed as His-tagged fusion protein and purified by nickel-affinity chromatography. A kinetic analysis will be used to analyze the effect of mutations on activity and substrate specificity for phosphoethanolamine. Our results probe the contributions of active site residues for EtPMT function.



Overal Structure of EtPMT

SERMACS 337

Salivary hormonal study on individuals of African ancestry living in different socio-economic environments, in order to understand etiology of prostate cancer

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Prostate cancer ranks high among some of the most serious public health problems that significantly impact the lives of men globally. Established risk factors for this disease include age, family history and African ancestry. While incidence and mortality of prostate cancer has decreased in the US in recent decades, men of African descent are disproportionately affected. To better understand the etiology of prostate cancer among men of African ancestry, this study examined hormonal differences among men of African descent living in different socio-economic environments by using their saliva samples to study their hormone levels. Using ELISA kits specific to either testosterone or cortisol, hormone levels were determined for each individual's saliva using standards and low and high quality control samples for validation. The saliva samples collected from individuals living in African countries (n=21) had a mean testosterone concentration of 93.43 pg/mL and standard deviation of 35.924 pg/mL while the mean cortisol concentration was 0.120 mg/dL and the standard deviation was 0.078 mg/dL. The saliva samples collected from individuals with African ancestry in the United States (n=84) had a mean testosterone concentration of 94.680 pg/mL with a standard deviation of 35.218 pg/mL while the mean cortisol concentration was found to be 0.136 mg/dL with a standard deviation of 0.101 pg/mL. This poster will explain data collected for both hormones for males living in African countries and the United States, and will discuss whether these hormone levels can be used to determine individuals at risk for prostate cancer. Any observed effects from socio-economic differences will also be discussed.

SERMACS 338

Detecting prostate cancer associated glycosylation patterns from human serum using a boronic acid functionalized synthetic lectin array

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Prostate cancer is predicted to be the most common, non-skin cancer diagnosed in men in the US during 2019, accounting for nearly 10% of all new cancer cases. However, the false-positive and false negative rates associated with the common PSA test, as well as health risks accompanying follow-up procedures lead to a need for a novel diagnostic tool. The research presented here intends to develop a screening/early diagnostic tool that utilizes boronic acid functionalized synthetic lectins (SLs) as an approach for the direct detection and prognosis of prostate cancer. This method is based on the knowledge that during the onset and throughout the progression of numerous diseases, including cancer, aberrant glycosylation occurs which involves the over-, under-, or neo-expression of specific carbohydrates, also referred to as glycans, on membrane-bound and secreted glycoproteins. This design presents a unique opportunity for the detection of cancer at the earlier stages of the disease when cancer is the most treatable as well as providing an opportunity to identify the virulence of the disease.

Initial studies using this SL array resulted in a 93% classification accuracy when discriminating human prostate derived cell lines based on metastatic potential. However, to use this SL array as a clinically relevant screening and early diagnostic tool, the SLs must be able to identify aberrant glycosylation patterns from human blood samples rather than cell lines. Subsequently, current efforts are focused on evaluating the ability of the SL array to assess cancer status using human blood samples from normal/healthy donors and newly diagnosed prostate cancer patients with varying prostate cancer status.

SERMACS 339

Identification of a novel transcriptional repressor gene in Kumao, a novel temperate bacteriophage

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Bacteriophages are viruses that infect bacteria and are the most abundant and genetically diverse entities on the planet. During the lytic replication cycle bacteriophage infection results in cell death and the production of many new infectious bacteriophage particles. However, it is now known that many bacteriophages are temperate and can also enter into a long-term relationship with their bacterial hosts. Temperate bacteriophages express an integrase protein that allows them to integrate their genome into the bacterial chromosome. The integrated bacteriophage is called a prophage, and the bacterial cell containing it is called a lysogen. During lysogeny, bacteriophage lytic gene expression is silenced via the expression of a transcriptional repressor protein. While it is known that many bacteriophages are temperate, only a few repressor proteins have been biochemically characterized. Due to the collective efforts of the SEA-PHAGES program 1,766 bacteriophages that infect the host *Mycobacterium smegmatis* have been sequenced and viral stocks archived. This collection of Mycobacteriophages is a powerful genetic resource to examine fundamental questions in bacteriophage biology.

Kumao is a genetically unique bacteriophage that infects *Mycobacterium smegmatis* and was selected for further study because of its noncanonical genome arrangement. Kumao contains an integrase gene on the right side of the genome, but bioinformatic analysis has failed to identify a repressor gene candidate. We have successfully generated Kumao lysogens, proving that Kumao is indeed a temperate bacteriophage. Our current work is focused on identifying Kumao’s repressor gene using two different functional screens. The first involves overexpressing individual Kumao genes in *Mycobacterium smegmatis* and performing a viral challenge experiment. Ten genes have initially been selected based on their proximity to the integrase gene and nearness to a transcriptional direction change or promoter region. The second approach involves CRISPR interference of Kumao’s operons during lysogeny. If the operon containing the repressor is silenced during lysogeny, Kumao should reenter the lytic replication cycle. Currently in progress of testing four operons located at the far left, middle, and right end of the viral genome. The results of these experiments and future plans for the biochemical characterization of Kumao’s repressor protein will be discussed.

SERMACS 340

Isolation, whole-genome sequencing, and antimicrobial activity of the slow-growing aquatic *Pseudomonas* sp. RIT623

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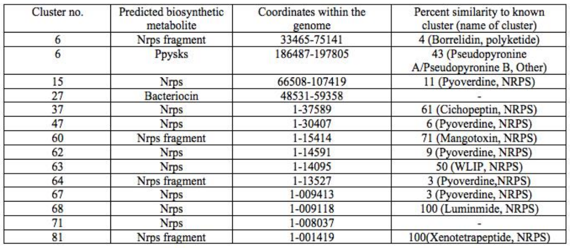
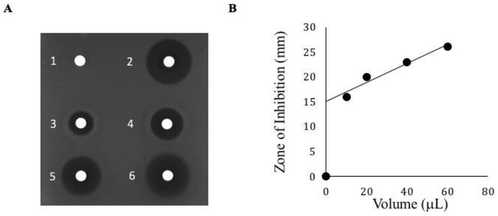
The rise in antibiotic resistant bacteria has led to increase bacterial infections that are resistant to antibiotics. Slow-growing bacteria, which could be potential antibiotic producers, can be difficult to isolate on rich media due to competition from fast growing bacteria. *Pseudomonas* sp. RIT 623 was isolated from pond water located on the campus of RIT using pond water agar. The genome was sequenced and analyzed for potential secondary metabolite gene clusters and antibiotic resistance genes. Antimicrobial production was also tested using extracts from the spent growth medium by means of disk diffusion tests. Fourteen gene clusters were identified as secondary metabolite genes. To date this is the first slow growing aquatic *Pseudomonas* strain which produces antibacterial compounds. Isolation of the bioactive compounds by liquid chromatography is underway with the aim of identifying the chemical structures and the genes responsible for the biosynthesis.



Cluster no.	Predicted biosynthetic metabolite	Coordinates within the genome	Percent similarity to known cluster (name of cluster)
6	Nrps fragment	33465-75141	4 (Borrelidin, polyketide)
6	Ppysks	186487-197805	43 (Pseudopyronine A/Pseudopyronine B, Other)
15	Nrps	66508-107419	11 (Pyoverdine, NRPS)
27	Bacteriocin	48531-59358	-
37	Nrps	1-37589	61 (Cichopeptin, NRPS)
47	Nrps	1-30407	6 (Pyoverdine, NRPS)
60	Nrps fragment	1-15414	71 (Mangotoxin, NRPS)
62	Nrps	1-14591	9 (Pyoverdine, NRPS)
63	Nrps	1-14095	50 (WLIP, NRPS)
64	Nrps fragment	1-13527	3 (Pyoverdine,NRPS)
67	Nrps	1-009413	3 (Pyoverdine, NRPS)
68	Nrps	1-009118	100 (Luminmide, NRPS)
71	Nrps	1-008037	-
81	Nrps fragment	1-001419	100(Xenotetrapeptide, NRPS)

Summary of predicted secondary metabolite gene clusters using the antibiotics and secondary metabolite analysis shell (antiSMASH4.0) webserver for *Pseudomonas* sp. RIT 623



(A) Disk diffusion assay using ethyl acetate extract of spent medium of *Pseudomonas* sp. RIT 623 against *Bacillus subtilis* BGSC 168. (1) Methanol, 20 µL; (2) Tetracycline, 20 µL (10 mg/mL); and (3, 4, 5, 6) 10 µL, 20 µL, 40 µL, and 60 µL of RIT 623 extract, respectively. (B) Positive correlation of the diameter of the zone of inhibition (ZOI) with increasing volumes of extract.

SERMACS 341

Isolation, sequencing, and antibacterial properties of *Exiguobacterium* sp. RIT452

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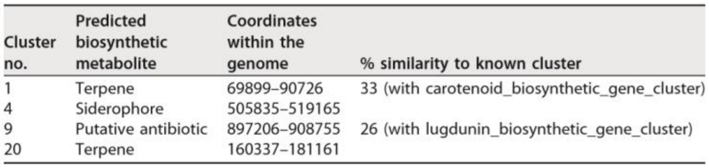
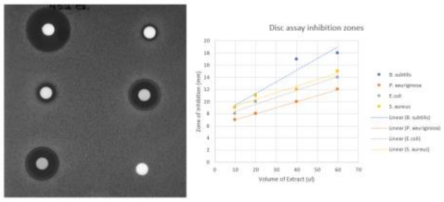
Bacteria are becoming resistant to the antibiotics that were historically effective in clinical settings and there is a need for new molecules. The goal of this study is to identify novel bactericidal/bacteriostatic compounds produced by bacteria isolated from the environment. Bioprospecting approaches were employed to identify unique bacteria from the environment. The variable 3 (V3) regions of the 16S rDNA were amplified using polymerase chain reaction (PCR) followed by nucleotide sequencing. A selection of these unique isolates were subjected to whole genome sequencing using the Illumina MiSeq sequencer including the strain RIT 452. RIT 452 was shown to produce a variety of secondary metabolites in addition to bactericidal compounds. Disk assays were employed to test the inhibitory effects of organic compounds isolated from RIT 452 against other bacteria. Fractions were collected using FPLC chromatography to facilitate the identification of compound/s that are responsible for the antibiotic effect.



Cluster no.	Predicted biosynthetic metabolite	Coordinates within the genome	% similarity to known cluster
1	Terpene	69899–90726	33 (with carotenoid_biosynthetic_gene_cluster)
4	Siderophore	505835–519165	
9	Putative antibiotic	897206–908755	26 (with lugdunin_biosynthetic_gene_cluster)
20	Terpene	160337–181161	

A summary of RIT452 secondary metabolite gene clusters predicted by antiSMASH 4.0 online software.



Discs containing extracts from RIT452 create zones of inhibition in *Bacillus subtilis* growth. Zones show a graded increase in *Bacillus subtilis, Escherichia coli, Pseudomonas aeruginosa,* and *Staphylococcus aureus* growth, shown by graph.

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Directed evolution of a natural product prenyltransferase towards alkyl-diversification of isoprenoids

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The attachment of an isoprenoid moiety to an acceptor compound is a frequent modification in the biosynthesis of a wide variety of important natural products. Prenylation often requires regioselective C-H functionalization or activation of one of multiple nucleophilic heteroatoms. In nature, many of these transformations are catalyzed by aromatic prenyltransferases which have been demonstrated to have modest, tunable promiscuity with respect to both the prenyl donor and aromatic acceptor. We are leveraging a novel high-throughput prenyltransferase assay to apply directed evolution to increase activity towards non-natural prenyl donors and to expand its reactivity towards diverse aromatic acceptors. The engineered biocatalysts will be used to diversify the structures of several clinically significant natural products. In addition, studying the structure and mechanism of the evolved enzymes will improve our understanding of the molecular basis of prenyltransferase substrate specificity and catalysis.

SERMACS 343

Prey-associated quorum signals impact specialized metabolism and predatory features of predatory myxobacterium *Cystobacter ferrugineus* Cbfe23

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The diverse antibacterial and antifungal activities of specialized metabolites from soil-dwelling myxobacteria are typically associated with their predatory lifestyles. The model myxobacterium, *Myxococcus xanthus* intercepts and responds to acylhomoserine lactone (AHL) quorum signals produced by prey bacteria by activating features associated with predation such as motility. Quorum signaling AHLs are a common class of quorum sensing molecules (QSMs) produced by several soil-inhabiting Gram-negative bacteria that facilitate group activities such as biofilm formation and virulence. Considering the association between myxobacterial specialized metabolism and predation, we hypothesize that exposure to AHLs will impact the specialized metabolism of myxobacteria. To broaden our understanding of such quorum signal interception by myxobacteria, we have performed untargeted mass spectrometry and RNA-seq analysis on a myxobacterium *Cystobacter ferrugineus* Cbfe23 after exposure with *N*-hexanoyl-L-homoserine lactone (C6-AHL) molecule that is produced by a number of bacteria including *P. chlororaphis* and *P. aureofaciens*. Crude extract analysis indicates that *C. ferrugineus* produces numerous metabolites when exposed to C6-AHL and shuts down the production of several others including toxins such as isopimaric acid and tubulysins. Furthermore, RNA-seq data reveals activation of lytic endolysin secretion and modulation of various genes associated with specialized metabolism during C6-AHL exposure experiments. In conclusion, these data depict the robust response of the predatory myxobacterium *C. ferrugineus* when exposed to prey quorum signals and suggest that the chemical signals within soils impact neighboring populations and not only producing organisms.

SERMACS 344

Simplifying molecular probes for interrogating bacterial surface polysaccharide bioassembly

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Microbes have a profound influence over our health, both to our detriment and benefit. The highly unique surfaces of bacteria are critical for distinguishing the role that these microbes play in our health. In particular, polysaccharides at the cell surface are highly variable among bacteria of even the same species and provide a unique “thumb-print” identifier used in serotyping. Our knowledge of the bioassembly of these surface glycans is sorely limited because of the considerable diversity in glycan composition that is inherent to these highly complex structures. Research herein addresses the need for simplifying molecular probes necessary for the elucidation of surface polysaccharide bioassembly in various bacterial species. We then assess these probes in vitro as functional substrate replacements with a representative pool of initiating phosphoglycosyltransferase enzymes which commence surface polysaccharide bioassembly. Our findings demonstrate that these probes are indeed utilized for building polysaccharides, and have unique solubility considerations for efficient enzymatic turnover.

SERMACS 345

Structure-based design of INGAP peptide analogs to promote viability and function of pancreatic islet beta cells

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Diabetes mellitus is a metabolic disease characterized by a high level of glucose in the blood. Methylglyoxal (MG), a by-product of glucose metabolism, is believed to cause the deleterious effects observed in diabetes by causing oxidative stress and death in various cell types. Toxicity of MG to pancreatic islet β-cells contributes to a further loss of pancreatic β-cells mass and/or dysfunction of β-cells, which augments deficiency of the hormone insulin that regulates blood sugar level. We found a synthetic pentadecapeptide segment of Islet Neogenesis Associated Protein (INGAP-P), Ac-IGLHDPSHGTLPNGS-NH_2, is able to protect RINm5F cells (rat β-cells) against the toxicity of MG in MTT-based cell viability assays. INGAP-P presented at micromolar concentrations was able to reverse 50% of the cell death in the presence of 1mM MG for 24 hours. We then used a free online peptide structure prediction program PEP-FOLD 3.5 to design analogs of INGAP-P and identified several sequences that favor the b-hairpin structure with a short loop containing the DPSHG segment. Among the analogs synthesized and tested, the sequence Ac-LHDPSHGLTQ-NH_2 and a cyclized analog of INGAP-P showed stronger cytoprotective effects on MG-treated RIN5mF cells than INGAP-P, both reversing cell death at submicromolar concentrations. These two analog peptides also maintained the glucose-stimulated insulin secretion ability of RINm5F cells. Because of its easier synthesis and lower cost, the shorter linear peptide analog may serve as a better lead compound than INGAP-P in development of β-cell promoting agents.

SERMACS 346

Characterization of lipid binding by full-length NoxO1

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NADPH oxidases are multi-protein enzyme complexes that catalyze the generation of superoxide, which is a molecule important for many biological functions ranging from host defense, cell signaling, and the regulation of cell growth. Aberrant NADPH oxidase function is associated with many inflammatory conditions including vascular disease and certain cancer types. The NADPH oxidase complex contains both membrane-bound and cytosolic components; proper arrangement of the cytosolic components to the membrane-embedded enzyme is necessary for proper complex function. NoxO1 is one cytosolic protein found within certain NADPH oxidase complexes that acts as an organizer, helping position cytosolic components correctly at the membrane. To achieve this function, NoxO1 is capable of binding both membrane lipids and other proteins within the NADPH oxidase complex. NoxO1 contains a well-studied lipid binding domain, the PX domain, which binds phospholipids. The lipid binding of the isolated PX domain of NoxO1 has previously been characterized, but lipid binding by full-length NoxO1 has yet to be studied. Here we present the expression and purification of recombinant full-length NoxO1 as well as preliminary lipid binding data. Work from this project will help to further characterize the lipid binding of NoxO1 which can provide insight into the basis of NADPH oxidase regulation through the lipid binding function of NoxO1.

SERMACS 347

Isolation, sequencing, and antibacterial properties of *Paraclostridium* sp. MH636

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Bacteria are becoming increasingly more resistant to current antibiotics. The goal of this experiment is to find and identify new antibacterial compounds produced by bacteria isolated from the environment, specifically crab apples. Bio-prospecting approaches were used to identify these bacteria from the environment. The variable 3 (V3/V4) regions of the 16S rRNA were amplified using polymerase chain reaction (PCR) followed by nucleotide sequencing. A few of these isolates were subjected to whole genome sequencing using the Illumina MiSeq sequencer including MH636 (Paraclostridium). MH636 was shown to produce various secondary metabolites including antibacterial properties. Disk assays were used to test the inhibitory effects of organic compounds isolated from MH636 against other bacteria. Fractions were collected using FPLC chromatography to facilitate the identification of compound/s that are responsible for the antibiotic effect.

SERMACS 348

Decoding the machinery behind the thermodynamically unstable disubstituted β-branch formed in difficidin

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Difficidin is a broad spectrum antibiotic polyketide product from *Bacillus velezensis* FZB42. Although most of the difficidin structure is made by conventional polyketide synthase (PKS) chemistry, it also contains a small structural feature that is not fully understood. This novel “β-branch” structure is unusual because it is a disubstituted exocylic olefin that is likely thermodynamically unstable compared to the tri-substituted β-branching groups found in other polyketides, such as bacillaene. Our hypothesis is that that the *B. valezensis* difficidin biosynthetic pathway utilizes a mechanistic route that avoids the thermodynamically stable conjugated trisubstituted double bond while forming the less stable disubstituted β-branch olefin. Using mass spectrometry and recombinant proteins, we investigated the biochemical steps for the biosynthesis of the difficidin β-branch. We reconstituted the early steps of the difficidin β-branch biosynthetic pathway involving the construction of the acetyl-DfnX substrate that provides the extra carbon of the β-branch. We also successfully used two enzymes to complete the β-branch, starting with a hydroxymethylglutaryl (HMG) group tethered to the acyl carrier di-domain of the modular polyketide synthase, DfnJ. We will describe these and ongoing experiments designed to complete this pathway. Once this pathway is reconstituted we will be able to study how the difficidin system constructs the unusual di-substituted β-branch.

SERMACS 349

Design of mimic peptides for inhibition of methyl-binding proteins

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The study of epigenetics has shown how the effects of post-transcriptional modifications can critically change the expression of genes. In one case, repression of methylated gene segments, or CpG islands, can lead to a multitude of pathologies such as certain cancers or an overactive immune response resulting in inflammation. Transcription factors such as Methyl-CpG binding domain protein 1 (MBD1) bind specifically to hyper-methylated promoters of genes, effectively silencing them. One approach involves designing peptides which mimic specifically the binding sites of transcription factors that control this repression, and which can competitively bind to CpG islands to prevent the silencing of target genes. Using a peptide synthesizer, mimic peptides can be produced and compared to known binding segments of methylated binding domain proteins (MBD proteins), resulting in a designed mimic with a specific binding affinity competitive to that of the MBD1 protein’s binding domain (β2-l1-β3). Synthesized peptides will be purified by HPLC and their masses will be analyzed using MALDI-ToF. Initial results indicate that Isothermal Titration Calorimetry (ITC) serves as a promising method for binding analysis compared to fluorescence methods which rely on fluorophores or intrinsic tryptophan amino acids within the peptide. Circular Dichroism (CD) data will be used to understand what role peptide secondary structure plays in binding when compared with ITC data. CD will also be used to compare peptides’ thermal stability using thermal denaturation data. Competition assays can be conducted once the most optimal peptides are determined, and data gathered may lead to discovery of new methods of treatment for these pathologies.

SERMACS 350

Biological evaluation of botanical extracts against *Staphylococcus aureus* and methicillin resistant *Staphylococcus aureus*

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Antibiotics were first prescribed to treat serious infections, however; their overuse eventually resulted in drug resistance. Multidrug resistant infections are an increasing universal problem, responsible for more than 700,000 annual morbidities and mortalities. There is an increasing need for more the discovery of new antimicrobial leads. *Rumex crispus*, also known as curly dock, is a plant of the Polygonaceae, Buckwheat family and native to Europe and Western Asia. Emodin, an anthraquinone and known antimicrobial, was identified as an active compound in *Rumex crispus* using liquid chromatography and mass spectrometry. Extracts of *Rumex crispus* (roots, seeds, and leaves), and Emodin were dissolved in dimethyl sulfoxide at concentrations of 10 µg/mL and 100 µg/mL and tested against MRSA and MSSA to observe bacterial inhibition. Targeted analysis using ultra high-performance liquid chromatography coupled to high resolution mass spectrometry was used for quantitative analysis. Untargeted metabolomics was employed to identify other secondary metabolites that may contribute to biological activity. Preliminary results of promising leads will be presented. Follow-up studies for this project are on-going.

SERMACS 351

Peptides as model systems for sequence specific transcriptional regulation

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Transcriptional regulation remains a major hurdle in biochemistry. Overexpression of certain genes has been linked to various diseases such as cancer and neurological disorders. One method successfully proposed for modulating overexpressed genes in some systems is to bind DNA sequences specifically using small molecules which can displace the native transcription factor and halt transcription, thereby regulating the expression of those specific genes. This research involves designing beta-sheet peptides as sequence selective mimics of natural transcription factors and targets specific DNA sequences including methylated sequences. Using peptides to determine sequence specificity may provide not only a set of template sequences which could bind DNA and regulate transcription but could also afford insight into the guidelines that govern sequence specificity. Two transcription factors will be used as model systems. The protein nuclear factor-kappa B (NF-kB) will be studied for its binding mode to kappa B DNA sequences, and the methyl-CpG binding domain family of proteins will be analyzed to determine mechanisms of selectivity for methylated sequences of DNA. To accomplish this goal, peptides mimicking each family of proteins will be designed and analyzed to determine their structural features and their DNA binding affinities. Binding affinities will be determined utilizing Isothermal Titration Calorimetry (ITC) and fluorescence techniques while secondary structures of peptides will be analyzed using circular dichroism (CD). Certain ions have been implicated in affecting DNA binding, peptide structural integrity, and various biochemical pathways, and their potential role will be analyzed as well. The culmination of this research should lead to a series of peptides which can be manipulated to specifically target various DNA sequences with the long term goal of regulating transcription. The initial steps of this project will be reported.

SERMACS 352

Analysis of enzymes involved in polymyxin resistance in *Escherichia coli* using fluorescent bactoprenyl phosphate

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Lipid A is a hydrophobic glycolipid that anchors lipopolysaccharide (LPS) in the outer membrane of a gram-negative bacterium. Modification of lipid A with 4-aminoarabinose (Ara4N) confers resistance to cationic antimicrobial peptides such as polymyxin. In *Escherichia coli*, this modification is conferred by the expression of genes in the *arn* operon. In this work, cell envelope fractions of two strains of *E. coli* (B and K-strains) were evaluated for precursors of Ara4N lipid A modification using a fluorescent, tagged bactoprenyl phosphate (2CNA-BP). Precursors of lipid A modification were identified using reversed-phase high-performance liquid chromatography (RP-HPLC) and mass spectrometry (LC-MS). Single, in-frame deletion mutants were used to evaluate the production of lipid A modification precursors compared to wild-type. *In vitro* analysis suggests that modification of lipid A with Ara4N is reversible. Our results also demonstrate that overexpression of a critical enzyme in this pathway confers growth defects. Overall, we demonstrate the utility of fluorescent BP coupled with LC-MS for evaluating Lipid A modification systems and the activity of enzymes involved in polymyxin resistance.

SERMACS 353

Characterization of novel protein domains in the DNA polymerase gamma from the human pathogenic yeast *Cryptococcus neoformans*

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Cryptococcus neoformans is a pathogenic fungus that causes infection in the lungs and central nervous system. DNA polymerase gamma (polG) is an essential enzyme in the replication of mitochondrial DNA, and since *C. neoformans* is an obligate aerobe, we hypothesize that polG is essential for *C. neoformans* infection and survival in the host. The polG from *C. neoformans* has not been

biochemically characterized, and it contains two domains of unknown function that are not present in the well-characterized human or *Saccharomyces cerevisiae* polG enzymes. The goal of this project is to characterize the *C. neoformans* polG to learn more about the function of these novel domains. Using bioinformatics, we have discovered that the N-terminal uncharacterized domain is only found in cryptococcal species. The second domain of unknown function, which lies internal to the protein between the spacer and polymerase domain, is found in polG enzymes in a variety of other species. Some of these species include *Aspergillus bombycis* and *Penicillium roqueforti.* Along with bioinformatics, we are also characterizing the polymerase activity of the full-length enzyme on short and large DNA substrates. Our kinetic results show that while the *C. neoformans* polG is an active DNA polymerase, it appears to lack the ability to perform strand-displacement DNA synthesis. This differs from the polG enzyme from *S. cerevisiae*, which functions as a monomer and shows robust strand-displacement DNA synthesis activity. From these results we hypothesize that unlike the *S. cerevisiae* enzyme, the cryptococcal polG requires additional protein factors for strand-displacement DNA synthesis, and these additional proteins may be recruited to polG by interactions with the novel domains. Current efforts are focused on identifying partner proteins in *C. neoformans* that may bind these novel domains. Using pull-down assays with the novel domains as bait, we are currently hunting for novel interacting partners that play a role in cryptococcal mitochondrial DNA replication.

SERMACS 354

How sweet it is: Using table sugar to teach single crystal X-ray crystallography at all levels of the undergraduate laboratory curriculum

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We have developed a laboratory experiment to introduce single crystal X-ray crystallography to undergraduate students at any level of the curriculum. We chose the single crystal X-ray crystal structure of sugar because X-ray quality crystals are easy to acquire, they diffract well, and all students are familiar with it. Students can execute this experiment even if supervising faculty have no background in X-ray crystallography. Selected research students and faculty vetted the laboratory protocol during the summer, and it is successfully being used in East Tennessee State University laboratory classrooms this fall.

Our goal in this research project is to popularize single crystal X-ray crystallography. While the current J. Chem. Ed. papers describing single crystal X-ray crystallography are intriguing, it appears that they require an academic institution with both a practicing crystallographer and a single crystal X-ray diffractometer. Unfortunately, few academic institutions have faculty with crystallography experience and fewer institutions have a single crystal X-ray diffractometer. Even fewer institutions have a single crystal X-ray diffractometer which can be devoted to a large amount of undergraduate use.

In this experiment, we used a version of CrysAlisPro which is available from Rigaku Oxford Diffraction. ShelX, the structure solution and refinement software, is available through the Structural Chemistry Department at the University of Göttingen, Germany. Olex2, the graphical user interface, is available from OlexSys. At the time of this writing, all versions of the necessary software are free.

For the experiment, we mounted a sucrose ($C_{12}H_{22}O_{11}$) crystal on a fishing line and analyzed it using a Rigaku XtaLAB Mini diffractometer (built 2011). We analyzed the data and generated a model of sucrose using CrysAlisPro, Olex2 and ShelX. However, if an institution without a diffractometer wants to adapt this experiment, we can easily send the data set and it can be processed at the home institution. Further, we are happy to collect a data set on a crystal for use in any laboratory experiment.

SERMACS 355

Cross curricular themes of water quality in introductory general biology and chemistry courses

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As we continue to adapt to changes in 21th century, it becomes increasingly important that students become science literate and learn the skills early in their academic career. Most students sign up for general biology and chemistry courses in the same semester. But they treat them as a separate course, and just consider each as an abstract subject. In addition, students in our large general biology and chemistry courses comprise a diverse set of majors. These students often lack interest in the content and wonder how it fits into their career goal. Most students in these two courses are not prepared to do critical thinking. They do not attempt to correlate the material in general biology and chemistry courses. These factors can result in low performance on higher order questions. The objective of this project was to determine if the use of a system-based approach and merge of limited content from both general biology and chemistry would increase student's exam scores, interest in science, and reduce D/F rate. We modified the course by creating interdisciplinary teaching modules for both courses using the case study teaching with a theme on the impact of water quality on human health. Results from the project reveal that students in revitalized general chemistry course performed much better in the ACS final compared to students the previous fall semester (54.3% vs. 47.2%). A comparison between performance of students in Fall 2017 and Fall 2018 general biology course shows a slight improvement for the latter semester by 0.3%.

SERMACS 356

3D printed models of atomic, hybrid, and molecular orbitals

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Beginning chemistry students often have difficulty visualizing the 3-dimensional shapes of electron orbitals without the aid of 3D models. Unfortunately, commercially available models can be quite expensive. 3D printing offers a solution for producing models of atomic orbitals. 3D printing technology is widely available, and the cost of 3D printing "inks" is relatively low. Creation of models requires graphing electron orbital probability distributions in spherical coordinates and exporting as stereolithography (.stl) files (a common format for 3D printing). The free web-based applet, CalcPlot3D[1], is capable of both graphing and exporting the required electron orbital geometry, and 3D printing is possible with minimal modifications for structural stability. The 3D printed models are calculated using physical constants and experimental data, and thus can be related directly to scale. Worksheet activities have also been developed in the classroom which utilize these models, and students have responded well.

SERMACS 357

Teaching essential QA/QC in the undergraduate analytical laboratory through pharmaceutical analysis: Cephalexin (DPAL project)

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Conducting research at a small, primarily undergraduate institution often requires research be incorporated into the classroom and laboratory. The DPAL (Distributed Pharmaceutical Analysis Laboratory) Project is well-suited for both independent student research and adoption in the undergraduate analytical and instrumental laboratories. The requirements for analysis stress the importance of quality assurance in the analytical process: from system suitability to method validation and analytical control charts the students experience the rigors necessary for accurate precise work. Not only do students participate in real research and the analysis of real pharmaceuticals, but they are applying their skills to aid the WHO in identifying counterfeit and sub-standard drugs from countries across the globe. The work is rigorous in an analytical sense; it is also engaging and serves to broaden the STEM students' global perspectives and impact.

This presentation will discuss both successes and failures as we began our participation in the DPAL project through both independent undergraduate research projects and in the undergraduate teaching laboratory. From the development of a successful analytical method for Cephalexin analysis to the characterization of capsules from the WHO.

SERMACS 358

Evaluation of virtual reality resources for an Organic Chemistry laboratory

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Using Virtual Reality (VR) in educational settings is becoming increasingly popular. The feasibility of replacing an organic chemistry lab with a VR experience has been evaluated. A VR laboratory experience was designed to teach students how to use an infrared spectrometer and elucidate an unknown structure from the resulting infrared spectrum. The resulting first-person VR experience is immersive and realistic, with a teaching assistant guiding the user along the steps required to complete the experiment, including feedback as needed. The VR experience was developed in WondaVR with selections made using gaze navigation. The resulting product was tested with a group of students and the outcomes for short and long-term recall were compared with a group of students that did the same experiment in a traditional lab. Results indicate that there are no significant differences in learning outcomes between the two groups, which indicates the possibility of using this tool to offer this organic chemistry lab experiment via distance education. Students that tried the VR experience reported a high degree of satisfaction with the product and no significant usability barriers. These VR experiences could be useful for students who are unable to be present in lab due to disabilities, attendance challenges such as pregnancy, or safety concerns.

SERMACS 359

Making a case for hands on activities in spectroscopy

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A new hands on activity to help engage the students in their IR and 1H NMR problems was attempted in our Organic Chemistry 2 laboratory this past Spring 2019 Semester. The results (based on how the students performed on the subsequent problems in lecture) will be shared and the activity itself will be discussed.

SERMACS 360

Determining the quantity of acetic acid in household vinegar: Undergraduate laboratory titration experiment using three independent monitoring techniques

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We embarked on a program aimed at developing undergraduate laboratory experiments in the area of physical and analytical chemistry. Determination of acetic acid by titration method using an aqueous sodium hydroxide is a common undergraduate laboratory experiment. Three titration experiments based on this neutralization reaction will be presented. In these experiments, a known volume of a sample of household vinegar was placed in the cathode compartment of an electrolysis cell. Electrolytically produced $OH^-(aq)$ neutralized the acetic acid and the end point was determined by visual color change of an indicator. In the first experiment, the progress of the titration was monitored by measuring the volume of $O_2(g)$ produced at the anode. The perfect gas equation and the stoichiometric relations were applied to determine the amounts of $O_2(g)$, $OH^-(aq)$, and the acid in the sample. In the second experiment, the amounts of $H_2(g)$ and $O_2(g)$ were determined from the decrease in mass of the electrolysis cell. Stoichiometric relations were applied to determine the amounts of $OH^-(aq)$ and the acid in the sample. In the third experiment, the amounts of $OH^-(aq)$ and the acid in the sample were determined by monitoring the charge passing through the cell. A special multicompartment electrolysis cell facilitated simultaneous coulometric titrations. Experimental procedures and quantitative results obtained by students will be presented.

SERMACS 361

NGS profiling of a mother culture used in the production of sour beer

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Beer fermentation is one of humanity's oldest biotechnologies. In many cases the methodologies and assessments used in American craft brewing are unchanged from traditional approaches and rely heavily in sensory assessments. Recently sour beer production has become widespread in American craft brewing with consumer demand increasing faster than any other beer style. Orpheus Brewing Company was established in Atlanta, GA in 2013 with a portfolio focused on sour beer. While the general trend in sour beer production relies on pure culture inoculum and kettle souring, Orpheus has achieved notoriety for the flavor of their products due to their use of a mother culture that incorporates diverse microorganisms resulting a complex sensory experience. In an effort to determine the community composition of the Orpheus mother culture both targeted and global community analyses were conducted. Samples from each of the three dosing kegs containing the mother culture were extracted and a 16s/ITS library constructed using the QIAseq 16s/ITS screening panel. Whole genome libraries were constructed using QIAseqFX DNA library kit. Each library was sequenced with Illumina technology and processed with the CLC Genomics tool kit. The results indicate that the mother culture is dominated by Lactobacilli with several species being highly represented. The fungal population is dominated by *Saccharomyces cerevisiae*, however diverse fungal genera were detected, including organism routinely identified in brewing operations that may significantly contribute to the sensory profile of packaged products. This study highlights the power of NGS to understand the communities responsible for the production of a unique sour beer portfolio as well as allow brewers to diagnose community changes that may result in undesirable changes to a product's sensory profile.

A dosing keg in the Orpheus brewery, Atlanta, GA.

SERMACS 362

Bypassing the malting process with Koji

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Malted grain is one of the necessary ingredients in the production of beer, spirits and other grained-based beverages. For grains to be of any use in the brewing process, enzymes that break down soluble sugars within the grain must be accessible in order to develop a medium that yeast can ferment. This is done via the malting process, which generally takes several days, and may consume up to 1,140 gallons of water and 800kWh of energy to produce 1 ton of malted grain. The goal of this project is to determine if *Aspergillus oryzae,* commonly called Koji, can be used with grains to bypass the lengthy and energy intensive malting process and if it can be used to develop fermented beverages comparable to those that use malted grains. Koji is a fungus utilized in the production of many fermented Asian foods and beverages where it is used in the saccharification of grains and other substrates. In addition to its ability to yield important enzymes, Koji also produces unique flavors and aromas not traditionally found in malted grains. For this project unmalted barley grains were inoculated with various strains of Koji spores to determine its effectiveness in producing enzymes and soluble sugars within the grains. After proofing in a controlled climate, the inoculated grains will be analyzed qualitatively for appearance, aroma, and flavor. The koji grains will then be used in the production of a simple beer recipe where sugar yield, presence of marker compounds, and attenuation are determined as well as the organoleptic properties of the finished product.

SERMACS 363

Investigation of volatile and semi-volatile aroma compounds in beer originating from either sorghum or barley malt

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The consumer desire for gluten-free products has extended into beer. There are currently several beers produced from gluten-free grains, specifically sorghum. The beers produced from gluten-free grain have a distinct flavor, which is significantly different from beer produced from barley. It is therefore of interests to determine the differences in the volatile and semi-volatile chemical profiles of beers brewed from these two grains. A series of brews were produce using either malt or sorghum extract using US 05 yeast. The aroma profile was sampled using SPME with chemical separation and identification and relative quantification by GCMS. The statistical analysis of the profiles developed shows that the differences result not from distinct compound differences but from a wide number of compounds present in different amounts.

To further explore these differences the effect of four additional yeast strains, Wyeast 1056, Wyeast 1098, Wyeast 1010, and Wyeast 1214 was explored. Another series of brews using both malt and sorghum extract were produced and the volatile and semi-volatile compounds were detected using HS-SPME-GCMS. The effect on the relative concentrations of a series of compounds was observed. As expected, the starting grain material and selected yeast strain influenced the relative amount of the volatile and semi-volatile compounds produced.

SERMACS 364

Effect of yeast strain on distilled spirit aroma and flavor: Sensory perception

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Multiple spirits were generated using a total of five yeast strains. Various fermentable material was used, ranging from a simple sugar solution to an all-grain mash. The various aroma and flavor profiles generated by the yeast were analysed by gas-chromatography mass-spectrometry, including quantification. These spirits were analyzed for aroma and flavor and typed against standard spirits (whiskey, rum, vodka, tequila). The typing of a particular spirit led to investigations as to which compounds contributed to that typing.

SERMACS 365

Testing and characterizing a novel bioactive glass containing nanoceria

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Cerium oxide nanoparticles, called nanoceria, have gained significant importance for biomedical applications due to the switching of cerium ions between its two oxidation states, Ce+3 and Ce+4, on the surface of the nanoparticle. The ratio of Ce+3/Ce+4 sites on the nanoceria is strongly correlated to the antioxidant/enzyme mimetic activity of the cerium oxide nanoparticles, introducing exciting biomedical applications for nanoceria as potent antioxidants. Bioactive glasses are well known biodegradable and biocompatible materials often used in tissue engineering to enhance new bone formation. This project involves the creation of a novel bioactive glass containing nanoceria with a range of specific Ce+3/Ce+4 ratios sealed within the glass. Dissolution of the bioactive glass in aqueous media releases the mixed valence nanoceria. Thus, the novel bioactive glass acts as a creator and delivery system for mixed valence nanoceria. In this present study, nanoceria from the glass matrix has been extracted and tested for bioactivity. Characterization of nanoceria containing bioactive glass by UV-absorbance spectroscopy shows a peak at 290nm. Preliminary data from a colorimetric cell viability assay shows that cell growth is inhibited in presence of the glass without nanoceria. However, in presence of glass that contains nanoceria, cell growth is stimulated. The antioxidant properties of the glass containing nanoceria have been identified using the Fenton reaction and further tests will be done to determine the enzyme mimetic properties of the novel nanoceria containing glass. This study will provide valuable data on the biological function of these novel, never before tested bioactive glass samples and the potential therapeutic uses of this glass in treating diseases caused by oxidative stress as well as a way to coat implants to improve surgical wound healing.

SERMACS 366

Design and synthesis of new aminoflavonol benzyl quinolone carboxylic acid (BQCA) analogs as potential Alzheimer’s disease drugs

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As the 6th leading cause of death in the United States and the most common type of dementia among older adults, with no real cure, Alzheimer’s Disease is projected to affect a more significant number of populations. Our research goal is to develop small libraries of potential Alzheimer’s Disease drugs. The analogs are benzyl quinolone carboxylic acid (BQCA) analogs in which BQCA, an allosteric potentiator of the M1 muscarinic acetylcholine receptor (mAChR), shows a promising therapeutic property by reducing the acetylcholine needed to activate the mAChR. An automated docking tool, AutoDock Vina, is utilized to design novel analogs and predict their binding affinity. Our research design is to synthesize new aminoflavonol BQCA analogs that have a higher binding affinity and water solubility, to increase their efficacy and oral availability, and evaluate their drug efficacy in a novel zebrafish AD model.

SERMACS 367

Small molecule inhibitors of MEMO1: Biochemical and biological evaluation

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MEMO1 is a scaffolding protein found in high levels in aggressive breast cancers. We have recently identified small molecules capable of binding to MEMO1 and disrupting its interaction with other proteins. We have characterized the inhibition using fluorescence polarization and examined phenotypic responses in breast cancer cells.

SERMACS 368

Expression, purification, and characterization of the *Staphylococcus aureus* pasta kinase STK1

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The PASTA kinases found in gram-positive bacteria act as major regulators of a variety of cellular pathways including antibiotic resistance, toxin expression, and biofilm formation. Recently they have emerged as attractive targets for overcoming antibiotic resistance mechanisms. In order to identify small molecule inhibitors of the PASTA kinase Stk1 from *Staphylococcus aureus*, we have expressed and purified the kinase domain. In addition, we have optimized a luminescence based kinase assay to evaluate enzymatic activity.

SERMACS 369

Regulation of pyrimidine degradation in *Pseudomonas chlororaphis*

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The microorganism *P. chlororaphis* was studied to determine if the reductive pathway enzymes were expressed and the effects of the activities relative to nutrient sources. *Pseudomonas* species have been found to be opportunistic pathogens and are agriculturally and environmentally important. The pyrimidine reductive catabolic pathway is one of two mechanisms that can be utilized by microorganisms to degrade nucleic acid bases for their carbon and nitrogen end-products. The other pyrimidine catabolic pathway is oxidative, and its end products include urea and malonic acid. It has been previously shown that some *Pseudomonas* species are able to utilize pyrimidines as sole nitrogen sources, and this could be a mechanism for either negative or positive growth control. Therefore, the reductive pathway was studied in this *Pseudomonas* strain and subjected to various nutrients to demonstrate the effects on the reductive pathway enzymes. The degradative pathway enzymes (dihydropyrimidine dehydrogenase, dihydropyrimdinase, and N-carbamoyl-β-alanine amidohydrolase) were assayed to determine their specific activities after the microorganism had been grown in Stanier minimal media with either glucose or succinate serving as the carbon source, while the nitrogen sources were varied. The three reductive pathway enzymes were detected regardless of the nutrient sources. It was found that glucose has a depressive effect on the dehydrogenase enzyme relative to succinate when uracil serves as the nitrogen source. Ongoing projects will analyze the production and specific activity of pyridine nucleotide transhydrogenase. This enzyme converts the oxidized form of nicotinamide adenine dinucleotide to the reduced form that is involved in the reduction of uracil to dihydrouracil in the reductive pathway. It is of interest to investigate the various cationic metals to analyze the effects on the three pathway enzymes.

SERMACS 370

Pro-ligands of estrogen receptor beta and implications in neurodegenerative diseases

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Activation of estrogen receptor beta has been linked to neuroprotective effects in a variety of neurodegenerative diseases such as Parkinson's disease, multiple schlerosis, and Alzheimer's disease. Taking advantage of the high levels of reactive oxygen species in these environments, we have masked an estrogen receptor beta ligand as a boronate ester . We have characterized the selective release of the active ligand in the presence of hydrogen peroxide kinetically as well as in a cellular environment. We have recently begun to examine the phenotypic effects on a cellular model of neurodegeneration.

SERMACS 371

Encapsulation of small molecules in the virus-like particle qβ

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Virus-like particles have gained interest in recent years due to their potential applications in vaccine development, drug delivery, and imaging capabilities. We have generated rationally designed hydrophobic mutants of the bacteriophage Qβ and begun to characterize their differential ability to encapsulate small molecules such as crystal violet, the cancer drug doxorubicin, and fluorescein. Different loading capacities with the mutant Qβ particles have been observed.

SERMACS 372
Expression and characterization of mutant virus-like particles

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The use of virus-like particles for a variety of biotechnology applications relies on the ability to mutate and optimize the protein structure and function. Therefore, we have generated rationally designed point mutations of the Qβ virus-like particle. Expression and purification of the mutated capsid proteins has been successful. The particles have been characterized using thermal denaturation, transmission electron microscopy, and spectroscopic techniques.

SERMACS 373
Autoinhibitory loop of endothelial nitric oxide synthase: Structural characterization and kinetics with MAPKs

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Mitogen-activated protein kinases (MAPKs) ERK and p38 participate in signaling networks with endothelial nitric oxide synthase (eNOS). eNOS contains a putative MAPK binding site associated with the autoinhibitory loop (AI), a major eNOS control element. Our reported pentabasic MAPK binding site and the site phosphorylated by ERK S600 are within the AI and have important enzyme control elements between them. Despite extant crystal structures of homologous NOSs, nothing is known of the structure of the AI beyond secondary structure prediction. To address this lack of knowledge, we constructed a synthetic gene encoding a maltose binding protein (MBP)-AI fusion and expressed and purified the protein. Biolayer interferometry (BLI) showed that MBP-AI bound p38 with low µM affinity, as expected, confirming the presence of the MAPK binding site within the AI. BLI and surface plasmon resonance (SPR) will be used to perform a complete kinetic characterization of AI-p38 binding. MBP-AI will be labelled with ^{15}N and characterized with ^{1}H, ^{15}N heteronuclear NMR methods. Transverse Relaxation Optimized Spectroscopy (TROSY) and Saturation Transfer Difference (STD) experiments to determine the p38-bound structure of the AI will be described, along with other NMR and biophysical characterization methods. The results will be incorporated into an updated model of MAPK regulation of eNOS, which may have implications for understanding diabetic physiology, atherosclerosis and cancer.

SERMACS 374
Synthesis of multi-metallic acetylide compounds of D^{10} transition metals

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Transition metal acetylide compounds have been studied for their applications in non-linear optics, luminescence, and molecular conductivity. Herein, we report a series of *cis*-alkynyl d^{10} transition metal compounds and explore their interactions with additional metal centers. For instance, ^{t}bpyPt(C$_2$Fc)$_2$ (where Fc = ferrocenyl) displays two 1e- Fe$^{III/II}$ couples, which are impacted by Cu(I) complexation between the alkynes. Other structures investigated involve purely organic acetylide ligands, where the secondary metal interaction occurs between the alkynes, or a Lewis basic site attached to the alkyne.

SERMACS 375
Synthesis of ^{t}bpyPt(C$_2$2Py)$_2$ and its interactions with Cu(I) and Pd(II) metals

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Metal-ion interactions with Lewis bases are of interest in the field of supramolecular chemistry and ligand design. Our group has been particularly interested in exploiting *cis*-alkynyl transition metals to form *trans*-bidentate ligands. Herein, we report the synthesis and characterization of ^{t}bpyPt(C$_2$2py)$_2$, and its interactions with Cu(I) and Pd(II). Crystallographic studies are used to compare this Pt(II) ligand to a previously reported *trans*-bidentate titanocene ligand, Cp*$_2$Ti(C$_2$2py)$_2$.

SERMACS 376
Synthetic strategies for generating 4-ethynyl-2,3,5,6-tetrafluoropyridine

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Tuning emissive transition metal (TM) compounds has direct application in developing efficient optical devices, i.e., organic light emitting diodes. Alkynyl ligands have been used to tune emission properties of their corresponding TM compounds. For instance, ethynyl-pentafluorobenzene, an electron deficient ligand, is commonly utilized to blue-shift emission. Herein, we discuss synthetic methodologies to generate 4-ethynyl-2,3,5,6-tetrafluoropyridine and theoretical studies that compare the electronics of this ligand to ethynylpentafluorobenzene. A preliminary screening of reactions suggests that a Sonogashira coupling strategy is the best method to append an alkynye on tetrafluoropyridine.

SERMACS 377

Third-row molecules in space

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The extremely harsh conditions of space make it the perfect breeding ground for many interesting molecules in both the interstellar and circumstellar media. Since the discovery of carbon-sulfur bonded molecules in the interstellar medium, many sulfur analogs of carbon-oxygen containing molecules, such as thioformaldehyde, may yet be detectable. Additionally, magnesium-bearing molecules in circumstellar media may be essential for grain formation in proto-planetary disks. This work provides predictions of the vibrational and rovibrational spectra of isomeric forms of H2CS, as well as MgC2H2 and MgC3H2, using quantum chemical methods. These methods employ quartic force fields that are shown to provide accurate spectral data when compared with experiment. The computed anharmonic quantum chemical spectral frequencies of H2CS in this work compares favorably with gas phase experiment. The brightest computed mode is the antisymmetric C-H stretching at 3021.6 cm−1, which is 4 cm−1 less than the gas phase experiment. The observation of the spectral frequencies of the isomeric forms of H2CS, as well as MgC2H2 and MgC3H2, in the interstellar and circumstellar medium, respectively, will provide further evidence of the detectability of organosulfur compounds and magnesium-bearing, possibly grain-forming, molecules.

SERMACS 378

Investigating sulfur and selenium antioxidants and the role plasmid DNA conformation has on data collection using PCR, CGE, and gel electrophoresis

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Oxidative damage of DNA is linked with DNA mutations, cancer, and aging. Free radicals formed due to reactions with unbound metals in vivo are a common cause of oxidative damage of DNA. Free radicals are characterized by an unpaired electron, which results in short lifetimes and high reactivity. In the Fenton reaction, iron reacts with hydrogen peroxide to form a hydroxyl radical that is able to oxidize DNA. This oxidation leads to changes in the DNA structure, in the form of single and double stranded breaks, that can be examined through various analytical techniques. Baseline damage and the ability for the DNA to replicate is examined using pre and post PCR data analysis. The compounds N,N'-dimethylimidazole thione (dmit) and selone (dmise), as well as methimazole (MetIm) and 2-mercaptoimidazole (MerIm) are being studied for their ability to mitigate the damage of DNA caused by free radicals via a preventative metal-binding mechanism. PGEM-3z, a DNA plasmid, has been utilized to collect previous data on the compounds. Due to the various conformations of plasmids that exhibit different characteristics, linearization of the plasmid DNA has been performed and comparative data collected.

SERMACS 379

Competitive reduction of ferrihydrite and nontronite and implications for lacustrine sediments

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Detrital Fe (III)-bearing minerals (e.g. ferrihydrite) are often converted to Fe (II)-phases (e.g. pyrite, siderite) in lake basins through reduction in organic-rich, oxygen-depleted sediment. Various phases may subsequently form depending on complex redox reactions in diagenetic pore waters, including greigite, goethite, hematite, magnetite and others. These processes are poorly understood, but are important contributors to the mineral record in lacustrine sediments, affecting our understanding of paleolimnology and paleomagnetic records.

To better understand the diagenetic history of Fe-bearing phases in lakes, we are conducting abiotic water-rock interaction experiments to isolate variables identified from natural systems. Fe-bearing phases such as ferrihydrite (fhy) and clay minerals such as Fe rich nontronite (nont.) were used in this experiment. We performed abiotic reduction experiments in carbonate brine to test the hypothesis that ferrihydrite reduction is kinetically more favorable than that of nontronite. Trials were run with varying mineral proportions and trial durations. Samples had 100% nont, 80/20 nont/fhy, 50/50 nont/fhy, 20/80 nont/fhy and 100% fhy. Trials one through three ran two, six and ten hours respectively. Samples were reduced using a sodium dithionite-citrate-bicarbonate solution (Stucki et al, 1984). We characterized the relative abundance of Fe-bearing phases pre- and post-reduction by detailed X-ray diffraction analysis.

The sample containing 100% nontronite exhibited small changes in its octahedral layer after each trial. In trial one through three, 060 reflection values shifted from 1.5012 Å, 1.5015 Å and 1.5019 Å. This suggests partial reduction of a component of the Fe (III) in its octahedral layer. There was no siderite production from the reduction of nontronite, suggesting that Fe (II) remained in the smectite structure rather than being released into solution. In contrast, every sample containing ferrihydrite showed loss of ferrihydrite with subsequent precipitation of siderite (Fe (II)-carbonate). These results indicate the importance of ferrihydrite in lacustrine iron biogeochemistry, with important implications for interpreting the sedimentary mineralogy and paleomagnetic records of lacustrine sediments.

SERMACS 380

Predicting reactivity of homologous sulfohydrolases via bioinformatics

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The goal of this project is to understand a class of enzymes belonging to the metallo-beta-lactamase superfamily whose members serve unknown biological purposes. The first of these enzymes identified was SdsA1, an alkyl sulfohydrolase that allows the *Pseudomonas aeruginosa* bacterium to utilize the man-made detergent sodium dodecyl sulfate (SDS) as its sole carbon and/or sulfur source. Homologous proteins exist in diverse prokaryotic and eukaryotic species, raising questions about the biological roles of these proteins. SdsA1 and the *Saccharomyces cerevisiae* homolog Bds1 are alkyl sulfohydrolases, while the *Rhodococcus ruber* homolog CddY may be a lauryl lactone esterase. Here we used a bioinformatics approach to compare these enzymes and predict their reactivity based on gene clusters and amino acid alignment.

SERMACS 381

Assessing the release and transformation of metal additives from consumer plastics

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The use of consumer plastic spans a very broad range, including electronics, food packaging, and even clothing. While the major constituents of plastics are organic polymers, many also contain trace metal additives, which are potentially toxic to humans and the environment. These trace metals are often added to plastics to reduce degradation/discoloration, as well as increase strength and flexibility. However, there is a gap in knowledge on how these metal additives may be unintentionally released from consumer plastics. Polyvinyl chloride (PVC), commonly used in piping, is specifically known to contain large amounts of tin (0.5 – 2 wt%). Previous research has investigated the release of tin compounds from PVC piping under bench-scale flow systems. However, these studies do not address other exposure routes, including inhalation of secondary particles produced during PVC construction activities (cutting, sanding, grinding, etc.) The proposed project will focus on two avenues. The first is tin and organotin mobility and fractionation during construction activities. Subsequently, tin release from these different size fractions will be tracked after incubation in a variety of synthetic biological fluids (SBFs). We hypothesize that incubation time and SBF pH will affect tin bioavailability, with lower pH’s increasing the release rates. The results of this project will give the scientific community insight into the likely environmental and human health consequences from the use of PVC, due to tin additives.

SERMACS 382

Mycoremediation of atrazine and its metabolites from soil utilizing high-performance liquid chromatography

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Atrazine is a commonly used photosynthetic inhibitor herbicide. As a Persistent Organic Pollutant (POP), it remains in the soil long after its initial use causing damage to the environment and aquatic life. Mycelium has demonstrated the ability to convert atrazine into its metabolites, specifically desisopropylatrazine (DIA), desethyldesisoproylatrazine (DEDIA), hydroxyatrazine (HA), and deethylatrazine (DEA). We are interested in the bioremediation process that different varieties of mycelium undergo to convert atrazine its into metabolites, and thereby reducing the concentration of atrazine present in the soil. Specifically, Pleurotus Ostreatus (Oyster), Lentinus Tigrinus (Tiger Sawgill), and Ganoderma Curtisii (Reishi) are the species of interest. Additionally, we are interested in the abilities of each variety of mycelium to combat contaminants while degrading atrazine. Results from High-Performance Liquid Chromatography (HPLC) have shown that mycelium have successfully degraded atrazine into its metabolites and reduced the quantity of atrazine present in soil samples.

SERMACS 383

Hydrothermal syntheses and crystal structures of molybdenum tellurites

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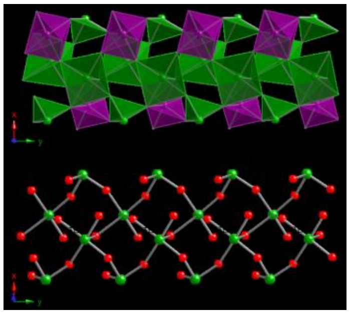
Hydrothermal reactions of MoO3, TeO2 and KCl in acidic conditions resulted two new molybdenum tellurites, MoTeO5 (1) and MoTe2O7 (2). Within the structures of these two compounds, all Mo(VI) atoms adopt distorted MoO6 octahedral in a 2+2+2 mode with two short, two normal, and two long Mo-O bonds, while Te(IV) atoms are observed to be coordinated by three and five oxygen atoms and result TeO3 tetrahedral and TeO5 square pyramid polyhedra with Te-O bond distance cut off at 2.45 Å. In compound 1, two MoO6 octahedral are joined together by sharing an edge to form a Mo2O10 dimer and these dimers are further connected by corner-sharing two TeO3 polyhedral and result a neutral MoTeO5 one-dimensional chain structure. Compound 2 also exhibits a one-dimensional chain structure but in a more complicated way. Four crystallographic Te atoms adopt two difference coordination geometry, TeO3 trigonal pyramid and TeO5 square pyramid polyhedral, and them are joined together by corner-sharing and results a [Te4O10]4- chain. The negative charge of Te chain is balanced by incorporating Mo6+ as MoO6 polyhedra which are connected to edge-sharing one TeO5, corner-sharing other two TeO5 and two TeO3 polyhdedra. Crystallographic data: compound 1, monoclinic, space group P2(1)/c, a = 4.7106(3) Å, b = 13.5827(11) Å, c = 6.0962(5) Å, β = 93.898(3)°, V = 389.15(5) Å3, Z = 4; compound 2, orthorhombic, space group Pna2(1), a = 17.5632(5) Å, b = 4.9107(2) Å, c = 12.9518(4) Å, V = 1117.06(7) Å3, Z = 8.



SERMACS 384

Development of an oxidative [3+2] photocycloaddition reaction for the synthesis of huaspenone D

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Huaspenone D is a furopyridone natural product isolated from an endophytic fungus whose host plant, *Huperzia serrata*, is an herb used in traditional Chinese medicine. Despite the known antibiotic and antifungal activity of other members of the furopyridone family of natural products, huaspenone D has not yet been tested for biological activity. As existing methods for the synthesis of furopyridones from 4-hydroxy-2-pyridones involve multiple steps, we are developing an oxidative [3+2] photocycloaddition to accomplish the annulation in a single step. Initial efforts toward identifying a photocatalyst and co-oxidant for the photocycloaddition and progress toward the furopyridone core of huaspenone D will be detailed. Successful completion of the synthesis of huaspenone D will enable biological testing of huaspenone D and unnatural analogues.

SERMACS 385

Oxidative [3+2] photocycloaddition reactions of 4-hydroxy-2-pyrones

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Furopyrone-containing natural products are a family of heterocyclic fungal metabolites with clinical significance, possessing antimicrobial or anticancer activity. Among this family of natural products, phellinstatin holds promise for highly selective inhibition of bacterial fatty acid synthesis in *S. aureus* and MRSA. We have been investigating an oxidative [3+2] cycloaddition reaction of 4-hydroxy-2-pyrones for the synthesis of furopyrones in a single step. Progress towards the synthesis of the furopyrone core of phellinstatin will be discussed.

SERMACS 386

Measuring heat related to the dissociation and reformation of ferritin using isothermal titration calorimetry

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Ferritin is an iron storage protein that is responsible for the accumulation of excess intracellular iron. Native ferritin self-aggregates into a nanocage structure containing a ferroxidase center that regulates the uptake and release of iron. In recent years, researchers have begun to explore the idea of using ferritin as a component in the delivery of drugs throughout the body. Ferritin is an attractive candidate because it is a native human protein that has the ability to encapsulate small molecules. Furthermore, it can be chemically or genetically modified to target very specific cells. One major limitation of drug delivery by ferritin lies in its inherent stability; harshly acidic conditions are needed to drive the disassembly of the nanocage. It was recently discovered that replacing the E-helix of human light chain ferritin with a GALA peptide repeat (hFtnL-GALA) would allow for the pH-induced disassembly to occur at a pH below 6. As a result, ferritin is able to become more applicable as a drug carrier under physiologically relevant conditions.

This project focuses on the expression and purification of modified human L-chain ferritin with a subsequent thermodynamic characterization of the disassembly and reassembly of the hFtnL-GALA nanocage. The chimeric protein is largely localized to the insoluble lysate pellet after sonication; consequently, the published purification protocol failed to produce enough protein for subsequent experiments. An alternate protocol was developed that leveraged 4 M Urea to resuspend the insoluble lysate fraction. The urea was diluted slowly to allow the hFtnL-GALA protein to fold properly. Analysis of the sample by size exclusion chromatography on a sephadex G200 column showed that the protein eluted around 9 mL, consisted with an intact nanocage structure. Currently, the amount of protein that was isolated using this approach is insufficient for a thermodynamic characterization. In the future, the goal is to adjust the most recent purification protocol in an attempt to produce a larger yield of pure protein as well as use isothermal titration calorimetry to explore the heat exchange associated with the dissociation and reformation of ferritin.

SERMACS 387

Capillary electrophoresis as a screening technique for atrazine and atrazine metabolites

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Mycelium have been found to have the ability to break down the widely-used herbicide atrazine into natural metabolites and other simple organic decomposition products. The identification of atrazine and related products is environmentally important, as this compound has been identified as a persistent organic pollutant (POP) and is found as a contaminant in runoff and well water. The mechanism for action for atrazine is based on blocking electron transport during photosynthesis in grass and broad-leaf plants; mycelium are thus effective in metabolizing atrazine without being adversely affected owing to their lack of chloroplasts. Capillary electrophoresis (CE) is an analytical technique used in the separation of charged species present in a small-volume aqueous samples, based on intrinsic differences in electrophoretic mobility (i.e., charge/solvated ion radius). In the work presented, separations of atrazine (AT), desethylatrazine (DEA), hydroxyatrazine (HA), desethyldesisopropyl atrazine (DEDIA), and desisopropylatrazine (DIA) are explored and compared using a variety of running buffer compositions including an ionizing pH (pH < 2.0), the use of complexing additives including myristyltrimethylammonium bromide (TTAB), and micellar electrokinetic chromatography (MEC).

SERMACS 388

Thermostability characterization of tetrahedrite nanoparticles synthesized by a modified polyol process

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Amidst the current energy crisis, thermoelectrics are utilized to convert waste heat into electricity and are possible materials useful for sustainability. Tetrahedrite ($Cu_{12}Sb_4S_{13}$) is a unique thermoelectric material composed of earth-abundant elements. Tetrahedrite produced by conventional solid-state methods typically requires weeks at elevated temperatures (>600° C). To reduce the cost and energy consumption of the material synthesis, we developed a bottom-up, modified polyol synthesis. This unconventional method efficiently produces high yields (2+ grams) of surfactant-free nanostructured and phase-pure tetrahedrite materials with one hour of heating at 220° C. We employ powder x-ray diffractometry, scanning electron microscopy, and energy dispersive x-ray spectroscopy to characterize the nanoparticles. To determine the quality of thermoelectric performance (figure of merit, ZT), thermopower, electrical resistivity, and thermal conductivity measurements were collected from the samples produced via the modified polyol synthesis. Our solution-phase synthesis outperforms tetrahedrite compounds made by conventional methods and successfully incorporates a range of dopants, such as Fe, Zn, and Co on the copper-site. We are investigating the thermostability of undoped and doped tetrahedrite samples by employing differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Sample degradation is examined by TGA, which has only shown minor differences between doped and undoped samples when heated from 325K to 825K. However, in DSC, the undoped tetrahedrite sample exhibits a significant endothermic transition around 750K, and the addition of dopants to the tetrahedrite appears to eliminate this transition, enhancing its overall thermostability. Additionally, DSC heat-cool-heat measurements have been employed to investigate the effect of heating on subsequent heating cycles. We will further utilize the DSC and TGA to identify trends in thermostability across samples formulated with varying synthetic methods, dopants, and concentration of dopants.

SERMACS 389

Electrophoretic investigation of the inhibition of ROS-induced DNA damage using n,n'-dimethylimidazole selone

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Free radicals are reactive molecules that possess an unpaired electron capable of inducing oxidative damage to DNA, which may in turn lead to mutagenesis, cancer, and aging. The production of such free radicals can be facilitated by uncomplexed metal ions in vivo that react with the byproducts oxygen metabolism, e.g., reactive oxygen species (ROS) such as superoxide, which then lead to damage to DNA. Numerous natural defense strategies reduce the action of such free radicals by reacting with them directly, including physiological antioxidants such as glutathione or other antioxidants consumed in the diet. A second, potentially more effective mechanism for protection from damage of ROS involves direct binding to free metal ions, thus inhibiting the formation of ROS from the onset. Among such possibilities are compounds of sulfones and selenium selones including N,N'-dimethylimidazole selone (dmise), a selenium-containing antioxidant under investigation for its ability to complex with Fe(II). To simulate the production of free radicals for in vivo study, the Fenton reaction is utilized, where Fe (II) reacts with hydrogen peroxide to produce hydroxyl free radicals. In the work presented here, native polyacrylamide gel electrophoresis and agarose gel electrophoresis are utilized to provide complementary studies of dmise with multiple DNA types as a means to measure its ability to inhibit or prevent ROS-induced oxidative damage.

SERMACS 390

Investigating the mechanism of eukaryotic heme A synthase

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The cofactor heme A is essential for function of the mitochondrial electron transport chain, where it enables electron transfer within cytochrome c oxidase. In the cell, heme A is synthesized from heme B via a pathway dependent upon the evolutionarily conserved enzyme heme A synthase. However, the structure and mechanism of this enzyme have not been established in eukaryotes, and recent studies have suggested an additional chaperone role for heme A synthase during cytochrome c oxidase maturation. Taking advantage of recent structural data available for the bacterial homolog CtaA, we have used site-directed mutagenesis and structural modeling to investigate the mechanism of mitochondrial heme A synthase in the model eukaryote *Saccharomyces cerevisiae*.

SERMACS 391

Interactions between heme biosynthetic proteins in mitochondria

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Heme A is an essential cofactor of cytochrome c oxidase (CcO), the terminal protein complex of the mitochondrial electron transport chain. Several evolutionarily conserved enzymes have been implicated in the biosynthesis of heme A, including ferrochelatase, heme O synthase, the assembly factor Pet117, and heme A synthase, which collectively synthesize and modify iron protoporphyrin IX. We have shown that oligomerization of heme A synthase is important for the process of heme A biosynthesis and/or transfer to maturing CcO and that the evolutionarily conserved assembly factor Pet117 is necessary for heme A synthase oligomerization and function. We are currently assessing protein-protein interactions between biosynthetic enzymes and assembly factors to elucidate the mechanism of heme A synthesis in eukaryotes.

SERMACS 392

Novel tris-indolyl compound possesses anti-cancer properties

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The focus of this research is on the synthesis of a novel tris-indolyl compound and testing it for possible anti-cancer affects. Viability was measured via apoptosis assays using flow cytometry. Current results show a decrease in cell viability in a human prostate cancer cell line (PC3). Furthermore, it was determined the compound has a specific concentration range of toxicity to the cancer cells. This characteristic warrants further investigation for the compound's potential use as a chemotherapy agent that ideally would have limited harmful side effects to a patient. Further testing and analysis are still underway.

SERMACS 393

Quantum mechanics study of QSAR in synthetic cathinones

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Synthetic Cathinone's (Bath salts), are man-made stimulants based on cathinone, a substance derived from the Khat plant, a shrub commonly found in East Africa and Southern Arabia. Bath salts were initially designed as plant fertilizer and multi-purpose cleaners for phone screens and jewelry. However, over time the hallucinogenic effects of bath salts have led to a misuse of these substances leading to societal problems related to drug abuse and addiction. In our research we have investigated the Qualitative structure-activity relationship (QSAR) to determine which structural components such as aromatic rings, ketone moeties, and carbon side chains, correlate with biological activities. A well designed QSAR model will guide future research of the human brain, drug design, and the human dopamine transporter. These studies were completed using the B3LYP Density Functional Theory in Gaussian 09' on both R and S enantiomers of each bath salt molecule. This computational data will be compared to experimental data.

SERMACS 394

Introduction of fluoroaromatic probes into peptides and proteins via nucleophilic aromatic substitution

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Due to the idiosyncratic nature of proteins, examination of the local electronic environment in their folded structure represents a formidable challenge. 3,4,5-Trifluorobenzonitrile (TFBN) is a small molecule that contains IR active (nitrile groups) and NMR active (fluorine atoms) moieties that can monitor local properties of the surrounding environment. TFBN has been shown to readily react with the sulfur atom of free cysteine via nucleophilic aromatic substitution with minimal byproducts. Using proton and fluorine NMR, we investigated the reactivity of similarly structured fluorinated electrophiles for comparison and examined the selectivity of TFBN against other amino acids that could provide reaction sites in proteins. We examined how the use of different bases or different protecting groups on the cysteine substrate impact the yield and purity of the desired substitution product. We assessed the viability of TFBN for tagging more complex substrates, such as synthetic peptides and complete multimeric proteins, using UV spectrophotometry and mass spectrometry to monitor product formation. We found that TFBN provides excellent reactivity and selectivity under mild conditions, and can effectively label cysteine residues in peptide chains and complex proteins with minimal side-products, providing an effective tool for monitoring conditions in complex protein environments.

SERMACS 395

Photoredox-mediated alkylation of imines with potassium organotrifluoroborates in the presence of an organic photocatalyst

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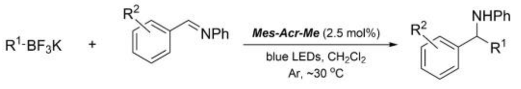
Recently, the use of visible light combined with a suitable photocatalyst to promote key bond-forming steps in organic synthesis has emerged as a viable strategy to achieve a number of important synthetic transformations. The photocatalyst involved is often a ruthenium or iridium polypyridyl complex, which absorbs light in the visible range to give a relatively long-lived excited state, which may engage organic substrates in a series of single-electron-transfer (SET) events. The organic radicals thus generated participate in downstream reactions leading to the final product(s). Our group has previously employed this strategy for the alkylation of aldimines with potassium organotrifluoroborates using transition-metal photocatalysts. However, because of the much lower cost of organic photocatalysts (~$50/mmol for acridinium-based catalysts vs ~$1000/mmol for Ir-based catalysts), we desired to explore the use of organic photocatalysts in this transformation. Optimization studies using the reaction of potassium isopropyltrifluoroborate (**1**, $R^1 = {}^{i}Pr$) with benzalaniline (**2**, $R^2 = H$) revealed that the photocatalyst 9-mesityl-10-methylacridinium tetrafluoroborate (***Mes-Acr-Me***) in dichloromethane gave the best yields of alkylation product **3**. In this presentation, we will describe the results of our current efforts to expand the scope of the protocol to other imines and potassium organotrifluoroborates.



1 2 3

SERMACS 396

Discovery and evaluation of small molecules that potentiate antibiotics in methicillin-resistant *Staphylococcus aureus* (MRSA)

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Methicillin-resistant *Staphylococcus aureus* (MRSA) is an extremely virulent pathogen that causes a wide variety of localized and systemic infections. MRSA is resistant to many common β-lactam antibiotics and many strains display resistance to several other antibiotic classes as well. MRSA is one of the hardest infections to treat and kills over 20,000 Americans annually. Novel therapies that potentiate existing antibiotics, also known as antibiotic adjuvants, could provide treatments for this superbug. We sought to identify novel antibiotic adjuvants that could potentiate β-lactam antibiotics in several clinically relevant strains of MRSA. We identified a novel scaffold capable of potentiating β-lactam and cephalosporin antibiotics in several strains of MRSA. Evaluation of structurally related compounds based on this scaffold was pursued to develop a structure-activity map. Interestingly, the structure-activity relationships differed across several strains, suggesting that this class of molecules could be optimized for exquisitely narrow applications. Biological data, structure-activity relationships, and putative target identification studies will be presented.

SERMACS 397

Syntheses and structures of manganese tellurite chloride

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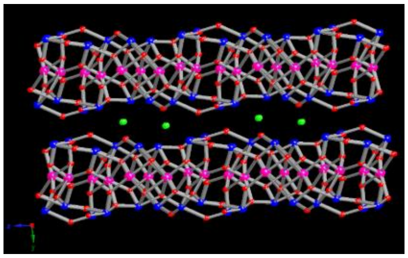
Two new manganese tellurites, $Mn_4Te_5O_8Cl_2$ (1) and $Mn_7Te_{12}O_{30}Cl_2$ (2), were synthesized under hydrothermal reactions of $MnCl_2$ and TeO_2 in molar ratios of 1:1 and 1:2, respectively. Single crystal XRD measurement revealed that these two manganese tellurites adopt cationic layer structures composed by Mn and Te polyhedra with Cl^- ions incorporated in the interlayer space. Within the structures of these two compounds, Mn(VI) atoms are coordinated by four, five six oxygen atoms with Mn-O bond distance ranging 2.048 (1) to 2.406 (2) Å, while Te(IV) atoms adopt three types of coordination polyhedra, TeO_3 tetrahedral, TeO_4 see-saw and TeO_5 square pyramid with Te-O bond distance cut off at 2.45 Å. The presence of Mn, Te, Cl and O in two compounds were confirmed by SEM-EDS and the average atomic ratios analyzed were consistent with the results from single-crystal X-ray structure analyses. Crystallographic data: compound 1, monoclinic, space group P2(1)/n, a = 8.6865(2) Å, b = 5.4786 (1) Å, c = 15.8559(3) Å, β = 103.9285(8)°, V = 732.39(3) $Å^3$, Z = 2; compound 2, orthorhombic, space group P-1, a = 7.9043(3) Å, b = 9.1124(3) Å, c = 11.2085(4) Å, α = 91.725(2) °, β = 93.382(2), γ = 106.871(1) V = 770.28(5) $Å^3$, Z = 1.



SERMACS 398

Temperature dependent stabilities of various isomers of C_{32} and C_{36} endohedral metallofullerenes

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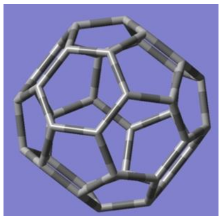
Fullerenes smaller than C_{60} have gained special interest because of the interesting chemical and physical properties that accompany their smaller curvature radius and higher chemical activity. C_{32} and C_{36}, the fullerenes of interest in this study, both fail to obey the Isolated Pentagon Rule, allowing small alterations to each fullerene's conformation to potentially result in large impacts upon their

stabilities. The Gibbs Free Energy stabilities of the six isomers each of C_{32}, K@C_{32}, Ca@C_{32}, and Sc@C_{32} and the fifteen isomers each of C_{36}, K@C_{36}, Ca@C_{36}, and Sc@C_{36}, were computed using density functional theory (DFT) at temperatures between 298-6000 K. In the case of C_{32}, isomer 6 by Fowler's algorithm (D_3 point group) was found to be the most stable at all temperatures studied in the empty cage case and in all three endohedral cases. In the C_{36} case, isomer 14 (D_{2h}) was the most stable overall in the empty cage and K@C_{36} . For Sc@C36, isomer 15(D_{6H}) was the most stable at all temperatures. Finally, for Ca@C36, isomer 14 was the most stable up to 2300 K, then isomer 15(D6h) became the most stable from 2300 K to 6000 K.



SERMACS 399

Recipe for a great scientist: Geometry, music, and mechanical drawing

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In previous projects, we studied the thought processes of Paul Dirac and Albert Einstein and how those processes led to difficulties for them in accepting new science later in their careers. During our research, we discovered that both Dirac and Einstein had a passion for geometry that began very early in their educational endeavors. When we followed up on this apparent coincidence, we found that each of them had an artistic hobby. For Einstein, it was the violin, for Dirac, it was mechanical drawing. In this work, we show a connection between study and practice of a combination of geometry and various arts with Nobel Prize winning abilities in science, and in particular, quantum mechanics.

SERMACS 400

Synthesis and reactivity of bioinspired mononuclear copper(II) complexes

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<p style="margin: 0px; line-height: normal;">The selective oxidation of hydrocarbon substrates in an environmentally friendly way remains a challenging and fascinating area of study within chemistry. Functionalization of C-H bonds is an essential step in many biological processes and is catalyzed under physiological conditions by enzymes such as particulate methane monooxygenase and lytic polysaccharide monooxygenase. These enzymes are copper-dependent and have been the inspiration for a number of synthetic copper complexes investigated for their potential for hydrocarbon functionalization.</p><p style="margin: 0px; line-height: normal;"></p>The synthesis and characterization of mononuclear copper(II) complexes supported by a series of substituted bispicen-type ligands (N2/Py2) is reported. The formation of active oxidants using H_2O_2 as the oxygen source is explored spectroscopically and the oxidative chemistry of these intermediate species toward external hydrocarbon substrates similarly explored. Likewise, the effect of structural variations to the ligand framework on catalytic activity is evaluated and discussed in the context of bioinspired copper-mediated hydrocarbon functionalization.

SERMACS 401

Kinetic isotope effect on the Kemp elimination

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The Kemp elimination is a benchmark reaction in the computational design of enzymes. In this reaction, proton abstraction from the benzisoxazole substrate concurrently leads to an irreversible ring opening, resulting in *ortho*-hydroxybenzonitrile. The kinetic isotope effect on the base-catalyzed Kemp elimination of 5-nitrobenzisoxazole is large (between 4 and 6) when the hydrogen at C3 is replaced with deuterium. This suggested significant cleavage of the bond between the proton/deuterium and C3 in the transition state of the rate-limiting step of the reaction. Recent studies have suggested an alternative pathway for the Kemp elimination involving an internal redox mechanism. We found that several heme proteins promote the Kemp elimination, and likely use a redox mechanism. When we measured the isotope effect in the heme systems, using 5-bromo-3-deuterobenzisoxazole as the substrate, we found not only a reduced isotope effect, but one that was significantly inverse (about 0.35). We speculate that sterics contribute significantly to this inverse isotope effect. However, the elimination of the bromo substrate is relatively slow, which is a hindrance because it allows for the hydroxide reaction to compete with the redox pathway. In an effort to minimize competing side reactions, we synthesized deuterated 5-nitrobenzisoxazole-- which eliminates at a faster rate-- to repeat measurements of the isotope effect in heme systems. Herein, we report of our results with this additional deuterated substrate.

SERMACS 402

Surface tension and critical micelle concentration measurements of seawater and estuarine water

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Surfactants are surface active organic compounds that have the ability to absorb at surfaces, self-aggregate, and decrease the surface tension of water. Surfactants have been observed in environmental samples, such as seawater and atmospheric aerosol particles. Surfactants can affect the properties of aerosol particles and their abilities to act as cloud condensation nuclei (CCN). One source of surfactants in aerosol particles is from bubble bursting at the ocean surface, which emit primary marine aerosol particles. A defining characteristic of a surfactant is its critical micelle concentration (CMC), which is the concentration where micelles form. Surfactants in excess of this concentration do not further decrease the surface tension of the solution. In this work, surface tensions and CMCs of known standard surfactants and surfactants extracted from ambient samples of seawater and estuarine water were measured using pendant drop tensiometry, which measures the equilibrium surface tension of a solution. Surface tension curves of standard solutions demonstrate how structural differences in the compounds such as polar head group, alkyl chain length, and counter ion, affect the CMC. Additionally, mixtures of standard surfactants change in CMC, depending on the strength of the individual surfactants in the mixtures. In this study, we also compare the surface tension of estuarine water collected from Skidaway Island in summer 2018 to that of the surfactant standards and the surfactants extracted from the estuarine waters. In this study, we observed that the CMC and strength of surfactants from estuarine water was similar to that of the nonionic surfactant standards. Additionally, measurements of surfactants extracted from samples collected off the coast of Skidaway Island in spring 2019 demonstrated differences in their strengths, compared to those of the estuarine waters.

SERMACS 403

Employing a binol based ligand for the design of chiral metal-organic frameworks

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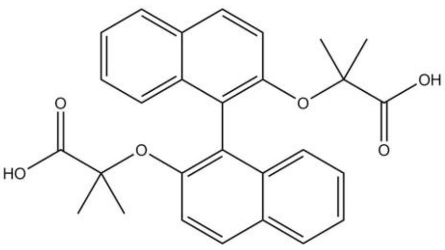
Metal-Organic Frameworks (MOFs) are three-dimensional porous structures consisting of metal ions linked together through coordinating organic ligands. MOFs have various applications within gas separation and storage, chiral separations, and drug delivery. In this work, a chiral dicarboxylic acid ligand (**CL1**) was synthesized using (±)-1,1'-binaphtalene-2,2'-diol (BINOL) as the starting material. Given the axial chirality from the BINOL group in **CL1** it has the potential be used to generate chiral MOFs. Porous chiral MOFs have significant potential for applications in chiral separations. The structure of the organic ligand was identified by FT-IR, ^{1}H NMR, and ^{13}C NMR. We have explored the coordination chemistry of this ligand using solvothermal reactions with copper(II) and zinc(II) metal salts. Our efforts to characterize the crystallized metal-organic products using single crystal X-ray diffraction, powder X-ray diffraction, gas sorption analysis, and thermogravimetric analysis are described herein.



CL1

SERMACS 404

Synthesis of metal-organic frameworks using four-connected imide containing linkers

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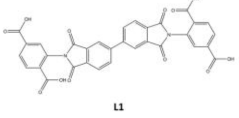
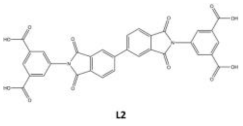
Metal-Organic Frameworks (MOFs) are hybrid crystalline compounds that are highly porous. These microporous materials are made by coordinating organic ligands to metal ions. Some of the applications for the use of these MOFs include gas storage, separation, magnetism, luminescence, drug delivery, and catalysis due to the high surface area and many pores. In this work, a series of tetracarboxylic acid containing ligands were synthesized from 4,4'-biphthalic anhydride and 2-aminoterephthalic acid (**L1**) and 5-aminoisophthalic acid (**L2**). These ligands were analyzed by ^{1}H NMR and ^{13}C NMR. The coordination chemistry of each ligand has been investigated through solvothermal synthesis using zinc(II) nitrate and copper(II) nitrate in an effort to obtain novel porous MOFs. Our attempts to characterize the crystalline metal-organic products of these reactions using powder X-ray diffraction, single-crystal X-ray diffraction, thermogravimetric analysis, and gas sorption analysis will be delineated.



L1



L2

SERMACS 405

Constructing metal-organic frameworks from unique tetracarboxylic acid ligands

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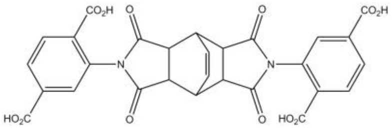
Metal-Organic Frameworks (MOFs) are a class of flexible materials made from synthesizing metals and organic ligands, resulting in three-dimensional crystalline structures. These structures have various important applications due to their very high surface areas and low densities. These characteristics result in MOFs having the potential to surpass other porous materials in areas such as gas storage and separation, catalysis, luminescence, drug delivery, and alternative clean energy production. In this study, a novel tetracarboxylic acid ligand (TL1) was synthesized. The structure of the ligand was confirmed by ^{1}H NMR and ^{13}C NMR. Subsequently, the coordination chemistry of this ligand was surveyed through a series of solvothermal reactions using metal salts of zinc(II) and copper(II). Our efforts to characterize these metal-organic crystalline products using powder X-ray diffraction, single crystal X-ray diffraction, gas sorption, and thermogravimetric analysis are outlined hereafter.



TL1

SERMACS 406

Metal phosphites: Synthesis, characterization, and susceptibility to oxidation

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Phosphorus is an important component in many biomolecules including nucleic acids (e.g., DNA and RNA), coenzymes such as ATP, and phospholipid cell membranes. Unfortunately, the most likely sources of phosphorus on the early earth were trapped in highly insoluble phosphate minerals. However, metal phosphites may be a solution to the so-called phosphorus problem in that they are far more soluble than phosphate minerals. We hypothesize that metal phosphites were a source of reactive phosphorus for the formation of prebiotic molecules on the early Earth. In order to test this hypothesis and because metal phosphites are not commercially available, we have synthesized and characterized our own metal phosphites. An aqueous dibasic sodium phosphite solution (Na2HPO3) was created by reacting phosphorus acid (H3PO3) and sodium hydroxide (NaOH). The pH was adjusted using phosphorus acid and sodium hydroxide. After pH adjustment, a soluble metal chloride (MClx) was added to the solution, and a metal phosphite (Mx(HPO3)x) precipitate was formed. Subsequently, Fourier-Transform Infrared spectroscopy (FTIR), Phosphorus Nuclear Magnetic Resonance spectroscopy (31P-NMR), and powder X-Ray Diffraction (XRD) were performed on each metal phosphite. In addition, Thermogravimetric Analysis (TGA) was used to determine the susceptibility of the metal phosphites to oxidation. Slight changes in pH were found to significantly change the percent yield and key characteristic of the samples (e.g., coupling constants in P-NMR). The optimal pH for synthesis varied depending on the metal cation.

SERMACS 407

Development of an active learning, organic chemistry laboratory experiment on extraction and LCMS identification of fragrant esters from fruits for use as a recruiting tool during UNC Asheville's NSF S-STEM "Chemistry First Day"

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Through an NSF S-STEM funded grant program, the Chemistry Department at the University of North Carolina Asheville has developed an interactive "Chemistry First Day" for high school students, their parents, and their chemistry teachers to enhance recruiting efforts geared toward students from underrepresented groups in western North Carolina to our program. For the upcoming 5thannual Chemistry First Day, a new laboratory experience was designed to allow potential students to have a hands-on, inquiry-based experience in an undergraduate laboratory setting. Additionally, the laboratory was designed so that some aspects could be directly translated into a high school chemistry laboratory by the teachers who also attend Chemistry First Day. Specifically, an organic laboratory for the identification of fragrant esters from fruits using qualitative and quantitative analysis was developed. First, esters are extracted from various fruits, such as citrus, pear, banana, pineapple, apricot, kiwi, and berry, using ethanol or isopropanol via sonication or distillation. The extracts are then concentrated, and the odor is qualitatively assessed and compared to known pure fragrant esters associated with fruits. After predicting which esters is present in their sample, specific esters are identified by LCMS.

SERMACS 408

Synthesis of polypeptides via emulsion polymerization of N-carboxyanhydrides

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Due to the overuse of antibiotic treatments leading to an increase in the quantity of antibiotic-resistant bacteria, the Centers for Disease Control has recently shown an increasing interest in the production of contemporary antibiotics. In this respect, recent research has demonstrated the synthesis of polypeptides comprised of distinct architecture and microstructure using N-Carboxyanhydrides under controlled conditions of polymerization as an auspicious means of achieving the production of said antibiotics. These syntheses, however, involve complex purification processes and meticulous control of the conditions in which the reaction takes place in order to induce the desired polymerization. A recent discovery has demonstrated that ring-opening polymerization of N-Carboxyanhydrides can be managed via completing the polymerization in a water-oil emulsion in-which undesired by-products are removed by the aqueous phase during the polymerization process. This research intends to explore the conditions through which this polymerization mechanism can be was expanded by producing a series of polypeptides derived from lysine and valine. Said polymers were characterized with respect to monomer distribution, molecular weight, and microemulsion particle size using gel permeation chromatography, infrared spectroscopy, proton nuclear magnetic resonance, and dynamic light scattering.

SERMACS 409

Synthesis, characterization, and reactivity of a heterobimetallic organometallic complex with a *trans* bidentate ligand for catalytic carbon-hydrogen bond activation

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Our group is interested in exploiting *cis*-alkynyl transition metals to form *trans*-bidentate ligands in order to explore C—H activation. The *p*-cymene-supported ruthenium(II) complex $(p\text{-cym})\mathrm{Ru}(\mathrm{PMe}_3)(\mathrm{C}_2 2\text{-py})_2$ (where $\mathrm{C}_2 2\text{-py}$ = 2-ethynylpyridine) has been prepared and characterized by NMR spectroscopy. We are interested in the interaction of palladium(II) acetate utilizing the Ru(II) center as a hinge in order to force the pyridine ligands to act as a *trans*-bidentate ligand. The synthesis and characterization of $(p\text{-cym})\mathrm{Ru}(\mathrm{PMe}_3)(\mathrm{C}_2 2\text{-py})_2$, reactivity with $\mathrm{Pd(OAc)}_2$, and comparisons to the previously reported $\mathrm{Cp}^*{}_2\mathrm{Ti}(\mathrm{C}_2 2\text{-py})_2$.

SERMACS 410

Acetate: Assisted C–H bond activation: Attempts to prepare and isolate a key Co(III)-cyclometallated intermediate

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Isolation of a *de facto* cyclometalled intermediate in cobalt catalyzed C-H activation is challenging due to the reversible nature of the reaction. Cobalt in the form {Cp*Co(III)} has been utilized for C-H activation involving heterocyclic substrates that have the potential to cyclometallate. This project employs non-sterically demanding phosphine (1,3,5 Triaza-7-phosphaadamantane (PTA)) and phosphite (Trimethylolpropane phosphite (POCage)) ligands in an electron-rich environment to isolate such an intermediate. Preliminary findings suggest successful deprotonation of 2-phenylpyridine and subsequent coordination to Co(III) in the presence of PTA or POCage. These findings, along with explorative chemistry in chiral amine-cobalt complexes will be presented.

SERMACS 411

Modification of head-groups on 10,12-pentacosadiynoic acid using click chemistry

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Polymerization of properly assembled diacetylenes forms highly conjugated containing polydiacetylenes (PDAs). Long-chain fatty acids containing the diacetylene moiety midway along the chain can be assembled into diacetylenes and in many cases, these are structured so as to allow for polymerization. Certain PDA-liposome derivatives have been examined as biological sensors as well as for vehicles for targeted drug delivery. Research in our group is centered around modification of 10,12-pentacosadiynoic acid (PCDA) liposomes. Through synthetic reactions involving 1-Ethyl-3- dimethylaminopropylcarbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS), the hydrophilic head-group on PCDA was transformed into an NHS-Ester, which was then further modified to leave a terminal alkyne. The presence of the terminal alkyne allowed for a copper-catalyzed azide-alkyne cycloaddition (CuAAC) "click" reaction to attach various compounds to derivatize monomers or to derivatize assembled liposomes. Proper modification of PCDA, along with utilization of click chemistry, yields unique liposomes able to be used as biological sensors and as nanomachines with potential for use in numerous applications.

SERMACS 412

Preparation, thermal properties and gelation studies of 3β-cholesteryl N-(9-acridinyl) carbamate as low molecular mass gelator and aggregation studies with DNA

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Acridine based compounds have known to exhibit many biological functions. In the present study 3β-cholesteryl N-(9-acridinyl) carbamate (CAC) was prepared by the reaction between 9-aminoacrdine and cholesteryl chloroformate as potential low molecular mass gelator (LMG). 5 and 10 wt % of CAC have been shown to gelate DMSO, tert-butanol mesitylene and safflower oil. Correlations between self-assembly and gelation properties of CAC in various liquids and thermal properties will be presented. Computational studies of complexation with DNA shows that CAC binds DNA with binding free energy of -12.13 kcal (Ki 1.27 nM). The interaction between CAC and DNA is stronger compared to pyridinyl cholesteryl carbamate or 9-aminoacridine that binds DNA with binding energy of -7.4 kcal/mol (Ki 3.6 mM). The CAC derivative binds DNA with inhibition constant (Ki) in the nanomolar range.

SERMACS 413

Preparation, self-assembly and gelation studies of *N*-(4-hydroxyphenyl)alkanamides as low molecular mass gelators

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Three derivatives of N-(4-hydroxyphenyl)alkanamides with varying alkyl chain length (n = 12, 14 and 18) have been synthesized and characterized using IR and NMR techniques. Gelation studies of N-(4-hydroxyphenyl)alkanamides were investigated in various polarity liquids. The gels formed were studied based on its physical appearance, solubility, gel formation time and melting point. It has been observed that both carbon chain length and the organic solvent altered gelation properties. Polarizing optical micrographic studies of 5 wt % Silicone oil gel of N-(4-hydroxyphenyl)alkanamides exhibit spherulitic textures.

SERMACS 414

Surface modified polydopamine-polypyrrole coatings

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Our laboratories have shown that polypyrrole films are easily surface modified with thiols, resulting in drastically altered surface energies. While electrochemically grown polypyrrole adheres well to electrode surfaces, the adhesion of chemically grown polypyrrole is less robust. This is unfortunate, because it limits the practical application of this process. Conversely, polyphenolic proteins excreted by mussel have been shown to be impressive adhesives. The key component is a polymer of 3,4-dihydroxyphenethylamine, or dopamine. The combination of the two polymers has been achieved electrochemically, but there are no reports of chemically grown composites. Here, we show how simultaneous polymerization of dopamine and pyrrole using chemical oxidants can be archived by putting both monomers together with an oxidizing agent and maintaining the PH at around 7-8. Polymer coating of the two will form slowly on a substrate put in during the reaction process. The adhesive strength of thin films prepared in this way will be discussed and the effectiveness of a thiol treatment to give anti-biofouling surfaces will be demonstrated.

SERMACS 415

Isolation methods for cannabinoids from hemp

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The therapeutic potential of tetrahydrocannabinol (THC) and cannabidiol (CBD) has been claimed anecdotally for many years with traditional medicinal uses dating back thousands of years, but only recently has the first *Cannabis* sp. derived drug, Epidiolex, been approved by the Food and Drug Administration (FDA). Currently, there is an extensive knowledge gap regarding the therapeutic potential of the minor cannabinoids, of which over 150 have been characterized from *Cannabis sativa*. The passing of the 2018 Farm Bill has legalized the cultivation of Hemp-varieties of *C. sativa* on a federal level, making the research into the minor cannabinoids possible without legal threats. The aim of this project is to conceive methods for the isolation of cannabinoids with industrial scalability in mind. Thus far varying chromatography techniques have been utilized to isolate cannabinoids found in hemp samples grown in South Carolina.

SERMACS 416

Synthetic progress towards asymmetrical pyridine-based CXCR4 modulators

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Chemokine receptor type 4 (CXCR4) is overexpressed in cells associated with autoimmune disorders, inflammation, and cancer. The binding interaction of CXCR4 with CXCL12 can be partially blocked with small molecules which can hinder the mechanism of cancer metastasis or inflammation. The overall goal for this research is to synthesize asymmetric, pyridine-based compounds as potential modulators of CXCR4-CXCL12 activity.

SERMACS 417

Control of encapsulation and embed magnetic nanoparticles within the aqueous interior bilayer of liposomes prepared from 10,12-pentacosadiynoic acid

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Encapsulation of magnetic nanoparticles within the aqueous interior of liposomes can be used for medical imaging or for externally directed localized drug delivery. Here, liposomes were assembled from 10,12-pentacosadiynoic acid (PCDA) via the thin film rehydration method. Magnetic nanoparticles consisting of Fe_3O_4 (magnetite) were prepared and suspended in water prior to liposome formation, allowing them to be encapsulated in the aqueous lumen. In addition, very small nanoparticles were synthesized through thermal decomposition in the presence of hydrophobic surfactants. The small size and coating encouraged them to be embedded in the ~6nm bilayer of the liposomes after rehydration. The ability to both encapsulate nanoparticles in the aqueous interior and embed the particles in the bilayer of the same set of liposomes illustrates how size and surface modification of particles permits the design of complex multifunctional vesicles.

SERMACS 418

Siloxy functionalized nanoclays and nanosilica towards automotive crashworthiness applications

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Nanoclay in the form of tubes or platelets can be functionalized with various organosilane groups and be used as a filler in order to increase durability and strength of a composite. To explore this avenue, various nanoclays, including halloysite nanotubes (HNTs), nanobentonite (BNT, platelets), and nanosilica (spheres) were each functionalized with an organosilane group with a terminal epoxy, as these have exhibited a trend of increasing strength upon functionalization. The final products were confirmed and characterized with infrared spectroscopy (IR), scanning electron microscope (SEM), energy dispersive x-ray spectroscopy (EDS), elemental analysis, x-ray powder diffraction (PXRD), and thermogravimetric analysis (TGA). This study also aimed to determine the effect of nanofillers on the fracture toughness of compact tension specimens of an epoxy, SC-15, under uniaxial tensile testing state. A 2D full-field optical technique, digital image correlation (DIC) was also used to measure the strain fields during experimental tests. With this increase in strength, the new composites can be placed in automobiles, trains, planes and other engineering applications to assist in improving the energy absorption during a crash.

SERMACS 419

Exposure of hepatocellular carcinoma cells (Hep-G2) to CDSTE quantum dots

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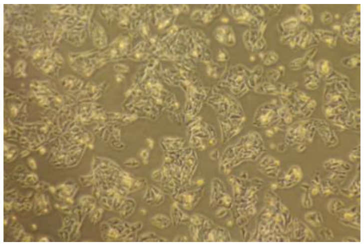
Nanomaterials with optical properties such as Quantum Dots (QDs) have possible uses in diagnostics, photodynamic therapy or drug delivery. Living organisms can be in contact and absorb this nanomaterial which can participate in oxidation/reduction reactions inducing oxidative cell stress. Lipids, located on the plasmatic membrane, can suffer peroxidation that induces cellular apoptosis and death of living systems. A critical point to understand is how QDs enter cells and how they interact with the biological chemistry of cells. Small crystals should produce more reactive oxygen species (ROS) due to more surface area by mass. Liver human cells from hepatocellular carcinoma (HEP-G2) were cultivated in Eagle's Minimum Essential Medium (EMEM) at 37°C and 5% CO_2. HEP-G2 cells were exposed to CdSTe QDs (96-well plate) with concentrations of 0.1, 1.0, and 10.0 mg/L and incubated for 24-48 hours. Fluorescence of the QDs in the EMEM was monitored during the exposition time to corroborate integration of the QDs. Incorporation of QDs inside HEP-G2 was observed by fluorescence microscopy (changes in cell shape was also monitored). The number of viable cells was determined by the quantification of ATP production as an indicator of metabolically active cells. It was observed that the viability was affected by the oxidative stress produced due to the crystal size accumulation of the QDs. The oxidative stress was evaluated through the production of ROS, such as H_2O_2. ROS (H_2O_2) production increased when higher concentrations of QDs were added to the cells, and large crystal sizes (CdSTe 150 and 180 °C) produced more ROS. Overall, the viability and oxidative stress response of HEP-G2 were dependent on the concentration and crystal size of the QDs.



HEP-G2 Cells

SERMACS 420

Cytochrome P450 activity of Hep-G2 cells after the exposition of quantum dots

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Nowadays the field of nanotechnology has emerged as one of the most important influencers in the development of new applications in the different fields of science and technology. Quantum dots (QDs) are nanoparticles with unique optical and electronic properties that have been used to develop better applications in the fields of sensing, drug therapy, biomedical imaging, and environmental applications. However, concerns have arisen due to the possible cytotoxic effects that QDs may induce on living organisms. The small size of the QDs allows them to enter the body and reach organs and tissues. They can interact with biological structures, and produce reactive oxidative species (ROS), thus damaging their normal functions. The purpose of this study was to evaluate the effects of cadmium sulfide/selenide (CdSSe) and cadmium sulfide/telluride (CdSTe) QDs on the activity of the 3A4 cytochrome P450 of liver cancer cells from hepatocellular carcinoma (HEP-G2). HEP-G2 cells were cultivated in Eagle's Minimum Essential Medium (EMEM) at 37°C and 5% CO_2 in a 96-well plate for 48hrs then exposed to CdSSe and CdSTe QDs at a concentration of 1.0 mg/L. After 48 hours of incubation, CYP substrates were added and incubated for 4 hours. Finally, luciferin detection reagent was added to measure 3A4 cytochrome P450 activity. Blank of cells and medium and cadmium ionic was used as controls. The results suggest that CdSSe and CdSTe QDs increase the activity of the 3A4 cytochrome P450 isoenzyme.

SERMACS 421

Determination of fluorescence quenching constants

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The purpose of this work is to study the quenching effect of two halide ions on two different fluorescent compounds using an Agilent Cary Eclipse Fluorescence Spectrophotometer. The analytes used in this experiment were calcein and disodium fluorescein; two structurally similar fluorescent dyes. Potassium chloride and potassium bromide were used as quenching agents. Using serial dilutions, 150nM solutions of analyte in 0.01M sodium hydroxide with varying concentrations of quenching agents were prepped for analysis. The concentration of quenching agent in each solution ranged from 1mg/L to 25mg/L. The fluorescence data obtained for the four of analyte-quencher pairs were plotted against the quenching agent concentration. A calibration curve for each pair was made utilizing linear regression statistics to determine the quenching constant.

SERMACS 422

Electrochemical synthesis of polyoxometalate based organic-inorganic hybrids

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Inspired by previous work alongside a graduate student mentor, an electrochemical synthetic system for the design of polyoxometalate (POM) based complex metal oxides has been adapted for use in exploring organic-inorganic hybrid crystals. This represents a key step in adaptation of the mild reaction system for use in the synthesis of polyoxometalate-organic-frameworks (POMOFs), a class of compounds previously dominated by synthesis via conventional hydrothermal or solvothermal methods, and more recently, ionothermal methods. Applications of such materials include use in lithium ion batteries owing to the multi-electron reduction of polyoxometalate clusters and tunability of pores allowing lithiation. Interestingly, the emerging electrochemical (e-chem) synthetic method enables synthesis of many micrometer scale single crystals and does not require a polymer matrix, differing from previous reports of electrodeposition used to grow thin film organic-inorganic hybrids. Most notably, conventional hydrothermal techniques prove destructive to POM anions with low thermal stability, precluding synthesis or creating reliance upon self-assembly of POM anions. This bench top, one-pot reaction system allows control of potential or current density, temperature, concentration, pH, timescale, and electrode material resulting in potential for enhanced tunability. Furthermore, the electrochemical pathway utilized allows greater selectivity for the synthesis of conductive materials. Reported herein are four crystalline materials obtained using POV (polyoxovanadate, $[V_{10}O_{28}]^{6-}$) anion and $C_6H_{15}NO_3$and 4,5-diazafluoren-9-one (DF) from e-chem method, namely $K_2[Cu(H_2O)(C_6H_{15}NO_3)]_2(H_2V_8{}^{V}V_2{}^{IV}O_{28})\_2H_2O$ (**I**), $[Cu(DF)_2]_3V_{10}O_{28}\_5H_2O$ (**II**),$(DF)_2[Cu(DF)_2]_2V_{10}O_{28}$, (**III**), and $(DF)_4[Cu(H_2O)_2(DF)_2]V_{10}O_{28}$(**IV**). Remarkably, structural diversity observed in crystals **II~IV**results from alteration of reagent concentration yielding copper-linked frameworks ranging from 1D chain-like to 2D layered. X-Ray Diffraction (XRD), Thermogravimetric Analysis and Differential Scanning Calorimetry (TGA/DSC), and X-Ray Photoelectron Spectroscopy (XPS) will be discussed for the respective structure and crystallinity, thermal stability and behavior, and oxidation state of these new organic-inorganic hybrid compounds.

SERMACS 423

Synthesis of boronate ester derivatives of triphenylphosphine

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Triphenylphosphine is commonly employed in both organic and organometallic synthesis because of its nucleophilicity, reducing character, and ability to act as a ligand. Despite, its versatility, triphenylphosphine cannot be easily modified for specific applications The synthesis of a hybrid triphenylphosphine-catechol molecule and its boronate esters is described, which addresses this issue. The triphenylphosphine-catechol compound can be treated with commercially available boronic acids to prepare boronate ester derivatives of triphenylphosphine. Boronic acids of varying steric and electronic properties are tolerated. The synthesis of boronate ester ligands from these boronic acids and the hybrid catechol-triphenylphosphine molecule offers a fast and affordable way to produce ligands with a broad range of steric and electronic profiles. Additionally, we have prepared late metal complexes that are supported by these compounds.

SERMACS 424

Analysis of lanthipeptides produced by *Salinispora* and characterization of the cyclase

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Lanthipeptides are a family of ribosomally synthesized and post-translationally modified peptides with a wide array of biological activities. We are investigating three species of *Salinispora*, a marine actinomycete, for its biosynthetic potential for producing lanthipeptides. Using the lanthipeptide sequences predicted by antiSMASH, BLAST, and Cytoscape, we generated a web showing the relationship between lanthipeptides putatively produced by *Salinispora*. We analyzed genomes of 122 *Salinispora* strains and identified 240 putative lanthipeptide clusters. Each cluster was evaluated for the three essential components of lanthipeptide formation: a pre-peptide, dehydratase, and cyclase. Using comparative genomic analysis, we divided these clusters into 8 groups and were able to predict the structure of the lanthipeptides produced by each group. We are now working to characterize the cyclase by heterologous expression in *E. coli*. Preliminary results reveal that the cyclase is being expressed in the insoluble fraction; therefore, further experimentation is needed to determine optimal expression conditions. Upon soluble expression of all components, we will biosynthesize the lanthipeptide and assess its biological activity.

SERMACS 425

Synthesis of bidentate bis(phosphino) pyrrole ligands and their complexes for nickel catalysis

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The synthesis and characterization of a variety of bidentate bis(phosphino) pyrrole ligands for nickel-catalyzed cross-coupling is described. These ligands were designed to facilitate reductive elimination in challenging coupling reactions. The electronic and steric properties of nickel complexes bearing these ligands are examined and our data support the hypothesis that these ligands produce nickel complexes with electron-deficient metal centers that are primed to accelerate rate-determining reductive elimination in C–N coupling reactions. Preliminary reactivity studies demonstrate that these ligands are suitable for cross-coupling and for examining the elementary steps of nickel-catalyzed cross-coupling.

SERMACS 426

Expression of electron transport chain complexes following exposure to tumor-suppressant α-TOS

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Cancer refers to a class of diseases characterized by abnormal cell growth, and can be caused by a number of genetic or epigenetic mutations. Currently, it is the second-leading cause of death worldwide. Creating a therapy directed at an organelle possessed by all cancer cells may be a more realistic goal for widespread cancer treatment than developing individual cures for each type of cancer. Mitochondria, responsible for generating ATP and regulating cellular metabolism, have recently become potential targets for anticancer therapies. Altered mitochondrial metabolism has been observed in a number of cancer types, leading to the discovery of a class of tumor-suppressing drugs known was mitocans, which selectively interact with mitochondria and can lead to apoptosis. One example, alpha tocopheryl succinate (α-TOS), is an analogue of vitamin E that directly targets the electron transport chain (ETC) and hinders the growth of cancer cells. The interaction of α-TOS with specific ETC complexes and its ability to act as an antioxidant via metabolism into tocopherol has been described; however, the exact mechanism of the tumor-suppressing behavior of α-TOS has yet to be fully elucidated. This study focuses on whether cells modify their expression of ETC complexes in response to different exposures to α-TOS. Other factors analyzed include growth rates and levels of oxidative stress. This data improves our understanding of α-TOS interactions in proliferating cells, and could act as a starting point for future research focusing on the specific ETC targets of α-TOS to better understand its role inducing mitophagy or apoptosis.

SERMACS 427

Synthesis of bis-(2-phosphinopyrrole) pincer ligands and their respective metal complexes

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Pincer ligands continue to remain of increasing interest for their rigid meridional configuration to metal centers, which provide excellent thermal and chemical stability in organometallic systems. The predictable arrangement of such ligands allows them to be effective complexes in catalytic cycles. We explore the synthesis of new and versatile pincer ligands based on a bis-(2-phosphinopyrrole) motif with methylene, silyl and phosphino linkers. Their respective metal complexes have been prepared and heavily characterized. These complexes are currently being examined as catalysts for cross-coupling and small molecule activation.

SERMACS 428

Structure activity relationship (SAR) studies of neurotoxin quinoline-derivatives

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Structure activity relationship (SAR) studies are performed in order to identify the core structure that is responsible for the biological activity of an organic molecule. Recently, we have synthesized a drug prototype which contains several functional groups, such as an alcohol, an ester, fluorine, and an aromatic ring. While studying in vivo toxicity of this molecule in zebrafish (Danio rerio) embryo, we observed that it has a unique biological activity that causes a sudden inactivity in embryo movement. Continued investigation revealed that this molecule blocks sodium channels in neurons causing a temporary anesthesia in Danio rerio embryo. We have also observed that after transferring the embryo to fresh water, the embryo resumed normal behavior. As our next step, we would like to synthesize a variety of structural analogs and determine their activity. The ultimate goal of this project was to develop effective methods of synthesizing various molecules that have one of the functional groups removed in order to identify its role in biological activity.

SERMACS 429

Readily accessible microfluidic devices using conventional 3D-printers

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Microfluidics is the science of controlling and manipulating fluids in a network of channels of dimensions in the range of 10 -100 micrometers (µm). These channels, often as thick as a human hair, enable microfluidic devices to perform physical and chemical processes using minuscule amounts of reagents, space, and human effort. Microfluidic devices can sort through multiple processes in a short amount of time while consuming minimal resources. They can prove as valuable tools where reagents are expensive or only available in small quantities such as early detection of cancer biomarkers in blood. A major hurdle in expanding the capabilities of microfluidic devices is their accessibility. The current state-of-the-art fabrication process is demanding on space, equipment, and technically trained professionals. Typically, the desired pattern of channels is imprinted on silicon wafers using soft lithography techniques and then transferred to polymeric casts used to assemble the device. Recently, 3D printing has gained traction as a less expensive, faster, and accessible alternative for the fabrication of microfluidic devices. However, this unorthodox method tends to yield extremely varying results since most entry and mid-level 3D printers are not manufactured to operate on such a small scale. The science of adapting conventional 3D printing to microfluidics is in its infancy. We are investigating the optimal parameters to create microchannels using conventional 3D printers which will help us build microfluidic devices for biomedical applications in the future. We report our results comparing two different 3D printers to create microfluidic channels. The Afinia h800+ printer uses melted extrusion modeling of filaments made from different polymers, while the Formlabs Form 2 printer uses photopolymerizable resins. We optimized the printing conditions for both instruments to create channels of uniform dimensions reproducibly. The channel morphology was also scrutinized for deformations occurring during the printing process. Inspired by our success at printing uniform channels, we are creating microelements to facilitate fluid mixing and comparing their efficiency with existing designs. Our initial results in this direction are also presented in this poster.

SERMACS 430

Determination of trace amounts of pesticides in green tea

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Over the last several years, a significant amount of articles have been published documenting the presence of pesticides and herbicides in various brands of tea. Our focus for this project was to develop a simple analytical method utilizing GC-MS that would allow for the detection of small quantities of pesticide components in a green tea sample previously verified to contain considerable amounts of known toxins. Herein, we report our method development and efforts to isolate some of these same toxins using a relatively straightforward extraction and analysis procedure.

SERMACS 431

Exploration of controlled release properties of polypyrrole films

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Intrinsically conducting polymers (ICPs) such as polypyrrole, poly(3,4-ethylenedioxythiophene) and polyaniline are polycations in their conducting form. This necessitates a counterion (or dopant) to be incorporated into the system in order to achieve charge balance. Reduction of the polymers results can drive the dopant out of the film and this has been exploited as a means of electrically controlled release, particularly when the counterion has biological activity. Here, polypyrrole films were grown electrochemically on gold coated quartz crystal microbalance (QCM) sensors in the presence of dodecylbenzenesulfonic acid (DBSA). DBSA acts as both the electrolyte for film growth and the dopant of the resulting film. The surfaces of these films were modified with varying molecular weight polyethylene glycol oligomers that were terminated with thiols. After being rinsed thoroughly, the modulation of the DBSA release was monitored under various conditions, including DI water, in phosphate buffer (PBS) and in the presence of 20% fetal bovine serum in PBS. DBSA dopant release was monitored by the use of Q-Sense Electrochemistry Module flow cells. As FBS solution was flowed through the cells, the sensors exhibited controlled release properties as well as resistance to protein deposition.

SERMACS 432

Bio-based materials to synthesize a novel surfactant used in the production of polyurethane foams

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Polyurethane (PU) foams are used world-wide and have a multitude of applications such as insulation, furniture, and vehicle interiors. Surfactants are a key component of PU foam synthesis, promoting mixing and drainage. Until the early 2000's these foams, and their surfactants were produced using non-renewable petroleum-based resources. To combat the ecological and economic issues accompanying the use of non-renewable resources, novel green surfactants have been synthesized to allow for the green synthesis PU foams. These surfactants are based on the coupling between hydrido and methyl siloxane groups followed by a fatty acid allyl ester coupling. In an effort to increase the effectiveness of these green surfactants different synthetic strategies were applied to increase coupling and vary the distribution of Si-H sites necessary for the fatty acid allyl ester coupling. These green surfactants will be used to synthesize soy-based PU foams and will be compared to traditional petroleum-based PU foams.

SERMACS 433

Purification and characterization of Notch TM by NMR

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γ-Secretase cleavage at the amyloid precursor protein transmembrane domain (APPTM) is the last step resulting in the formation of Aβ protein, which is a molecule that can aggregate to form plaques in the brain, a pathological hallmark of Alzheimer's disease (AD). Efforts have been made for decades to inhibit γ-secretase cleavage of APPTM to prevent AD. While there were drugs found to inhibit γ-secretase, all clinical trials on these drugs have failed due to side effects. Notch signaling pathway is a pathway that is crucial in several normal cellular processes. The cleavage of Notch transmembrane domain (TM) is a critical step in the pathway, and its cleavage is also done by γ-secretase. For most clinical trials, not only do γ-secretase inhibitors hinder the cleavage of APPTM, but they also inhibit Notch cleavage, which is the common reason for the side effects of γ-secretase inhibitors. To find a compound that

selectively inhibits APPTM cleavage, drug discovery targeting APPTM instead of γ-secretase has been carried out and several compounds were screened as promising hits. It is then important to demonstrate that the APPTM specific inhibitors do not bind or bind in different manners with Notch TM and also do not inhibit Notch TM cleavage. In this project, we worked on the purification and characterization of Notch TM by NMR for future testing of interactions between APPTM inhibitors and Notch TM, which is an anti-screen strategy in AD drug discovery.

SERMACS 434

New pathway for CO_2 reduction: Amine-CO_2 activation followed by traditional hydride reduction

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Hydride donors can reduce CO_2 to form CO or formate. This mechanism is promising for developing efficient methods for carbon capture and storage. While most mechanisms that effectively reduce CO_2 to CO or formate rely on metal hydrides, we were interested in investigating alternative pathways that may be accessible *via* activation of CO_2 with Lewis bases, such as amines. In this case, CO_2 is first activated by interaction with the amine to form a carbamic acid, and then carbamic acid reduces to formate by attack of a negatively charged hydride. The goal of this density functional theory (DFT) study is to obtain an atomistic understanding of the proposed reaction pathway and investigate the energetics, structures and reactivities of various amine candidates for CO_2 activation. Three solvent environments (water, acetonitrile and DSMO) were used in our study. Solvent was included to better correlate with experimental results, and because preliminary computational results indicated that the gas phase hydride is unstable with respect to electron transfer to any proximate species. We utilized the M05-2X functional with the 6-31G* basis set to probe the potential energy surfaces (PESs), which provided important clues into the mechanisms of the new pathway for efficient CO_2 reduction.

SERMACS 435

Ligand exchange of PbS quantum dot thin films: Mechanism and kinetics

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The formation of compact, thin films of lead sulfide quantum dots (PbS QDs) with a tailored surface chemistry is a key goal for integrating these materials into nanoelectronic devices. This process typically involves the deposition of a QD thin film with an as-synthesized ligand shell followed by subsequent ligand exchange. Common exchange targets include primary carboxylic acids, thiols, and amines. We have followed this exchange process in real-time by imaging the contraction of a PbS QD thin film floating on a liquid subphase as it undergoes exchange of its native oleate shell for a shorter organic ligand. The rate of this QD reorganization is limited by the rate of oleate displacement, and we have been able to correlate changes in film contraction rate with changes in the underlying ligand exchange kinetics. We have applied this analysis to track the kinetics of the displacement of oleate for primary carboxylic acids, thiols, and amines of various lengths. The lifetime for primary carboxylic acid exchange is highly sensitive to the length of the entering ligand, but this same length dependence is not observed for thiols or amines. In general, thiols and carboxylic acids produce faster exchange than amines. The rate and yield of ligand exchange are positively correlated for the ligands tested. These results are explained in the context of an associatively-activated ligand exchange mechanism.

SERMACS 436

Study of the lysine deprotonation mechanism in UBC13

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Ubiquitin (Ub) is a regulatory protein with the ability to flag proteins to be degraded by the proteosome. Ub is covalently attached to a lysine on the target protein by a series of reactions catalyzed by three types of enzymes: ubiquitin activating enzymes, E1; ubiquitin conjugating enzymes, E2; and ubiquitin ligases, E3. Before Ub is transferred to its target, it is bonded to the E2 via a thioester linkage. In this study, we examine the E2 enzyme, Ubc13, which catalyzes the formation of K63-linked polyubiquitin chains. The chains are formed when a lysine on the target Ub (K63) attacks the thioester bond between Ubc13 and the substrate Ub. To initiate this reaction, K63 on the target Ub must be deprotonated, turning it into an active nucleophile. There are two possible deprotonation sites: a conserved aspartate in Ubc13 (D119) and a conserved glutamate in the target ubiquitin (E64). We are utilizing classical molecular dynamics, Born-Oppenheimer molecular dynamics and single point QM/MM calculations to determine a preference between the sites D119 and E64.

SERMACS 437

Construction of an oligo(ethylene glycol)-based self-assembled scaffold using N-hydroxysuccinimide conjugation chemistry for the chemical attachment of enzymes to gold surfaces

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The attachment of enzymes and other functional biomolecules to surfaces has been of significant interest in applications ranging from industrial catalysis to biosensors and biofuel cells. Covalent binding between the biomolecule and specific surface functional groups

has generally been preferred over other types of non-specific interactions. Such approaches tend to improve biomolecule stability and retention at the surface, and can be engineered so that a preferred biomolecule orientation results from the binding process. The work described here has focused on using self-assembly methods to construct bilayer scaffolds on gold for the covalent attachment of enzymes. Construction of these scaffolds is being accomplished via a “layer by layer” methodology using separate α,ω-functional reagents for each layer in the scaffold. In the model currently being explored, the first layer is constructed using a self-assembled monolayer (SAM) of 11-aminoundecane-1-thiol (AUDT), which provides a compact inner region that blocks direct access of solution species to the gold surface. Formation of the outer layer is accomplished via N-hydroxysuccinimidyl (NHS) conjugation chemistry using a bis-NHS-derivatized oligo(ethylene glycol) reagent (NHS-OEG$_5$-NHS). Such an approach is expected to result in the formation of amide bonds between opposite ends of the OEG reagent and the amines on both the underlying AUDT SAM and the exterior lysine groups of the enzyme. Given the bioadhesion-resistant nature of the outer OEG layer, covalent binding of the enzyme to the outer surface is anticipated to predominate over nonspecific adsorption. Experimental data for the formation of each layer in the scaffold has been obtained by infrared reflection spectroscopy and X-ray photoelectron spectroscopy and will be presented and discussed.

SERMACS 438

Synthesis and characterization of copper proazaphosphatrane complexes as potential pre-catalysts for cross-coupling reactions

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Proazaphosphatranes are flexible ligands that are hypothesized to facilitate cross-coupling due to their ability to promote reductive elimination. Palladium proazaphosphatrane complexes using Verkade’s base have been shown to be effective in catalyzing cross coupling reactions; however, copper proazaphosphatrane complexes have yet to be investigated. To address this issue, we have synthesized copper proazaphosphatrane complexes as potential pre-catalysts for cross-coupling. Several proazaphosphatrane copper halide and silylamide complexes were successfully synthesized in high yield and were fully characterized. Preliminary catalytic reactivity with these complexes has been achieved.

SERMACS 439

Compositional analyses of potsherds from an ancient Jewish pottery industrial site by inductively coupled plasma optical emission spectrometry

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The long-term goal of this project has been to develop a better understanding of the production and distribution of pottery in Roman Galilee. The focus of the work presented here is to examine pottery taken from an identified production town (Kefar Shikhin) and to characterize the elemental composition of potsherds taken from that site. An important objective is to analyze pottery from different areas in order to determine how broadly the village of Shikhin distributed pots and oil lamps in the Roman period (37 BCE - 363 CE). Preliminary analyses of the elemental composition of Shikhin potsherds is being performed using inductively-coupled plasma optical-emission spectrometry (ICP-OES). These ceramics are primarily composed of aluminosilicates having compositions of approximately 50-60 w/w% silicon dioxide and 20-30 w/w% alumina. Microwave digestion of the ceramics is being achieved using mixtures of nitric, hydrochloric, and hydrofluoric acids. Presentation of results from this project will include information about the Shikhin Excavation Project, information about our ICP-OES methodology, as well as preliminary quantitative results from samples taken from the site.

SERMACS 440

Data-guided permeability estimations for polymeric membranes

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Gas separation is an important process for carbon emissions reduction, oxygen purification, and natural gas sweating. Using passive polymer membranes shows great potential to improve its energetic and economic efficiency. But the research field is daunting as there are countless polymers but few ways to determine each polymer’s potential gas separation utility. We present machine learning techniques to develop a model for predicting polymer permeability coefficients. To train the model, we introduce monomer structures and permeability coefficients from a database of approximately one hundred polymers with experimentally determined permeability coefficients for O_2, N_2, CO_2, and CH_4 gases. The machine learning model uses as input the monomeric structures in one of three molecular fingerprinting formats: a persistence image derived with persistence homology, a bag-of-bonds array, and a Coulomb matrix. In addition, we test a plethora of machine learning algorithms to optimize the prediction performance.

SERMACS 441

Investigating the oxidative mechanism leading to atherosclerotic lesions

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Oxidation of low-density lipoproteins (LDL) has been implicated in the formation of fatty plaques leading to atherosclerotic lesions. However, the exact mechanism by which this takes place is unknown. In this study, phosphatidylcholine was oxidized with the naturally occurring enzyme myeloperoxidase (MPO), in the presence of hydrogen peroxide, in an effort to better understand the biochemical mechanism behind atherosclerotic plaque formation. Phosphatidylcholine was chosen as the lipid of choice in this study since it is the most abundant LDL in humans and has the potential to be oxidized by MPO. The results of this study discuss the biological relevance of phosphatidylcholine in plaque formation, as measured by Km, and a partial mechanism based upon spectrophotometric and nuclear magnetic resonance data is proposed.

SERMACS 442

Evaluating the binding of a novel carbon POSs-based HIV protease inhibitor drug

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Human Immunodeficiency Virus Type-1 (HIV-1) is a widespread viral pathogen that causes Acquired Immunodeficiency Syndrome (AIDS) in humans. HIV-1 protease, a primary target of anti-AIDS treatment, is responsible for the regulation of the post-translational processing of pre-viral gag and gag-pol protein complexes during the viral budding step of the HIV life cycle. This post-translational processing allows the immature virus to transform into a mature virion. We seek to determine whether novel HIV-1 protease inhibitors based on the polyhedral oligomeric silsesquioxane (POSS) scaffold exhibit in-silico binding affinities favorable enough to warrant experimental evaluation. POSS is a cage-like structure composed of oxygen and silicon atoms that allow for a specific orientation of high-affinity ligand arms in the binding pocket of HIV-1 protease. Considering that there are no force field parameters for the Si-O bonds of POSS, we began the development of Carbon POSSderivatives that would give us an understanding of the chemical interactions of each derivative in the active site of the HIV-1 Protease. While Carbon POSS analogs are not true POSS derivatives, they can be used to accurately simulate the binding behavior of true silicon-based derivatives due to the similarities between carbon and silicon atoms. This is further bolstered by the fact that POSS is merely a scaffold. Any interactions that occur between HIV-1 Protease and a POSS derivative are due not to the scaffold itself but to the side chains attached to the scaffold. After the development of these derivatives, MD simulations will be tested on the most favorable derivatives based on their Glide Docking score with the goal of better understanding the dynamics and interactions of the POSS molecule with the HIV-1 protease.

SERMACS 443

Theoretical study of variable gas adsorption by the robust metal–organic framework NKMOF-1-Ni'

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Metal–organic frameworks (MOFs) represent a promising class of porous crystalline materials that are synthesized from metal ions and organic ligands. The pores exhibited by these highly tunable frameworks provide compartments for small guest molecules of interest to be captured and sequestered in hopes of addressing various environmental issues. Implications of small molecule storage have practical usages that include gas adsorption and separation, drug delivery, and catalysis. The MOF **NKMOF-1-Ni'**, synthesized by combining Cu^{2+} and Ni^{2+} metal ions and pyrazine-2,3-dithiolate ligands, was investigated through grand canonical Monte Carlo (GCMC) simulations to determine its efficacy in adsorbing different energy-related gases. These included CH_4, CO_2, C_2H_2, C_2H_4, CH_3CCH, H_2CCCH_2, and C_3H_6. Simulations of the adsorption of all seven gases were performed in the material at temperatures of 298 and 195 K and pressures up to 1 atm. The theoretical uptake at 298 K/1 atm, maximum adsorption capacity, and isosteric heat of adsorption (Q_{st}) for all gases in the MOF were obtained from the GCMC simulations. Computational modeling of the MOF–adsorbate interaction also revealed the locations of the binding sites for the different gases within the framework. Examination of the relative affinities that the MOF displayed toward each gas provided insights into the potential of using this material for adsorbing and separating particular guest molecules to solve certain environmental problems. Future investigations can be done to modify the structure of selected MOFs to induce a greater degree of adsorption for specific gases.

SERMACS 444

Photocatalytic oxidation of aqueous ethylene glycol using solar illumination

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Fracking wastewater is a major environmental concern. In this work, ethylene glycol was photocatalytically degraded as a representative fracking wastewater contaminant. The photocatalytic experiments were performed in solar reactors containing nanoscale TiO_2-poly (methyl methacrylate) composites. Compound parabolic concentrators were used in conjunction with a recirculating pump to treat 20 L of aqueous solution. Gas chromatography was used to quantify derivatized ethylene glycol concentrations that started at 255 ppm. After 26 h of solar exposure, the ethylene glycol concentration was reduced to 51.07 ppm. Photocatalysis is a promising option for the purification of fracking wastewater containing ethylene glycol.

SERMACS 445

Using chalcones to re-sensitize methicillin-resistant *Staphylococcus aureus* (MRSA) to antibiotics

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Methicillin resistant *Staphylococcus aureus* (MRSA) first appeared in the 1960s and was discovered to be caused by a mutation in the mecA gene. This mutation in the *S.aureus* bacteria is what transmits the bacteria's resistance to methicillin. MRSA infections come in two forms: Community-Associated (CA) and Healthcare-Associated (HA). The main difference between the two forms is where the infection was contracted. While there has been a general decrease in both CA-MRSA and HA-MRSA, there is still a prevalence of CA-MRSA today specifically in environments like daycare. The *S.aureus'* infections continued resistance has brought to question how to effectively treat the infection without furthering the resistance. In recent studies, chemically synthesized compounds called chalcones have been found to have bactericidal capabilities when used alone as well as in combination with antibiotics. The alpha beta unsaturated ketone within the parent carbon chain of the chalcone adds to the high reactivity and electronegativity of the compound. Chalcones are similar to flavonoids, which naturally contain medicinal compounds and can be extracted from plants directly. Disc diffusion testing and minimum inhibitory concentration (MIC) testing were performed on a variety of synthesized chalcones to test whether MRSA was susceptible, resistant, or intermediate to the chalcones and chalcone-antibiotic combinations in addition to testing this relationship at different concentrations in MRSA and Mueller Hinton broth. From testing it can be seen that chalcones do contain bactericidal capabilities and that when used in conjunction with antibiotics, they have an overall more prevalent effect than simply antibiotics alone.

SERMACS 446

Photochemistry of silver cluster: DNA conjugates

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DNA strands form a wide range of silver clusters with distinct spectra. These polymeric ligands block agglomeration, stabilize, and alter the shape of their cluster adducts. Furthermore, they create distinct environments and thereby tune the spectra of the clusters with ~10 atoms. In his work, we study the photochemistry of these complexes using modulated laser excitation. We describe the optical instrumentation and analysis of a green emitting silver 10-silver cluster with DNA templates that have different sequences and structures.

SERMACS 447

Silver cluster conjugates with a DNA template

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DNA strands are polymeric ligands that control and stabilize silver cluster adducts. Furthermore, they create distinct environments and thereby tune the spectra of the clusters with ~10 atoms. In his work, we use a DNA template to form a range of silver clusters. These have distinct optical spectra and their sizes and oxidation states are characterized by mass spectrometry. The combined approach of optical and mass spectra is a powerful approach for identifying key nucleobase interactions with the cluster.

SERMACS 448

Identification of toxic metabolites produced by *Batrachochytrium dendrobatidis* fungus

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Batrachochytrium dendrobatidis, or Bd, is a fungus that causes chytridiomycosis in amphibians, a disease responsible for the rapid decline in amphibian populations globally. The pervasiveness and mortality rates of the Bd fungus has spurred researchers to discover why the fungus is so lethal in various species of frogs, salamanders, and caecilians. While it is known that the fungus affects the skin of amphibians and causes death through suffocation via populating in the pores of adult amphibians, little is known about the active compounds in the fungus. An understanding of the methods of infection will aid in the creation of safe ways to treat amphibians and prevent further outbreaks. To determine the metabolites excreted by the fungus, the culture medium was filtered, dried, and analyzed by LCMS. Preliminary data suggests the presence of several compounds of interest in the dried metabolites. The masses of the peaks of interest were used to guide further isolation and identification of compounds.

SERMACS 449

Cracking the theobromine dimer through co-crystal formation with salicylic acid derivatives

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Multi-component crystals, such as co-crystals, are utilized throughout the Pharmaceutical industry in an effort to develop drug formulations with enhanced solubility and bioavailability. Improving our understanding of how molecules hydrogen bond in the solid-state is crucial towards enhancing our ability to design drugs and control the physicochemical properties of active pharmaceutical ingredients. Constructing co-crystals from theobromine, through non-covalent interactions was attempted using salicylic acid derivatives. Given its tendency to dimerize, theobromine's structure prevents salicylic acid from breaking the 2-point hydrogen interaction between imide groups on adjacent theobromine molecules in the solid state. Instead, the carboxylic acid moieties from salicylic acid molecules hydrogen bond to the aromatic nitrogen of theobromine outside of the dimer forming a 2+2 co-crystal. However, it was reported that 5-chlorosalicylic acid breaks the theobromine dimer and forms a 2:1 co-crystal. This project involved studying a series of salicylic acid derivatives and determining which ones could form co-crystals with theobromine, and subsequently which derivatives would involve breaking the theobromine dimer. Our efforts to synthesize and identify co-crystals using mechanochemistry, powder X-ray diffraction, and single crystal X-ray diffraction are described herein.

SERMACS 450

Studies toward functionalization of tenulin and isotenulin via Diels-Alder reactions

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This research focuses on functionalizing the molecules Tenulin and Isotenulin by adding substituents to the enone via Diels-Alder reactions. Preliminary work has looked at determining an optimized set of conditions to facilitate the reaction using Lewis acid catalysis with model compounds. Once optimized conditions have been determined, they will be applied to the Tenulin and Isotenulin.

SERMACS 451

Calculation of critical and incident angles of complex reflection-absorption infrared systems

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Surface-film-solution interactions are of great interest in surface chemistry today However, identifying the optimal incident angle for maximum signal intensity requires finding a balance between the critical angles of the interfaces. This study explores the necessary calculations required to study surface-film-solution interactions using reflection absorption infra-red spectroscopy (RAIRS). The system of interest includes air to a ZnSe prism to a urea-ammonium formate-water (UAFW) solution to a hydroxyapatite (HA) film finally reflected off a metal surface. The refractive index of UAFW in the region of 600-4000 cm-1 was determined using the Kramers-Kronig method. Snell's Law was used to determine the critical angles at each interface. In order to optimize the signal intensity, the greatest incident angle where the system has real critical angles at each interface was also calculated. The incident angle of light was calculated with respect to the plane of the underlying substrate and the plane of a 45-45-90 ZnSe prism. This method to determine the optimal incoming angle for a surface-film-solution system can be applied to other complex system RAIRS measurements.

SERMACS 452

Interaction of hydroxyapatite thin films with prebiotic solutions

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Recent experiments suggest that hydroxyapatite (HA) may have been the ultimate source of phosphorus for life on the early Earth. However, the mechanism by which HA dissolves in prebiotic solutions of urea, ammonium formate and water (UAFW) is unclear due to its highly insoluble nature. Additionally, whether the surface of HA plays a direct role in the subsequent phosphorylation of small biomolecules such as glycerol and adenosine in these HA and UAFW systems is unknown. Hydroxyapatite thin films conducive to surface-sensitive analytic methods were grown on a copper substrate using electrochemical deposition. The reaction of HA films with UAFW produced a bright blue solution, and upon centrifuging, a light blue precipitate was observed. Analysis of the supernatant and precipitate was performed by Fourier Transform infrared (FTIR) and electron backscattering (EDX). The results suggest that holes in the HA film expose a reactive copper (II) oxide layer between the metal substrate and the film. Evidence for the reaction of copper (II) oxide and the ammonium formate in the UAFW solution will be presented, including a proposed mechanism. Additionally, we will discuss adaptations to the system including varying the metal substrate, adjusting the pH, and varying the prebiotic deep eutectic solution. The changes of surface structure of hydroxyapatite as it reacts with prebiotic solutions will be monitored using a surface-sensitive infrared spectroscopy (i.e., PM-IRRAS).

SERMACS 453

Electrodeposition and characterization of hydroxyapatite thin films on metal substrates

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Hydroxyapatite or $Ca_{10}(PO_4)_6(OH)_2$ belongs to a class of minerals that are of interest to origin of life scientists because it may have supplied reactive phosphorous on early Earth. Hydroxyapatite thin films have been synthesized by electrodeposition onto several metal substrates including copper, iron, and stainless steel. The electrodeposition method uses a three-electrode cell connected to a potentiostat/galvanostat with the metal substrate as the working electrode coupled with a platinum metal counter electrode and a reference electrode respectively. The three-electrode cyclic voltammetry uses stock one molar solutions of calcium nitrate tetrahydrate and ammonium dihydrogen phosphate that are reacted in the system to form hydroxyapatite. Characterization of the films will be performed using scanning electron microscopy (SEM), powder x-ray diffraction (XRD), energy-dispersive x-ray spectroscopy (EDX), and reflection-absorption infrared spectroscopy (RAIRS). This was used to determine the thin film's morphology, crystallinity, chemical elemental composition, and qualitative thickness, respectively. Initially, characterization suggested that thin, uniform films were produced by electrodeposition; however, subsequent interactions with prebiotic solutions indicated the films were porous, with a reactive metal oxide layer between the metal substrate and hydroxyapatite. Adjustments to the electrodeposition method will be discussed to ensure future films are uniform, full-bodied, and no porosity.

SERMACS 454

Exploration of unexpected Ph-dependent acidic aromatic hydrogen in 1,8-diamino-2,7-naphthyridine-4-carbonitriles

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The acidity of aromatic hydrogens in heterocyclic compounds is very low (pKa= ~40) so the deprotonation of aromatic hydrogen does not occur under most conditions. However, the unexpected aromatic hydrogen exchange in 1,8-diamino-2,7-naphthyridine-4-carbonitrile systems has been observed in NMR analysis. 1,8-diamino-3,6-bis(1-pyrrolidinyl)-2-7-naphthyridine-4-carbonitrile and 1,8-diamino-3,6-bis(N-methylpiperazine)-2-7-naphthyridine-4-carbonitrile have been synthesized and characterized exhibiting unusual chemical properties. Both free and protonated forms of the compounds were studied by quantum calculation and NMR titrations, showing that the protonation alters the structure and reactivity of the compounds.

SERMACS 455

Phosphonates as a precursor to phosphonylated biomolecules

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Prebiotically plausible phosphorylation mechanisms have been an area of considerable interest due to the abundance of phosphates in important biomolecules such as nucleic acids, coenzymes, and cell membranes. However, phosphites may be a more plausible starting material than phosphate in these chemical processes, because they are more soluble in aqueous solution than phosphates. Reactions of metal phosphites with aqueous solutions of ethylene glycol and glycerol were performed under prebiotically plausible conditions of a pH of 4 along with overnight heating at 60ºC until dry. Analysis by NMR and LCMS confirms the formation of phosphonylated species in solution. The yield of phosphonylated product varies depending upon solubility of the metal phosphite used. Moreover, ammonium phosphite was observed to phosphonylate at multiple positions, while other phosphites targeted only the alpha position. These results and implications of the research on the phosphate problem will be discussed.

SERMACS 456

Developing small molecules selectively targeting the sequence-based secondary structure of SSDNA, CCG repeats

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DNA exists primarily as a duplex. However, single-stranded (ss) DNA is temporarily exposed in several cellular processes, such as DNA replication and transcription. ss DNA can form its self-folding (secondary) structure by sequences of DNA and the secondary structure of ss DNA affects the cellular processes. For example, the stable secondary structure of ss DNA can cause DNA mutations, both extension and contraction. Therefore, discovering selective binders that stabilize the secondary structure of ss DNA is important as a tool for understanding biological events more and as a potential treatment for diseases caused by the mutated DNA. The target DNA strand $(CCG)_7$, which builds the stable secondary structure, was assayed with selected 80 compounds which have more than 80 % of similarity of the known C-C mismatched base pair binder. The 10 hit compounds were tested for binding affinity and selectivity toward the secondary structure of $(CCG)_7$ repeats.

SERMACS 457

Tetrahedrite and Cu-Sb-S intermediates synthesized by a modified polyol process

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With the modern world facing an unprecedented energy and climate crisis due to past and current usage of fossil fuels resulting in global climate change, it has become a focus of scientific researchers to develop novel alternative energy sources. In this search, thermoelectrics have emerged as a field of particular interest due to the ability to convert heat into electricity via the Seebeck effect. Tetrahedrite ($Cu_{12}Sb_4S_{13}$) has proven to be a promising thermoelectric material due to its complex unit cell and the fact that it is composed of materials that are found in abundance on earth. Our research utilizes a cost effective synthesis via a modified polyol procedure, which produces high yields and requires only one hour of heating at 220° C. The majority of thermoelectric materials, in contrast, can often only be made with energy intensive solid state processes. An additional complicating factor is that most other popular thermoelectrics contain expensive and uncommon earth elements such as germanium, tellerium, or bismuth. To increase the efficiency of our modified polyol process, we have investigated the growth mechanism of tetrahedrite as a function of time and temperature. These syntheses were characterized by powder x-ray diffraction, scanning electron microscopy, and energy dispersive x-ray spectroscopy. While the modified polyol procedure is robust with the ability to incorporate a variety of dopants into tetrahedrite, the method is limited in that exotic dopants such as zirconium and calcium cannot be incorporated. With the goal of integrating these types of dopants dopants into tetrahedrite, we have fabricated other Cu-Sb-S compounds that we have identified as intermediates of the tetrahedrite growth mechanism using the modified polyol procedure. These intermediates will serve as starting materials for the future development of alternative synthetic routes, which may provide additional pathways toward incorporating exotic dopants.

SERMACS 458

Modification of polysiloxane surface coatings with zwitterionic thiols using thiol-ene click

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Silicones, or polysiloxanes, are a class of polymer that are characterized by a backbone consisting of Si-O linkages. Polysiloxanes are found in many products and may be prepared as liquids, rubbers, gels and coatings by modifying the extent of cross-linking and adding one or more alkyl groups around the silicon. They are usually highly thermally and oxidatively stable, electrically and thermally insulating, and resistant to microbial growth. Polysiloxanes prepared from allyltrimethoxysilane (ATS) are highly cross-linked and maybe used to coat various surfaces. We are interested in incorporating them into copolymers, allowing for phase

separation to provide complex topologies and patterned surface energies. Surfaces to be coated were cleaned by inserting the them into an UV/ozonizer chamber, followed by sonication in a solvent to remove any standing debris. Gels were prepared by hydrolyzing the methoxy groups by acid catalysis then inducing polymerization by base catalysis before letting the gels dry in ambient conditions. The surface was then altered by way of the thiol-ene click reaction using tris(pentafluorophenyl)borane as a catalyst. Polyzwitterionic thiols were attached under argon. Coatings were characterized by scanning electron and atomic force microscopies, Raman spectroscopy and contact angle goniometry. Samples were exposed to *Pseudomonas aeruginosa* to examine the effects of derivatization on cellular adhesion.

SERMACS 459

Investigating MOF ultra-thin film thickness by ellipsometry and atomic force microscopy

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Metal organic frameworks (MOFs) are crystalline, porous structures composed of metal ions coordinated with organic ligands. These materials have high surface to volume ratios as well as chemical and structural tunability. MOFs are able to store hydrogen gas, carbon dioxide, and other greenhouse gases from the air depending on chemical functionality and pore size. They can also be made of biocompatible, non-toxic materials to contain medication within their pores for controlled drug delivery and release. The optical and electrical properties of MOFs can be tuned so as to incorporate them in devices for applications in sensing. To incorporate MOFs into larger architectures, a thin film of a MOF can be formed by alternating deposition cycles of the inorganic and organic components using an automated slide stainer. Typically, the structure is assembled on a gold-silicon wafer using self-assembled monolayers to anchor the MOF to the surface. We have investigated film thickness as determined by the ellipsometer and atomic force microscope (AFM) to examine the thin film formation of surface-anchored metal organic frameworks. For ellipsometry, initial studies assumed the optical properties are comparable to that of ultra-thin organic films with 1.5 and 0 for the index of refraction (n) and extinction coefficient (k), respectively. For AFM, we use selective acid etching to pattern the film and thickness is physically determined by measuring the height difference between the top of the film and the substrate. The physical thickness obtained by AFM was then input into the ellipsometer to determine more accurate optical values for n and k. Ellipsometry is a non-destructive and simple method of determining film thickness, so the goal of optimizing the accuracy of the thickness output by this instrument is important for more efficient measurements. Additionally, an advanced understanding of the film’s optical properties is foundational for applications such as drug delivery and sensing.

SERMACS 460

3D printed laboratory accessories as a vital component of the undergraduate research experience

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Chemistry laboratories require a wide array of machinery and hardware for the efficient completion of experiments. However, many standard components of the modern chemistry laboratory are quite costly. As a result, frequent repair and replacement of these components can hinder research progress by diverting precious financial resources. The emerging field of 3D printing has the potential to provide a cost-effective solution to this dilemma, while also maintaining the quality of the off-the-shelf equivalencies. As 3D capabilities have progressed in recent years, its accessibility has also increased. Many academic communities, including colleges and universities, now offer individuals the ability to 3D print their own designs or pre-existing templates at a low cost. Furthermore, after a moderate initial investment, one can print their designs from the comfort of their own home or lab. In this work, we describe the benefits of designing and 3D printing laboratory equipment in a university setting. We further detail the design process for three 3D printing projects of routine laboratory equipment and demonstrate their applications in the research lab.

SERMACS 461

Screening and characterization of a commercially available lipase library for catalysis of a Morita-Baylis-Hillman reaction

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Over the last few decades, biocatalysts have become an important tool for the advancement of synthetic organic chemistry. In contrast to their organometallic counterparts, biocatalysts can be relatively inexpensive and more environmentally friendly while providing comparable yields and stereoselectivities. Synthetically useful biocatalysts may consist of biologically derived molecules (DNA, RNA and proteins), available from a wide array of plant, fungal and bacterial sources. Lipases, a class of protein biocatalysts previously shown to catalyze carbon-carbon bond forming reactions, are ideal components of libraries used in the screening of new biocatalytic transformations due to their high stability, mild reaction conditions, and excellent enantioselectivity. In addition, two promising attributes of lipases make them attractive catalysts for carbon-carbon bond forming reactions: i) catalytic promiscuity, or the ability to catalyze reactions beyond their standard in vivo chemistries, and ii) interfacial activation, or the enhanced catalytic activity of biocatalysts sometimes observed in non-polar media. In this work, we describe the screening of a library of commercially available lipases for catalysis of the Morita-Baylis-Hillman reaction (MBH), a synthetically useful carbon-carbon bond forming reaction. We utilize two solvent systems for this transformation, characterizing differences in reaction yields and biocatalyst-independent product formation.

SERMACS 462

Catalytic promiscuity versus stereochemical fidelity in enzymatic dynamic reductive kinetic resolution (DYRKR): Insights from biocatalytic studies and structural biology

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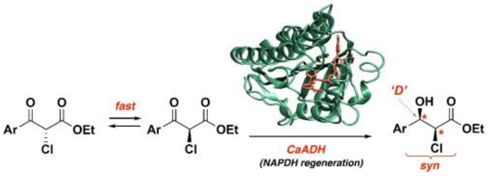
Our research group was the first to describe the expression, purification and characterization of a dehydrogenase enzyme from *Clostridium acetobutylicum* (CaADH) with considerable potential for stereocontrolled organic synthesis. *C. acetobutylicum* was chosen because it naturally traverses a solventogenic phase in its normal life cycle. Indeed, this underlies much of the effort to exploit this organism and its metabolic machinery for the production of biobutanol. Our group has established the ability of the CaADH enzyme to reduce a signifcant range of carbonyl compounds with high facial selectivity. This presentation will focus on dynamic kinetic kinetic resolution (DYRKR) processes by which this enzyme is able to formally deracemize an α-chloro-β-keto ester substrate and yield largely a single stereoisomer of the four possible. Kinetically, this requires that the racemization step be faster than the enzymatic carbonyl reduction step so that the disfavored enantiomer does not accumulate. Stereochemically, this process requires that the enzyme display two distinct modes of stereo-recognition. On the one hand, the enzyme must significantly favor one antipode of the racemic substrate; on the other, the enzyme must display high levels of facial selectivity in the reduction of the carbonyl center. This presentation will describe our synthesis and enzymatic reduction of a number of carbonyl substrates bearing α-stereocenters. This enzyme displays a remarkable degree of "active site plasticity" whereby substrates of entirely different structural classes are reduced stereoselectively, but with different facial preference depending upon the nature of the organic functional group(s) flanking the susceptible carbonyl center. This presentation will also describe our newest results in characterizing the three dimensional structure of CaADH by x-ray crystallography. This bifurcated organic substrate diversification-structural biological characterization approach provides our collaborative team with complementary information for the construction of predictive models to guide the use of dehydrogenase enzymes in hybrid, stereocontrolled synthetic ventures.



SERMACS 463

Exploring sequence-function space in the old yellow enyzme superfamily

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Biotechnology and bioinformatics have made it increasingly apparent that there is a vast wealth of protein 'dark matter', i.e., sequence and functional information that is yet to be discovered and harnessed for fundamental or applied gains.For example, the superfamily of Old Yellow Enzymes (OYEs) with ~88 characterized enzymes in the literature, is shockingly underexplored, despite >85 years of research and their proven industrial application. We have applied large scale bioinformatic and synthetic biology approaches to systematically sample and functionally characterize representatives across the entire OYE superfamily, which is comprised of >70,000 members. Our efforts have more than doubled the current OYE knowledgebase and have yielded native biocatalysts with improved activity and expanded substrate specificity. Furthermore, our multidisciplinary approach serves as an adaptable pipeline for the analysis of other superfamilies, improving the current standard of investigative processes for the field. The comprehensive characterization of enzyme superfamilies, especially those with proven biocatalysis capabilities, offers tremendous opportunities for future developments of green and sustainable chemical processes.

SERMACS 464

Understanding the limited stereo-complementary nature of old yellow enzymes 1 & 3: Loop movement dictated by a single amino acid

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Old Yellow Enzymes (OYEs) 1 and 3 are powerful biocatalysts in the reduction of enones, but tend to possess similar stereo-selectivity, not surprising, given their 80% sequence identity. The Stewart group has shown that mutations to the conserved Trp 116, such as W116A, alter the stereo-selectivity of OYE1 and OYE3 via a flipped binding orientation of multiple enone substares, but has yet to fully explain 7 notable exceptions to the conserved stereo-selectivity of OYE1 and OYE3. Thus, we examined the non-conserved position 296, which is Phe 296 in OYE1 and Ser 296 in OYE3, to explain this limited stereo-complementary nature of two wild-type enzymes. Site saturation libraries at position 296 of OYE1, OYE3, OYE1-W116A, and OYE3-W116A were screened for the reduction of a panel of enone substrates to characterize the stereo-selective role of position 296 and any combined effects with mutation to Trp 116. The results suggest that phenylalanine at position 296, in either OYE1 or OYE3, works with W116A to allow for a unique stereo-selectivity, with respect to all other mutants, during *R*-carvone reduction. Whereas, Phe 296 alone, provides a unique stereo-selectivity while reducing 2-methylcyclopentenone and (*E*)-2-methyl-1-phenylpent-1-en-3-one, the latter being 1 of the 7 substrates for which OYE1 and OYE3 provide opposite stereo-selectivity. In conjunction, molecular dynamic (MD) simulations were conducted on OYE1 and OYE3 solved structures, focusing on the active site loop-6 region, which contains position 296. These calculations show that Phe 296 hinders loop 6 movement, closing upon the active site, while Ser 296 leads to more loop 6 movement, despite the enzyme. We are starting to link a unique stereo-selectivity which arises from altered substrate binding to the movement of an active site loop by combining experimental data with computational MD data of mutations at position 296. X-ray crystallography and MD simulations need to be focused on OYE1, OYE1-F296S, OYE3, and OYE3-S296F complexed with (*E*)-2-methyl-1-phenylpent-1-en-3-one to accurately characterize loop 6 movement in response to the amino acid at position 296 in the presence of this substrate which OYE1 and OYE3 reduce to opposite enantiomers.

SERMACS 465

Bubble column enables higher reaction rate for deracemization of (*R*,*S*)-1-phenylethanol with coupled alcohol dehydrogenase/NADH oxidase system

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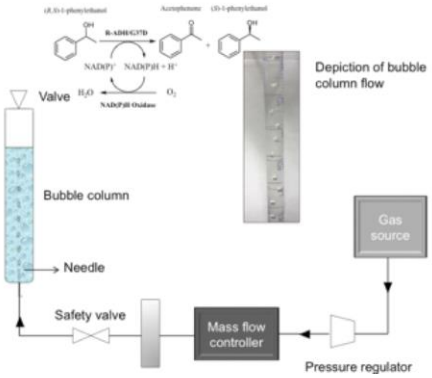
One of the major drawbacks for many biocatalysts is their poor stability under industrial process conditions. A particularly interesting example is the supply of oxygen to biooxidation reactions catalyzed by oxidases, oxygenases or alcohol dehydrogenases, coupled with oxidases which all require the continuous supply of molecular oxygen as an oxidant or electron acceptor. Commonly, oxygen is supplied to the bioreactor by air sparging. To ensure sufficient oxygen transfer from the gas to the liquid phase, stirring is essential to disperse the gas bubbles and create high gas-liquid interfacial area. Studies indicate that the presence of gas-liquid interface induces enzyme deactivation by protein unfolding which then readily aggregates and can subsequently precipitate. This contribution has examined the effects of stirring and the presence of gas liquid interface on the kinetic stability of waterforming oxidase. These effects were studied separately and a bubble column apparatus was successfully employed to investigate the influence of gas-liquid interfaces on enzyme stability. Results showed that NOX deactivation increases in proportion to the gas-liquid interfacial area. While air enhances the rate of stability loss compared to nitrogen, stirring causes faster loss of activity in comparison to a bubble column. Finally, deracemization of 1-phenylethanol, using a coupled alcohol dehydrogenase-NADH oxidase system ADH-NOX, proceeded with a higher rate in the bubble column than in quiescent or in a stirred solution, although, inactivation was also accelerated in the bubble column over a quiescent solution. In addition, we will also present unpublished work about the influence of antioxidants on operational stability in all three mechanical configurations.



SERMACS 466

Data-Rich Development of a Novel Biocatalytic Aerobic Oxidation Across Scales

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Recent advances in the biocatalytic retrosynthetic toolbox have transformed the way Merck conceives of novel synthetic routes, particularly for drug candidates with significant structural similarity to naturally occurring biomolecules such as proteins, peptides and nucleosides. This is particularly evident in the ongoing development of the biocatalytic route to MK-8591, a nucleoside reverse transcriptase/translocation inhibitor (NRTTI) currently progressing through Phase II clinical trials, displaying great promise as a next-generation anti-HIV drug. Broadly speaking, this synthetic pathway represents a ground-breaking application of cascaded biocatalysis for the synthesis of a complex, clinically relevant small molecule compound. Furthermore, the oxidation of alcohols to aldehydes represents key transformations in organic synthesis. Traditionally, many of these oxidation reactions have been carried out using stoichiometric amounts of transition metal-based oxidants while selective and green methods have remained largely underdeveloped. To surmount those obstacles, Merck has recently expanded its biocatalytic platform to include the copper-dependent galactose oxidases (GOases), which are highly efficient enzymes for the mild, regio- and stereoselective oxidation of a broad variety of primary and secondary alcohols, polyols and sugars. These enzymes are capable of catalytic oxidations in water, making direct use of the molecular oxygen from compressed air as the oxidant. In this submission, we will showcase how collaborative efforts across Process Research and Development are contributing towards building deep, fundamental understanding of the oxidation of 2-ethynylglycerol, a key intermediate in the MK-8591 synthesis. We will highlight past and ongoing efforts centering on enzyme discovery and reaction engineering, underpinned by data-rich experimentation methods including; high-throughput experimentation and analysis, automation, and insitu reaction analysis using novel analytical tools. Furthermore, development of a robust process optimized for a commercially relevant synthetic chemistry reactor (vs. for example a more optimal bioreactor or fermentor) will be reviewed including demonstration across scales.

SERMACS 467

Development of a commercial biocatalytic process to produce dextroamphetamine salts

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Dextroamphetamine salts, such as dextroamphetamine sulfate, dextroamphetamine saccharate, and Lisdexamfetamine mesylate (a dextroamphetamine pro-drug), are active ingredients in many pharmaceuticals to treat attention deficit hyperactivity disorder, narcolepsy, and eating disorders. Traditional manufacturing of these compounds has relied on chiral resolution by diastereomeric crystallization to afford enantiomerically pure dextroamphetamine from racemic amphetamine mixtures produced by reductive amination of phenylacetone. This classical chiral resolution is a costly inefficient low-yielding multi-step process. This case study covers the process development to replace an existing reductive amination of phenylacetone to produce racemic amphetamine followed by chiral resolution with an efficient one-step biocatalytic amination with a highly selective aminotransferase to produce dextroamphetamine. This case study covers the efforts from the initial biocatalysis screening to reaction optimization and modeling to final downstream process development (e.g., filtrations, extractions, and crystallization) to design a one-step process that can produce dextroamphetamine salts meeting current USP specifications and can be produced by GMP standards for pharmaceuticals. This process development afforded an improved process that can achieve a 5-fold increase in yield, 4-fold decrease in process mass index (PMI), and 4-fold decrease in cost of goods over the classical process and was demonstrated in several scale-up batches on a multi-kilogram scale prior to commercialization.

SERMACS 468

Recent advances in commercial scale biocatalytic processing

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Abstract hold. Final abstract is awaiting approval and clearance for the sharing of IP. Talking points will cover recent advances in the process and commercial scale manufacturing of API and API intermediates. The application of both existing biocatalysis and development of novel engineered catalysts. Full abstract will be uploaded once available.

SERMACS 469

Directed evolution of an amide bond-forming enzyme in organic solvent

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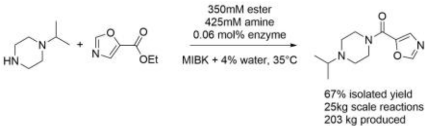
The catalytic synthesis of amides is a long-standing problem in organic synthesis, with only a few demonstrations of the cost-effective synthesis of pharmaceutically relevant amides at large scale and under desirable conditions. By comparison, biology is routinely capable of performing amide bond formation with exquisite activity and specificity, yet biocatalytic applications remain limited by narrow solvent scope and poor substrate promiscuity. To overcome these limitations, we have developed a platform for the evolution of enzymes as lyophilized powders in fully organic systems, and used it to evolve a thermostable esterase for the synthesis of diverse secondary and tertiary amides in fully organic systems. Using this platform we were able to dramatically alter our starting enzyme, yielding a variant >10,000-fold improved from its starting activity and enabling the synthesis of 203kg of a tertiary amide via a reaction run in water-saturated MIBK.



SERMACS 470

Quick discussion on multiomics with mass spectrometry and standardization in metabolomics

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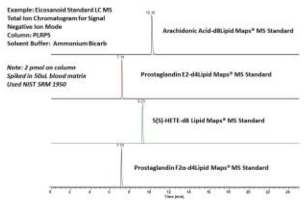
This presentation looks to first quickly discuss the fields of proteomics and metabolomics, as well as other applications that use LC MS as the detection device. Mass Spectrometry is found across all fields of research in the life sciences and biotechnology - we look to highlight this truth during the Joint Mass Spectrometry Symposium. As well as a discussion on the use of LC MS for different workflows, we will present current aspects of standardization in metabolomics. Improved standardization in the OMICS fields should lead to improvements in the drug discovery pipeline and precision medicine. Recently, we developed a global metabolomics experiment with isotopically labeled internal standards. The experiment is designed to capture improved information on different steroids, which are often difficult to detect in a global metabolomics. As well, we also developed an Eicosanoid heavy labeled spike method for the same sample. Because of the nature of the molecular species of interest, we used separate column chemistries (RPLC, C18, etc.) and mobile systems (Formic Acid and Ammonium Bicarbonate) to optimize the ionization and separation of molecular types. Results include information on separating steroid isobaric structures in complex blood matrix and interesting in-source fragmentation pathways of importance. As well, we present excellent separation and ionization of molecules from the eicosanoid family.



SERMACS 471

Mass spec applications to natural products drug discovery

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Natural products provide a significant source of new metabolites for drug discovery. Mass spectrometry is used widely in the analysis of natural products, including structure determination, quantification and myriad biomedical assays. Examples of new natural products from our lab will be highlighted in this presentation with emphasis on mass spectral techniques used for their analysis.

SERMACS 472

Mass spectrometry metabolomics in clinical research

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The metabolome encompasses the entire set of small molecules that may be found in a biological specimen under a given condition. It consists of metabolic intermediates, hormones, and even exogenous metabolites from food or the environment that have an impact on health. Metabolomics refers to the measurement of these metabolites. In Global metabolomics, the aim is to measure as many of these metabolites as possible (often in excess of 2000 for mass spectrometry) in a single injection and correlate the expression to health. The metabolome thus represents a unique opportunity to develop personalized diagnostics. Advances in mass spectrometry instrumentation have been a key driving force of this growth. New approaches to rapidly assess the metabolome, identify metabolites and find transient metabolites are necessary as the next step in development. Analytical advances in lipid identification, rapid sample analysis with PaperSpray, and opportunities to find transient metabolites using liquid micro junction surface analysis are key aspects that will lead to new clinical diagnostics.

SERMACS 473

Plant health, performance and metabolome perturbation measured by high throughput mass spectrometry and automated greenhouse technology

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Phenotypic plant health and performance are important to experimental breeding operations where advancement of genetic lines and engineered constructs from greenhouse to field is cost prohibitive. Therefore, deployment of a broad spectrum of analytical tools and statistical approaches for greenhouse plant performance monitoring is therefore necessary. Here, metabolomics mass spectrometry is presented as such a tool after introduction of genes, promoters, biotic and abiotic stresses. These tools are enabled by high throughput plant tissue sampling by automated greenhouse technology and chemometrics. Preliminary measurements were performed on two transgene systems. PLSDA modeling and variable statistic scoring were effective multivariate approaches for separating sample population from the wild type, and identification of the most transgene-sensitive and selective variables (metabolites). Marker statistic sensitivity score to noise ratio is proportional to the inverse square root of the number of biological repetitions or plants sampled. Highly sensitive transgene markers may contain a strong growth stage covariance, penalizing selectivity scoring during sampling. Mahalanobis distance measurements are also explored for quantitative measurement of metabolome perturbation.

SERMACS 474

Pharmacoproteomics: Mass spectrometry-based approach to determine drug targets and their effects in an unbiased manner

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Recent advances in mass spectrometry-based proteomics now enables the unbiased identification and quantification of thousands of proteins in a single experiment. We can apply this technology to determine drug targets and understand their cellular response and resistance on a global level, which is termed pharmacoproteomics. The failure rate of drugs in development is high due to poor pharmacokinetic properties. With pharmacoproteomics, drug mechanisms can be studied on a proteome level early in the development stage to potentially prevent drugs with poor PK properties from entering the preclinical or clinical phase. Proteomics can be applied is several ways to aid in drug development. To determine specificity of kinase inhibitors, cells are treated with the drug, then incubated with multiplex inhibitor beads (MIBs) which consist of multiple immobilized pan kinase inhibitors. Kinase targets of the drug will occupy the ATP binding pocket of the bound kinases, thereby prevent MIBs binding which will cause a dose-dependent decrease in abundance when analyzed by LC-MS/MS. To understand cellular response and resistance to kinase inhibitors in the context of cancer, MIB/MS is used to study kinome-wide changes in cancer cells after drug treatment over an extended timecourse and phosphoproteomics can be used to understand drug mechanism. Other types of drugs, such as PROTACS, can be profiled for drug specificity using deep, quantitative proteomics. This presentation will highlight several applications of pharmacoproteomics in drug discovery and development.

SERMACS 475

PepSAVI-MS for the identification of novel bioactive cyclotides

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Rapidly emerging multidrug resistant pathogens and a deficit of new antimicrobial compounds entering the clinical pipeline necessitate the exploration of alternative sources of therapeutics. Botanically-derived bioactive peptides are an attractive source of new antimicrobial compounds, with the potential to be highly selective, potent, and inexpensive to produce on a large scale. Our lab has developed the PepSAVI-MS (Statistically-guided bioActive Peptides prioritized VIa Mass Spectrometry) pipeline, an adaptable method for the rapid screening of natural product peptide libraries against pathogens of interest. Cyclotides, a class of cyclic plant-derived peptides, boast a diverse range of potent antimicrobial bioactivities and contain three interlocking disulfide bonds, conferring a highly stable, evolvable scaffold. Coupling a mass spectrometry based cyclotide identification strategy with PepSAVI-MS, we indentify previously uncharacterized cyclotide species with potent antimicrobial bioactivities.

SERMACS 476

High-throughput screening by adaptation of IR-MALDESI-MS

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The ability to rapidly and accurately characterize samples is of critical importance in the drug discovery process as well as in the clinical testing laboratory. However, for many screens and assays, the benefits of mass spectrometry analysis are outweighed by sample compatibility concerns and low throughput. Modern mass analyzers have sufficient speed, sensitivity and specificity if coupled with a “front-end” solution that does not require significant sample clean-up and create ions for analysis on the millisecond timescale.   Infrared matrix-assisted laser desorption electrospray ionization (R-MALDESI) has significant potential for high-throughput mass spectrometry; an IR laser is used to aerosolize a solution directly from the wells of a commercial microtiter plate. Analytes are desorbed and ionized from the ejected droplets through interactions with an intersecting electrospray plume, effectively combining sampling, extraction and ionization into a single concerted step. This electrospray post-ionization approach has been proven to have significant tolerance for contaminants such as buffer salts and surfactants, requiring no cleanup before sampling and ionization. This talk will present a selection of results acquired using an IR-MALDESI ion source coupled with high resolution Orbitrap mass spectrometry, and more recent experiments using ion mobility separation for isomer distinction.

SERMACS 477

Effects of buffers on the conformation and aggregation of an adalimumab biosimilar studied with hydroxyl radical protein footprinting

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Unlike small molecule drugs, therapeutic proteins must maintain the proper higher order structure (HOS) in order to maintain safety and efficacy. Due to the sensitivity of many protein systems, even small changes due to differences in protein expression or formulation can alter HOS. Hydroxyl radical protein footprinting (HRPF) can sensitively detect changes in protein HOS by measuring the average topography of the protein monomers, as well as identify specific regions of the therapeutic protein impacted by the conformational changes. However, HRPF is very sensitive to the radical scavenging capacity of the buffer; addition of organic buffers and/or excipients can dramatically alter the HRPF footprint without affecting protein HOS. By compensating for the radical scavenging effects of different adalimumab biosimilar formulations using real-time dosimetry, we identify that sodium citrate buffer causes a modest decrease in average solvent accessibility compared to sodium phosphate buffer at the same pH. We find that the addition of polysorbate-80 does not alter the conformation of the biosimilar in either buffer, but it does provide substantial protection from protein conformational perturbation during short periods of exposure to high temperature. Compensated HRPF measurements are validated and contextualized by dynamic light scattering (DLS), which suggests that changes in adalimumab biosimilar aggregation is a major driver in measured changes in protein topography. Overall, compensated HRPF accurately measured conformational changes in adalimumab biosimilar that occurred during formulation changes, and identified the effect of formulation changes on protection of HOS from temperature extremes.

SERMACS 478

Assessment in postsecondary chemistry courses: Results from a national survey

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How and why we assess in our chemistry courses impacts student learning. While much has been done to characterize instructional practices in STEM education, little has been done to characterize assessment practices. We will present results from a national survey of chemistry faculty members on what assessment tools are being used in postsecondary chemistry courses. A cluster analysis revealed a grouping of faculty members that regularly use surveys and concept tests. We will supplement these results will interview data from our respondents as to why such tools are integral to their assessment practices. Implications for the dissemination and development of innovative assessment tools will be offered.

SERMACS 479

Longitudinal investigation of changes in teaching beliefs of chemistry faculty at research-intensive institutions

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Literature at the secondary level has demonstrated a tight interconnectedness between ones' beliefs about teaching and learning and one's instructional practices. Despite the substantial influence of teaching beliefs on educational decisions, very little research has been conducted at the post-secondary level, which suggests the need to attend to the development of faculty's beliefs. This study aims to fill this gap, by investigating the overtime changes in the beliefs of early career chemistry professors from research-intensive institutions in the United States. The study followed a longitudinal design, where faculty were interviewed using the modified Luft and Roehrig's Teaching Beliefs Interview protocol in Fall 2016/Spring 2017 and then in Spring 2019. Combination of constant-comparative analysis and cluster analysis were utilized to characterize faculty's beliefs after pre- and post-data collection cycles. Overall, the participants expressed more unique beliefs about teaching and learning during the post-interviews. Despite this increase, the substance and the message of the beliefs remained fairly similar to the beliefs expressed during the pre-interviews, which suggests that beliefs do not change as an artifact of teaching experience. Additionally, although this study explored beliefs systems of a fairly homogeneous sample of participants, there was a noticeable variation in the sophistication of faculty's beliefs. These results highlight the need for instructional reform facilitators to recognize the diversity of beliefs present within a somewhat homogeneous group of instructors and differentiate the learning experiences accordingly by providing individualized support.

SERMACS 480

Characterizing observation feedback provided to trainee graduate teaching assistants

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Graduate Teaching Assistants (GTAs) are the backbone workforce for teaching chemistry in higher education, and whilst their roles overall may be similar between institutions, the level of training and feedback that they receive varies across the country. Teaching is a professional occupation and requires both a theoretical and practical understanding that can be developed through observations, critiques, and reflections. Here we present data from an observation feedback mechanism used to train our trainee GTAs (t-GTAs). The system is called the 'observation series', and is mirrored aspects of teacher development seen during K-12 teacher training. The data collected includes observations provided by supervisor TAs (e-GTAs), observation feedback provided by peers (t-GTAs) and focus group discussions. The data was subjected to content analysis to identify common themes amongst the feedback provided, and then the nature of these themes were probed. We will present the different focuses represented in the data between e-GTAs and t-GTAs and suggest mechanisms to improve the observation process to enrich the feedback provided to t-GTAs.

SERMACS 481

Improving the training of teaching assistants at Purdue chemistry: Incorporating what they really need and want

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The training of graduate student teaching assistants (GTAs) is recognized as important for many colleges and universities, since they often interact more closely with undergraduate students than professors do. Supporting graduate students with teaching will ultimately help create a better learning environment for undergraduate students to thrive. Research on GTAs is becoming more important in order to better understand how to design effective training programs. At Purdue's Department of Chemistry, we have developed a GTA training program for first-year GTAs, "trainee GTAs" (t-GTAs), that exposes them to evidence-based instructional practices and provides support regarding their implementation in order to build up professional skills and run a successful classroom. This work will offer insights regarding the lessons we have learned from our course, how to improve t-GTAs experiences, and the benefits identified by experienced GTAs (e-GTAs), who mentored these students. This discussion will highlight the next steps and how we see the future of GTA training in our department.

SERMACS 482

Specifications grading: Method to improve student retention and progression?

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Specifications grading, a type of mastery-based learning assessment protocol, has been employed in a wide variety of chemistry courses at Georgia Gwinnett College, including in courses that typically serve as "gateways" into a major or career path, such as general or nursing chemistry. These courses typically have high rates of D, F, and W grades, and the hope was that introducing a mastery-based system that encouraged students to make repeated attempts to demonstrate mastery of the material would help ameliorate this issue. This presentation will include a discussion of findings related to DFW rates and success in subsequent sequence courses, as well as an exploration of relationships between affective constructs and success in specifications grading courses.

SERMACS 483

Utilizing evidence-based pedagogies to make general chemistry more individualized and accessible to under-prepared students

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As governing bodies continue to reduce funding to higher education and resources become scarcer, instructors are forced to reckon with how best to serve much of our student populations. Implementing evidence-based pedagogies in large-enrollment chemistry courses has been shown to increase student learning gains. Application of literature-proven techniques, such as active-learning, flipped classrooms, student response systems, learning assistants, and metacognition, have occurred in a methodical fashion over a three-year period in large-enrollment general chemistry courses at USM. Students participated in weekly flipped class sessions facilitated by learning assistants that helped make instruction more individualized, promoted peer-to-peer learning, and fostered a sense of community. A review of assessments, challenges, and logistics experienced by the author regarding the implementation of these pedagogies in large general chemistry courses will be discussed. Regardless of the challenges of implementing these techniques, they have reduced the DFWI (% of students earning a D, F, W, or I) rate by more than 15%. Putting these research-based techniques into practice has led to greater student success and a new atmosphere surrounding General Chemistry at USM.

SERMACS 484

What student know and say about acid-base equilibrium

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Acid-Base Chemistry is an important but complex and difficult topic for students to grasp. This research study seeks to investigate students' understanding of acid-base equilibrium as they progress through general chemistry, organic chemistry, and biochemistry. This study is designed as a cross-sectional and a longitudinal study. Student interviews were conducted with semi-structured questions and a series of think-aloud questions were used to elicit students' understanding of acid-base equilibrium. The student interviews also included acid-base problems that the student should be able to solve depending on the course they were in at the time of the interview. The interviews were transcribed and analyzed qualitatively using the constant comparative method to code for recurring themes. This presentation will describe some of the preliminary results of this study and implications for teaching will be discussed.

SERMACS 485

Diversity and inclusion: Perspective from a quarter of a century in a minority serving institution

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According to the US Census Bureau report of Sept 2013 [1] while Blacks and Hispanics make up 11 and 15 % of the workforce they represent just 6 and 7 % of STEM jobs respectively. Similarly, the National Science foundation (NSF) in 2012 reported that of the 25,058 doctorates produced in the US, the minority breakdown was 0.27 % (American Indian/Alaskan Natives), 4.86 % (Blacks), 6.50% (Hispanics) compared to 73.5% whites. This presentation would review some of the underlying issues regarding this disparity and discuss strategies that might work toward achieving a diverse workforce and inclusion of all segments of the US population in the STEM field.

SERMACS 486

ACS PROF and NOGLSTP: Making history for LGBTQ+ chemical professionals

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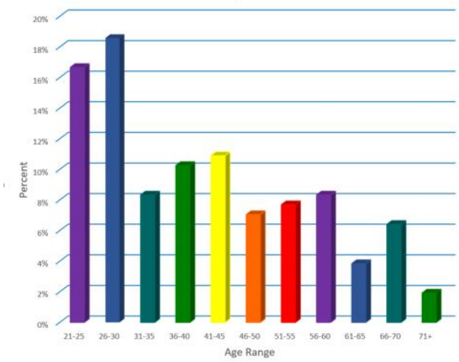
The American Chemical Society (ACS) Division of Professional Relations' (PROF) Subdivision of Gay & Transgender Chemists and Allies (GTCA) was created in 2010 to provide a home within the ACS and the division for LGBTQ+ chemical professionals not otherwise represented within the society. Since its founding, the group has grown to 185 members making it the second largest PROF subdivision. Also, with 44% of members classified as Younger Chemists (≤35 years of age), it is one of the youngest demographically – a critical population for the society overall. The subdivision has been responsible for programming at ACS National Meetings since 2011 with its most successful endeavor a symposium series highlighting the technical work of current graduate students and postdoctoral fellows – the first of which drew a standing room only audience of over 200. The first GTCA members were also members of the National Organization of Gay and Lesbian Scientists and Technical Professionals' (NOGLSTP) LGBT Chemists and Allies Caucus. This caucus had been holding social gatherings informally at ACS National meetings since the late 1990's. These gatherings became part of the official meeting program in 2002 and an ACS Presidential Event beginning in 2008. NOGLSTP serves LGBTQ+ STEM professionals in a vast array of technical fields and holds a biennial career summit known as *Out to Innovate*®. This presentation will further describe the history of these organizations' outreach to and support of the LGBTQ+ community through the years.



ACS PROF GTCA Member Age Demographics

SERMACS 487

American Chemical Society Committee on Chemists with Disabilities: Empowering ability

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ACS represents various aspects of the chemistry profession to help serve everyone as a member. It also represents the numerous interests of their wide-ranging membership base through the work of more than 40 committees. The Committee on Chemists with Disabilities (CWD) is one of them. The detail of how the CWD committee is working to promote awareness of chemists with disabilities. This includes their history, background, goals, internal and external involvements and results.

SERMACS 488

SACNAS: Achieving true diversity in STEM

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The Society for Advancement of Chicanos/Hispanics and Native Americans in Science (SACNAS) is an inclusive organization dedicated to fostering the success of Chicanos/Hispanics and Native Americans, from college students to professionals, in attaining advanced degrees, careers, and positions of leadership in STEM. Over the last 45 years, SACNAS has worked to ensure that those most underrepresented in STEM have the support they need to attain advanced degrees, careers, and positions of leadership. SACNAS has built a national network that is innovative, powerful, and inclusive, and has created opportunities for students and professionals to advance their education and careers. With over 6000+ members,115+ student and professional chapters, and the largerst cohort of emerging STEM leaders in the country, SACNAS represents a source of community that has generated a powerful peer network increasing the visibility of minority scientists at the local and national level.

SERMACS 489

Faculty research mentoring strategy at a PWI versus an HBCU

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A 2012 report from the President’s Council of Advisors on Science and Technology indicates that training scientists and engineers at current rates will result in a deficit of one million STEM workers to meet United States workforce demands over the next decade. The report further called for increased training of undergraduate students in STEM and to improve the first two years of STEM college experience in order to increase retention and graduation rates, and to maintain US competitiveness in global economy thereby meeting the technological challenges of the future. Furthermore, the Committee on Equal Opportunities in Science and Engineering (CEOSE) in its biennial report to congress in 2010 stated that achieving diversity in US education pipeline is essential to achieving a diversity in the domestic STEM workforce. CEOSE further recommended an augmentation of funding for Historically Black Colleges and Universities undergraduate program (HBCU-UP) and build capacity of Minority Serving Institutions (MSIs) to broaden participation of underrepresented minorities in STEM. Minority serving institutions face the challenges of attracting and retaining high achieving STEM majors in part due to severe financial needs of students coming into these colleges who are usually from low income families. It has been reported that mentoring involving hands-on activities and regular meetings between students and faculty enhance learning significantly at all levels of science education and increase retention of underrepresented minorities at HBCU’s. Diversity and inclusion has become an increasing focus on most college campuses with emphasis on attracting more students of color. However, recent reports have highlighted the inability of many institutions to provide the supportive environments for students of color to be successful and persist. Quality student mentoring provides professional personal support that enhances a student’s chances for degree completion and post-graduate admissions into a doctoral program. Beside learning knowledge and skills from mentors, mentees have hands-on training in research to increase STEM career readiness. Supportive mentoring and motivation are paramount to enhancing STEM career success of URMs irrespective of whether they attend an HBCU or a PWI.

SERMACS 490

Synthetic glycomics: Chemo-enzymatic synthesis of oligosaccharides, polysaccharides, glycolipids, glycopeptides and glycoproteins

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As one of the four fundamental classes of macromolecules that comprise living systems, glycans were found to play diverse roles in a wide range of biological processes. Understanding the structures and functions of glycans is central to understanding biology. However, glycans found in nature possess an inherited diversity, complexity, and in most cases low abundance, makes it extremely hard to access structurally defined glycans in sufficient amounts. Theoretically, due to the variable and multiple connectivity, five monosaccharides can form a pentasaccharide with over half a billion possible structures. On the other hand, in any real biological system, much smaller numbers of glycans than the theoretical number may exist since glycans are synthesized by glycosyltransferases (or other enzymes) with limited sugar to sugar connection variations. For example, it is estimated 20,000 to 30,000 glycan backbone structures may cover most mammalian glycomes. Thus, the perspective is that in the next decade majority of biologically important glycan backbone sequences will be synthesized by separation and chemo-enzymatic synthesis to provide structurally fullly defined **synthetic glycomics**. Post-glycosylational modification on the glycan backbone sequences will further produce the diversity and complexity of glycans. Here we will discuss Core Synthesis/Enzymatic Extension (CSEE) approach which offers a practical solution to synthetic glycomes. CSEE includes 1) convergent chemical synthesis of very limited numbers of small core structures, and 2) extension of the cores via enzymatic catalyzed reactions. For example, a library of N-glycans were prepared via CSEE in mg scales. Starting with 5 chemically prepared building blocks, 8 N-glycan core structures containing one or two terminal N-acetyl-D-glucosamine (GlcNAc) residue(s) were chemically synthesized via consistent use of oligosaccharyl thioethers as glycosylation donors in a convergent fragment coupling strategy. Each GlcNAc residue was then extended to 5 more structures (enzymatic extension I) by enzymatic reactions catalyzed by 4 robust glycosyltransferases, yielding a library of 73 N-glycans. Similarly, libraries of Human Milk Oligosaccharides and O-glycan have been synthesized. Our latest progress on chemo-enzymatic synthesis of N- and O-glycopeptides and glycoproteins, machine-driven production of oligosaccharides and glycopeptides, and large scale production of glycosphingolipids will be discussed.

SERMACS 491

Molecular basis for the evolution of methylthioalkylmalate synthase and chain elongation of methionine-derived glucosinolates

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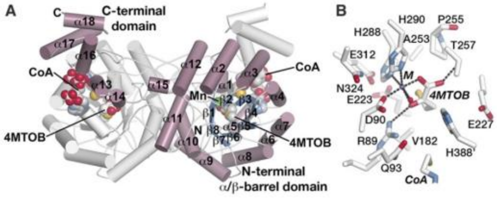
Methylthioalkylmalate synthase (MAMS), encoded by *MAM* genes, catalyzes the committed step in the side-chain elongation of methionine-derived aliphatic glucosinolates (GSL), and is believed to be evolved from the isopropylmalate synthases of leucine biosynthesis. The globally cultivated *Brassica* species possess diverse aliphatic GSL important for plant defense and animal nutrition; however, the molecular basis for the evolution of MAMS and elongation of methionine-derived GSL in *Brassica*e is poorly understood. Here we show that *Brassica* genomes encode multiple MAMS that are phylogentically interconnected but have differences in their expression profiles, 2-oxo substrate preference, and allelic conditions that account for diversity of aliphatic GSL across *Brassica* accessions. Further, the 2.1Å resolution x-ray crystal structure of *B. juncea* BjuA.MAM1.1 identifies key amino acid residues responsible for altering specificity toward 2-oxo substrates. Overall, these results provide the evolutionary and mechanistic foundation for diversification of different GSL profiles across globally-cultivated *Brassica* species.



Crystal Structure of B. juncea MAMS in Complex with CoA and 4MTOB. (A) Overall structure of BjMAM1-A. The dimer structure is shown as a ribbon diagram. In one monomer, the a-helices (rose) and b-strands (blue) of the structure are colored and labeled. The N-terminal a/b-barrel and the C-terminal extension domains are also indicated. Bound ligands are shown as space-filling models. (B) Residues interacting with 4MTOB and Mn21 (M) and surrounding the site are shown as stick models.

SERMACS 492

Fragment-based drug discovery targeting *P. aeruginosa* inhibitor of vertebrate lysozyme: Approach to active site-directed irreversible inhibition

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P. aeruginosa is an opportunistic pathogen that affects both the quality and longevity of life in patients suffering from cystic fibrosis. Antibiotic resistance complicates the efficacy of current treatments available for these patients. Further complicating matters, *P. aeruginosa* secretes a protein into its periplasm, named inhibitor of vertebrate lysozyme (IVY), to disrupt the bactericidal function of C type lysozyme. The H62 residue of an IVY monomer inhibits the active site of lysozyme through a strong interaction between amino acid residues E35 and D52 of lysozyme. The hypothesis that targeting IVY with drug fragments with a reactive warhead will irreversibly inhibit IVY, which will prevent it from binding lysozyme, allowing lysozyme to continue degrading the bacterium. Within this hypothesis, three objectives will be addressed: 1. Expression, purification, and backbone assignment of PaIVY 2. Primary and secondary screen by NMR and validation by biophysical methods 3. Optimization of lead fragments, which will be subject to biological assays. Primarily, the protein of interest will be transformed, expressed, purified, and subjected to backbone assignments by NMR. Second, a library of lead fragments is screened against IVY using a multiplexed NMR screening strategy along with quantification by other biophysical methods such as biolayer interferometry and thermofluor assay and covalently linked to a warhead. Fragment-based drug discovery is used as a method to develop novel leads in hopes of creating effective medications. The use of small organic fragments in conjunction with screening methods by heteronuclear single quantum coherence nuclear magnetic resonance showing chemical shift perturbation and saturation transfer difference nuclear magnetic resonance will be used to find binding capacity and location of the possible leads. binding fragments that localize near the active site residue of IVY is optimal. Crystallization of this compound with PaIVY will serve as a validation method for fragment binding. Other biophysical methods such as biolayer interferometry and thermofluor assay are utilized to determine the kinetics surrounding the interaction between the lead fragment and IVY.

SERMACS 493

More QACS, more questions: Investigation of next-generation quaternary ammonium compounds

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Quaternary ammonium compounds (QACs) have been used as disinfectants for years in residences, industries, and hospitals. While these compounds are some of the most effective methods of surface disinfectants available, their wide usage has also promoted the development of resistance in many pathogenic bacteria. This increasing threat necessitates a redesign of these remarkably simple and effective compounds. We have modified the structures of these compounds to develop bis-, tris- and tetraQACs which are much more potent than their original monoQAC counterparts. Previous work has investigated resistance mechanisms within methicillin-resistant *Staphylococcus aureus* (MRSA) in an attempt to design antimicrobials that will not promote resistance development. Our combined goal to design efficacious compounds with minimal toxicity continues through manipulation of QAC core structure, number and distribution of charges, and rigidity.

SERMACS 494

Human milk and the art of (microbial) war

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Bacteria are essential to maintaining host health and contributing to host illness. While growth and virulence are influenced by local parameters such as nutrient availability, our understanding of how a host and bacterium communicate to cause different outcomes is deficient. Accordingly, deciphering bacteria-host communication is necessary for understanding the evolution of chemical signal development and disrupting specific aspects of the information exchange. This seminar will focus on defining how human milk oligosaccharides (HMOs) maintain microbiome homeostasis over dysbiosis. We will also discuss the minimal pharmacophoric units responsible for antimicrobial activity and HMO potentiation of intracellular-targeting antibiotics.

SERMACS 495

Exploiting an NQO1 bioactivatable quinone for the selective treatment of *BRCA1/2*-mutant human breast cancers

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BRCA1/2 are tumor suppressor proteins involved in the maintenance of genomic stability by regulating DNA double-strand break repair through homologous recombination. Germ line mutations in *BRCA1/2* genes predispose individuals to developing breast and/or ovarian cancers. While these tumors exhibit sensitivity to platinum-containing therapy and poly(ADP-ribose) polymerase (PARP) inhibitors, there are few treatments that selectively target *BRCA1/2*-mutant breast cancers without normal tissue toxicity. Isobutyl-deoxynyboquinone (IB-DNQ) is an antitumor quinone that is selectively bioactivated in the presence of the two-electron oxidoreductase NAD(P)H:quinone oxidoreductase 1 (NQO1). NQO1 is constitutively overexpressed in a number of solid tumor types compared to associated normal tissues. NQO1 metabolizes IB-DNQ via a two-electron oxidoreduction, resulting in multiple rounds of redox cycling. Interestingly, *BRCA1/2*-mutant breast tumors also overexpress NQO1. However, the efficacy of IB-DNQ has not been evaluated in this subset of tumors. Here, we demonstrate that the NQO1-mediated metabolism of sub-lethal doses of IB-DNQ causes DNA damage in *BRCA1/2*-mutant breast cancer cells. DNA damage activates the repair protein PARP-1, leading to cell survival. However, inhibition of PARP-1 using Olaparib or Rucaparib after sub-lethal IB-DNQ treatment potentiates cell death. The findings gleaned from our studies provide insight into the mechanisms of IB-DNQ-induced lethality in NQO1$^+$, *BRCA1/2*-mutant breast tumors and thus expands the clinical use of PARP inhibitors for combination cancer chemotherapy.

SERMACS 496

Expanded genetic code to study protein post-translational modifications

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The activity of many proteins is controlled in vivo by post-translational modifications (PTMs). In particular, lysine residues are frequently modified by various acyl groups, and the small modifier protein, ubiquitin. A major limitation in the study of these modifications is preparing proteins that contain user-defined homogenous PTMs. Here I will discuss several tools we have developed that allow for genetic encoding of PTMs through the reassignment of the genetic code. These tools may useful in deciphering the molecular basis of PTM activity, and proteins that specifically recognize PTMs.

SERMACS 497

Unravelling the druggability of E3 ubiquitin ligase Nedd4 as a target for the alleviation of α-synuclein toxicity in Parkinson's disease

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Pharmacological strategies to treat Parkinson's disease (PD) are limited to replacement therapies and do not directly address the neuronal toxicity associated with disease pathology. Through efforts to better understand the mechanisms underlying PD and to identify novel druggable targets, E3 ubiquitin ligase Nedd4 was determined to be a target for the alleviation of cellular toxicity induced by aggregation of PD-associated protein α-Synuclein. Specifically, treatment with a small molecule with an N-arylbenzimidazole (NAB) scaffold alleviated α-synuclein toxicity phenotypes in a Nedd4-dependent manner. Despite its potential as a druggable target as determined through phenotypic screens, Nedd4 is a non-canonical target due to its lack of discrete active site and its complex mechanism which depends on protein-protein interactions and intramolecular conformational changes. Through biophysical, kinetic, and proteomics-driven investigations, we are using NAB as a chemical probe to unravel the tunability of Nedd4 conformation, activity, and specificity to improve our understanding of its druggability as a novel target in the context of α-synuclein associated PD.

SERMACS 498

Metabolomics-based differentiation of gram-positive bacterial strains

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The increase of drug-resistant bacterial infections has compelled health-care professionals to treat patients using a combination of antibiotics across a broad spectrum. It is crucial to determine methods for rapid and reliable susceptibility testing. Liquid chromatography coupled to mass spectrometry is an excellent tool for detecting secondary metabolites; however, the most abundant peaks on the chromatographic profiles are often ions from the complex growth media or commonly produced metabolites. In this study, we used multivariate statistical analysis to identify unique metabolites for 11 different strains of bacteria including Enterococcus faecalis, Listeria monocytogenes, Staphylococcus lugdunensis, Staphylococcus saprophyticus, 3 strains of Staphylococcus epidermidis, and 3 strains of Staphylococcus aureus. The ultimate goal of this study is to develop a library of unique metabolites that can be used for bioassay development, drug discovery, or for quick species identification.

SERMACS 499

Tunable chemistry for global discovery of protein function and ligands

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Covalent probes serve as valuable tools for global investigation of protein function and ligand binding capacity. Despite efforts to expand coverage of residues (e.g. serine, cysteine, and lysine) available for chemical proteomics, a large fraction of the human proteome remains inaccessible with current activity-based probes. Here, we introduce novel covalent chemistry for developing probes with broad applications for chemical proteomics. We show our chemoproteomic probes can be tuned for site specificity against nucleophilic residues detected in lysates and live cells. Using our novel probes, we discovered druggable sites that are enriched in enzymatic, protein-protein interaction, and nucleotide recognition domains, and can be targeted for modulating protein function. Collectively, we describe new biocompatible chemistries that offer vast tunability for chemical biology investigations of the human proteome.

SERMACS 500

Dynamic polymer biointerfaces

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A number of practically important problems related to medical treatment technologies, biotechnologies, sensors, food packaging, personal care, to name a few, involve interactions between biomaterials and synthetic materials in humid and aqueous environments. These soft materials are reach in functional groups and they typically reveal a complex phase behavior affected by variations in humidity, temperature and chemical composition of their environment. Ability to regulate a balance between attractive and repulsive interactions in such systems is a very efficient method to realize various scenarios for programming of the interactions between materials and trigger the response of biological systems (live cells and tissues). Such complex interactions of synthetic interfaces relay on their complex structures through combinations and 3D alignment of materials' microphases and functional molecules. Here, several examples of engineered polymer interfaces are discussed to demonstrate design concepts to approach preprogrammed responses at nanostructured interfaces.

SERMACS 501

Interfacial behavior of soft thermoreversible microgel particles on flat surfaces

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Poly-*n*-isopropylacrylamide (NIPAM) microgel particles are multifunctional materials, which possess the biocompatible properties of polymer hydrogel films and the emulsifying properties of solid colloidal particles. NIPAM microgel particles are best known for their ability to drastically change their volume in response to changes in temperature and pH. Others have gone to great length to describe the material properties of NIPAM microgel particles as dispersions in suspension, at the air/water interface, and at the fluid/fluid interface, to stabilize oil and water phases in complex fluids. Contrarily, far less is known on how these deformable microgel particles interact with flat surfaces, how as they adsorb and desorb to interfaces, and how adhesion to surfaces affect swelling behavior. In this work, the interfacial properties of deformable NIPAM microgel particles were investigated by measuring the adhesion between surface-functionalized NIPAM particles (ranging in crosslinking density and thereby stiffness) and flat, adhesive surfaces. Surface adhesion was characterized by exposing biotinylated-microgel particles to flat, avidin-functiontionalized surfaces and particle spreading was measured with atomic force microscopy (AFM). The measurements revealed that microgels with 0% n,n'methylenebisacrylamide (BIS) crosslinking agent were most deformable and spread farthest along the adhesive surface, compared to microgels containing 2% BIS. NIPAM microgels were surface-functionalized via EDC/sulfo-NHS carbodiimide chemistry with biotin and deposited on to avidin-functionalized glass coverslips. The results provide new information on the adsorption of deformable microgel particles to flat surfaces, which becomes specifically important for applying these materials to new applications, such as thermo-responsive coatings.

SERMACS 502

Polymer interpenetration and chain connectivity on the local glass transition and dynamical gradients near and across polymer interfaces

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The strategic use of interfacial interactions to perturb local properties, combined with an optimized morphology, could lead to numerous designer materials with advanced performance where the desired global properties are obtained from an amalgam of local property changes. To achieve this grand goal, a detailed understanding of how interfaces perturb local properties are needed, along with knowledge of the global macroscopic characteristics resulting from these local effects. I discuss our efforts to understand how various interfaces perturb local material properties and how different experimental techniques contribute to this picture. Our group has recently employed a localized fluorescence method to measure the profile in local glass transition temperature $T_g(z)$ across glassy-rubbery polymer interfaces. For a single interface between semi-infinite domains of polystyrene (PS) and poly(*n*-butyl methacrylate) (PnBMA), the local $T_g(z)$ profile was found to be extremely broad and asymmetric, spanning 350-400 nm as the local $T_g(z)$ transitioned the 80 K difference in bulk T_gs, with subsequent studies finding this profile to be common to a range of weakly immiscible systems. The observed $T_g(z)$ profiles were found to be strongly dependent on the interface formed between the two polymer domains during thermal annealing and on the finite size of domains. Related studies on polymer films have demonstrated similar long range $T_g(z)$ profiles near PS end-grafted silica substrates, with the largest $T_g(z)$ increase of 50 K next to the substrate corresponding to a low grafting density coinciding with the "mushroom-to-brush" crossover regime, and having a $T_g(z)$ profile comparable to that observed for a polymer-polymer interface. More recent efforts have focused on correlating these local measures of T_g with global measures of glassy physical aging dynamics using ellipsometry. By studying single layer PS films across a wide range of molecular weights, we have observed variations in glassy dynamics with chain connectivity, supporting the notion that chain connectivity may play an important role in modifying how dynamical perturbations propagate in the material. We also describe our attempts to develop a similar ellipsometric thermal analysis method to extract the physical aging response of glassy PS domains in contact with rubbery PnBMA domains. In doing so, we address the role that finite domain size has on this phenomenon.

SERMACS 503

Study of kinetics and functionalization efficiency of sonochemical assisted nanoscale anion exchange resins for water purification

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Atom transfer radical polymerization (ATRP) is one of the industrially useful controlled radical polymerization processes that can be synergistically linked to sonochemistry for initiation, chain growth and chain-end functionalization. This work focuses on sonochemical assisted atom transfer radical polymerization (SONO-ATRP) using no/low amounts of reagents achieving excellent control on polydispersity and high functionalization density of polyelectrolyte on single-walled carbon nanotubes (SWCNT) producing nanoscale functionalized resins for safe, fast and affordable water purification solutions. SONO-ATRP of vinyl benzyl trimethyl ammonium chloride (vbTMAC) was performed in aqueous medium in absence of any external initiator or reducing agent utilizing ppm levels of catalyst/ligand complex. Polyelectrolyte functionalized SWCNT (NanoResin) showed high capacity adsorption of analyte when used as thin films for water purification purposes. Kinetic plots indicated first order kinetics with respect to monomer concentration in presence and absence of sonochemistry. Apparent activation energy of poly(vbTMAC) for radical propagation using ARGET ATRP in aqueous medium calculated from slope of Arrhenius plot was 21.1 ± 1.42 kJ mol^{-1}. Well-controlled polyelectrolyte strands having low polydispersity were obtained having high monomer conversions (93%) at room temperature using thin probe sonicator (144 W cm^{-2}, 20 kHz) in 4 hours as compared to 37 hours reflux conditions. Low temperature (10 °C) functionalization of polyelectrolyte strands of vbTMAC on single-walled carbon nanotubes (SWCNT) was achieved in absence of reducing agent that show similar functionalization density in 2 hours duration as 12 hours reflux. Sonochemistry synergistically aids in ATRP synthesis of poly(vbTMAC), dispersion and conformal functionalization of SWCNT formulating nanoscale functionalized resins for water purification solutions. These functionalized NanoResin membranes demonstrated Thomas Model breakthrough curve fitting with a maximum adsorption capacity of 144. ± 0.984 mg g^{-1} and water flux of 285.92 L m^{-2} h^{-1} bar^{-1} at 1 atmospheric pressure. These few μm thick membranes could be easily regenerated and reused without degradation or loss in adsorption capacity. We will present study of influence of sonochemistry in providing a green and sustainable platform for SONO-ATRP modified nanocomposite and polyelectrolyte syntheses and kinetics for industrial applications.

SERMACS 504

Polymer coatings for aerospace applications

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Aircraft exteriors are painted with polymer coatings to protect the airframe from operational and environmental degradation and to meet appearance requirements, which include airline branding for commercial operators and camouflage schemes for military aircraft. Conventional qualified aerospace coating systems are formulated to meet many demanding requirements such as resistance to hydraulic fluid, corrosion, ultraviolet radiation, and rain and particle impact. The next generation of coating systems will additionally need to have multifunctional properties. Examples of such properties that can contribute to the design of fuel-efficient, light weight aircraft with reduced operating costs as well as the challenges associated with the development and application of multifunctional coatings at different substrates will be presented

SERMACS 505

Counterion condensation in polymer electrolytes and its role on ionic conductivity in electrochemical processes

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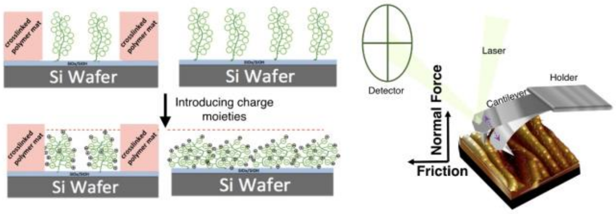
Ion-conducting polymer electrolyte membranes, resins, and binders are central components to many types of electrochemical processes (e.g., fuel cells, electrolysis, and electrodeionization). Ionic conductivity is an important property of these materials as it controls the thermodynamic efficiency of electrochemical systems operated at high current density. Many studies correlate nanostructure attributes in polymer electrolytes to ionic conductivity. However, the impact of counterion condensation, a proxy for the extent and strength of ion-pairing, on ionic conductivity has received less attention and is not clearly known. This talk highlights our effort to study counterion condensation in model thin film block copolymer electrolytes with precisely defined nanostructures that are defect free and have long-range order. These molecularly engineered nanostructures were attained through the principles of directed self-assembly and absolve interferences that structural defects cause when trying to correlate counterion condensation to ionic conductivity.



SERMACS 506

Pattern-based metal cation sensing at trace levels in water using fluorescent polymeric receptors

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Metal cations can have severe negative impacts on human health and the environment. Therefore, rapid *in situ* detection is important. Optical spectroscopic techniques such as UV-vis absorbance and fluorescence spectroscopy allow for an inexpensive, simple, and portable means to obtain data immediately after sample collection. The low concentrations relevant for environmental and biological applications, however, present a major challenge with this approach. Moreover, many sensors or receptors are only selective for one or two metal cations, and are not responsive to other metals that may be present in the sample. However, well established pattern recognition methods are able to recover selectivity for a large number of analytes using only a small number of receptors. A series of four synthetic, highly fluorescent polymers were used as metal ion receptors in a sensing array. These polymers contain a common fluorene core separated by conjugated spacer groups and a variety of pendant arms. These structural modifications can cause a significant change in the optical signature of the polymer. Compared to small-molecule fluorophores, conjugated polymers provide much greater sensitivity through π-mediated signal amplification along the backbone of the polymer. Moreover, polymers offer multiple binding sites, which can lead to improved observed affinity for the analytes of interest. These effects have allowed us to reach parts-per-trillion sensitivity, and are currently being used for trace metal cation detection in complex media such as seawater. As we continue to study the properties of these polymers, we will be able to optimize our array to achieve improved resolution and differentiation of metal cations even in natural seawater samples from the Gulf coast.

SERMACS 507

Ultra-stretchable conductive polymer complex with repeatable autonomous self-healing ability

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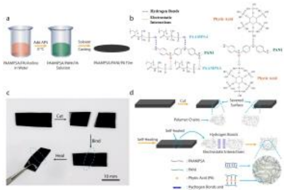
Wearable strain sensors are essential for the realization of applications in the broad fields of remote healthcare monitoring, soft robots, immersive gaming, among many others. These flexible sensors should be comfortably adhered to skin and capable of monitoring human motions with high accuracy, as well as exhibiting excellent durability. However, it is challenging to develop electronic materials that possess the properties of skin—compliant, elastic, stretchable, and self-healable. This work demonstrates a new regenerative polymer complex composed of poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAAMPSA), polyaniline (PANI) and phytic acid (PA) as a skin-like electronic material. It exhibits ultrahigh stretchability (1935%), repeatable autonomous self-healing ability (repeating healing efficiency > 98%), and quadratic response to strain ($R^2 > 0.9998$), linear response to flexion bending($R^2 > 0.9994$) — outperforming current reported wearable strain sensors. The deprotonated polyelectrolyte, multivalent anion, and doped conductive polymer, under ambient conditions, synergistically construct a regenerative dynamic network of polymer complex crosslinked by hydrogen bonds and electrostatic interactions, which enables ultrahigh stretchability and repeatable self-healing. Sensitive strain-responsive geometric and piezoresistive mechanisms of the material owing to the homogenous and viscoelastic nature provide excellent linear responses to omnidirectional tensile strain and bending deformations. Furthermore, this material is scalable and simple to process in an environmentally-friendly manner, paving the way for the next generation flexible electronics.



a) Schematic illustration showing the synthesis of PAAMPSA/PANI/PA polymer complex. b) Cross-links forming a regenerative dynamic network by hydrogen bonds and electrostatic interactions between PAAMPSA and PA with PANI. c) Photographs of autonomous self-healing process after 3 hours, blue dashed circles show the healed severed-strip. d) Schematic diagram of the self-healing process.

SERMACS 508

Beyond CP*: Mechanism guided design of a new rhodium complex for enantioselective C–H functionalization

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The development of new reactions and catalysts for the oxidative cross-coupling of C-H bonds with C-H, N-H and O-H bonds will be discussed. Strategically, these reactions allow for the synthesis of complex molecules from their constituent components, minimizing the need for functional group activation and manipulation. Specifically, rhodium and iridium catalysts for oxidative allylic C-H functionalization of terminal, di- and trisubstituted olefins will be presented. Mechanistic insights leading to new reaction protocols for regiochemical control, and new catalyst designs that facilitate enantioselective reactions will be described. Illustrative examples of emergent applications will be provided.

SERMACS 509

Understanding catalyst substrate interactions and reaction selectivity

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Electrostatic interactions, such as cation-pi interactions are hypothesized to be one of many controlling factors in reaction selectivity, and we are interested in obtaining a better understanding of this supramolecular interaction as it relates to asymmetric catalysis. Our group uses physical organic techniques, such as linear free energy relationships, to understand reaction mechanisms which includes the intermolecular interactions that aid in controlling these reactions. In this talk we will show how we use our silylation-based kinetic resolution as a model reaction to explore how changes in the pi system of the substrate affect the selectivity of the reaction. Since the hypothesized intermediate is a silylated cationic catalyst, changes in the substrate's pi system should affect the affinity to the catalyst which ultimately affects the selectivity. The effect of sterics and electronics will be presented as well as computational modeling to further understand this interaction.

SERMACS 510

Photochemical cyclization techniques: Synthesis of carbetocin

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Oxytocin (OT) is a naturally-occurring human hormone and neurotransmitter that is involved in myriad physiological and psychological phenomenon. Carbetocin (CT) is a heat-stable derivative of OT used in postpartum hemorrhage therapy, where one

sulfur atom of the native disulfide bond is replaced by a carbon atom. Drawing inspiration from the thiol-ene coupling (TEC) reaction, which has shown high efficiencies in polymer and materials chemistry settings, our research concerning photochemical construction of thioether linkages via TEC reactions in complex settings has facilitated improved synthetic access to carbetocin.

SERMACS 511

Pericyclic reactions in the total synthesis of natural products

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While there are many strategies for the construction of natural product scaffolds, one of the most powerful available to synthetic chemists is the use of pericyclic reactions. In this manner, it is not only possible to build complex skeletons but also to convey stereochemical information to distant positions that might otherwise be difficult to control. We will present some recent examples of this in our efforts toward the synthesis of several natural products.

SERMACS 512

Synthesis of α- and β-carbolines via tandem catalysis

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Pyrido[2,3-b]- and pyrido[3,4-b]indoles, commonly known as α- and β-carbolines, respectively, are unique pharmacophores found both in Nature and in drug-like molecules. Strategies towards their synthesis are numerous, but typically do not allow for the simultaneous construction of additional rings within the same flask. We will describe new methodology that employs transition metals to prepare annulated α- and β-carbolines. Specifically, we will demonstrate that two different pathways can be used to synthesize 1-aryl β-carbolines and 2-aryl α-carbolines. We will show that these molecules can be prepared using either a stepwise Rh(I)-catalyzed sequence or a tandem Pd(0)-catalyzed reaction with good yields and broad substrate scope.

SERMACS 513

Development of alkyne metathesis catalysts for organic materials synthesis

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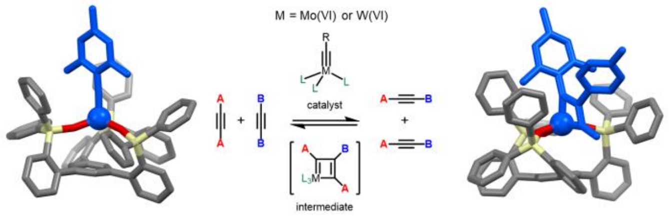
Alkyne metathesis is a powerful method to synthesize alkyne-linked molecules under thermodynamic control. It has recently seen a resurgence with the development of highly-active catalysts, typically based on Mo(VI) and W(VI) alkylidynes. Alkyne metathesis has been effective in preparing natural products, and variety of organic material such as shape-persistent macrocycles, cages and covalent organic frameworks. However, compared to olefin metathesis, alkyne metathesis catalysts are still in its infancy. There still exist great room for improvement in catalyst reactivity, substrate scope, solvent compatibility, and moisture/air tolerance. Here, new ligands and catalysts will be introduced to further understand and improve the design rule behind alkyne metathesis catalysts.



SERMACS 514

Benzimidazolyl-metal complexes as simple bifunctional templates in sustainable catalysis

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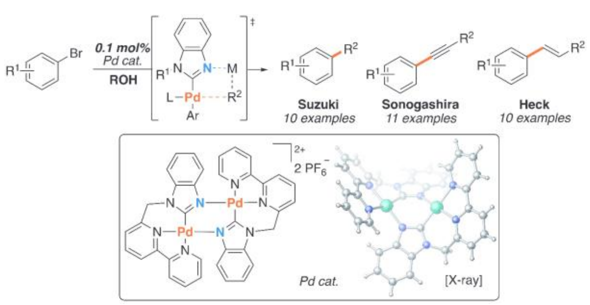
A new class of simple bifunctional complexes bearing 2-benzimidazolyl ligands is reported and shown to be a highly effective platform in diverse catalytic cross-coupling reactions. The effect of the rigidity and conformation of the ligand scaffold was evaluated and shown to have a crucial impact on catalytic activity. In optimal conditions, Suzuki-Miyaura, Heck and copper-free Sonogashira-type couplings can all be performed in excellent yields using only 0.1 mol% of catalyst, in aqueous or alcohol solvents. The bifunctional character of these complexes has been studied and is proposed to be responsible for their high catalytic activity, where the free *N*-functionality of the ligand is proposed to accelerate (trans)metalation events via intramolecular Lewis or Brønsted base assistance.



SERMACS 515

Activating silent biosynthetic gene clusters in fungi via co-cultivation

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Fungi have evolved strategies to survive in complex environments, such as the ability to respond chemically to different environmental cues. This, coupled with genomic data indicating that numerous biosynthetic gene clusters are silent, allows us to take advantage of these traits by co-culturing to activate the untapped biosynthetic potential of fungi. This study aims to uncover and activate silent gene clusters to search for unique bioactive secondary metabolites. To evaluate this, and to gain insight into the secondary metabolic arsenal fungi possess, we co-cultured *Aspergillus fischeri*, a genetically tractable fungus that produces a suite of mycotoxins, with *Xylaria cubensis*, a fungus that produces the fungistatic compound and FDA-approved drug, griseofulvin. The co-culture exposed the activation of several secondary metabolites that were not present in either monoculture. During this experiment a structurally novel secondary metabolite was characterized that was not previously present in the monocultures, and it exhibited cytotoxic activity. This demonstrates that by activating silent biosynthetic gene clusters within fungi structurally novel metabolites can be characterized that have the potential to be new drug scaffolds.

SERMACS 516

Bacterial and fungal ribosome RNA targeted antimicrobials

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Aminoglycosides inhibit bacterial growth by binding to the A-site decoding region of the bacterial 16s ribosomal RNA (rRNA) within the 30S ribosomal subunit. Herein, we describe an approach to develop compounds that are selective for bacterial rRNA and include motifs such as aminosugars, amino acids and nucleobases. First, we have developed a screening assay that rapidly identifies compounds that discriminate between the two model rRNA structures. This approach, coupled with a rapid solid phase methodology for aminoglycoside variants, has identified active antimicrobials (against wild type and mutant strains) that show large differences in binding affinity for the *E. coli* A-site and the human A-site. The methodology for synthesizing, screening for both ribosomal binding/selectivity and bacterial growth inhibition, and rapid analysis of the data provides a systematic method for identification of bacterial ribosome specific antibacterial that can evade bacterial resistance pathways.

SERMACS 517

Antibiotic resistance: Protons, promiscuity and polymerases

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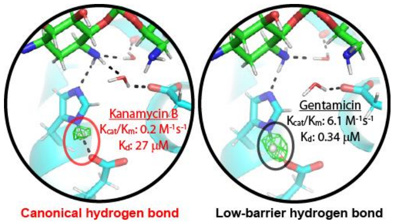
Pathologically relevant microorganisms have evolved elaborate mechanisms to escape the bactericidal effects of modern antibiotics. Entire classes of antibiotics are rendered useless through redundant processes, many of which are not fully understood in detail. Aminoglycoside antibiotics such as kanamycin, tobramycin, and neomycin are covalently inactivated through a class of enzymes known as aminoglycoside modifying enzymes (AGMEs). Although the aminoglycosides are chemically, structurally and topologically diverse, some AMGEs are able to inactivate as many as fifteen from the two main classes of aminoglycosides, the kanamycin- and neomycin-based antibiotics. The AGME mechanism of modification can be classified into three different subtypes based on the functional group they covalently transfer, namely, *O*-phosphotransferases, *O*-nucleotidyltransferases and *N*-acetyltransferases. Using a combination of X-ray and neutron crystallographic studies of aminoglycoside acetyltransferases and a nucleotidyl transferase we probe the underlying enzyme mechanism at a proton level of detail. These studies allow for unprecedented chemical insights into these pathologically relevant enzymes and protein superfamily, while suggesting the design requirements of the next generation of aminoglycoside antibiotics.



SERMACS 518

Computer-aided design and synthesis of potential pharmacophores

Siva S. Panda, *sspanda12@gmail.com. Chemistry & Physics, Augusta University , Augusta, Georgia, United States*

Computational tools are useful to interpret and guide to accelerate the drug design process. Computer-aided drug design (CADD) in drug discovery is to screen out a large number of compounds and identify the leads. Structure-based drug design (SBDD) and ligand-based drug design (LBDD) are the two general types comes under computer-aided drug design (CADD) approaches. We have utilized both SBDD and LBDD for our drug development program. However, we have used a quantitative structure-activity relationship (QSAR) and 3D-pharmacophore techniques more in the development of new drug-like molecules. We have successfully designed and synthesized potential drug-like molecules for microbial infections, inflammation, and breast cancer. We used SBDD and QSAR to develop potential antimicrobial drug candidates. Recently, we executed molecular docking study is to identify whether curcumin modified conjugates modulate T47D and to identify potential binding sites for well-established ER- Breast cancer target. The experimental data also validated by the computational data. The details of the studies will be discussed in the symposia.

SERMACS 519

Structure-based design of panthothenate kinase modulators for the treatment of COA deficiencies

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The discovery, design and structure-guided development of the Pantazine class of Pantothenate kinase modulators will be discussed.

SERMACS 520

Type IV inhibitors of B-Raf kinase that block dimerization and overcome paradoxical MEK/ERK activation

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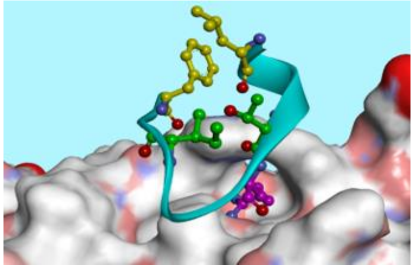
Despite the clinical success of B-Raf inhibitors like vemurafenib in treating metastatic melanoma, resistance has emerged through “paradoxical MEK/ERK signaling” where transactivation of one protomer occurs as a result of drug inhibition of the other partner in the activated dimer. The dimerization interface of B-Raf plays a key role in the signaling potential of wildtype B-Raf in cells with mutant Ras and has been proposed as a potentially druggable interface in targeting cancers resistant to ATP competitive drugs. Proof of concept for a structure-guided approach is described through the design and synthesis of macrocyclic peptides that mimic a loop region present in the B-Raf dimerization interface (DIF). High affinity DIF inhibitors of B-Raf that block paradoxical signaling in malignant melanoma cells have been identified through this approach and a structure-activity relationship defined. In addition, the REPLACE strategy has been applied to successfully identify fragments replacing key peptide determinants to generate more drug-like compounds. The lead compounds identified are type IV kinase inhibitors and represent an ideal framework for conversion into next generation BRAF inhibitors through macrocyclic drug discovery.



SERMACS 521

Data-driven construction of innate immune checkpoint inhibitors with controlled polypharmacology

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Controlling which particular members of a large protein family are targeted by a drug is key to achieving a desired therapeutic response. In this study, we report a rational data-driven strategy for achieving restricted polypharmacology in the design of innate immune-checkpoint anti-tumor agents selectively targeting the TYRO3, AXL and MERTK (TAM) family tyrosine kinases. Our computational approach, based on the concept of FRAgments in Structural Environments (FRASE), distills relevant chemical information from structural and chemogenomic databases to assemble a three-dimensional inhibitor structure directly in the protein pocket. Target engagement by the inhibitors designed led to disruption of oncogenic phenotypes as demonstrated in enzymatic assays and in a panel of cancer cell lines, including acute lymphoblastic and myeloid leukemia (ALL/AML) and non-small cell lung cancer (NSCLC). Structural rationale underlying the approach was corroborated by x-ray crystallography. The lead compound demonstrated potent target inhibition in a pharmacodynamic study in leukemic mice.

SERMACS 522

Navigating teaching, research, service and motherhood at a primarily undergraduate institution

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Though roughly half of the nation’s undergraduate students in chemistry are women, only 20% of the chemistry faculty at the top 50 universities are women. Women often cite work-life balance as a reason for bypassing an academic career. This talk will provide insights gained over twenty years navigating an academic career at a primarily undergraduate institution while also raising a family. Observations, literature, anecdotes, and advice stemming from a path through tenure to Department Chair will be discussed, focusing on practical advice for women in chemistry just starting this journey.

SERMACS 523

Barriers in the laboratory and perceptions of femininity

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Part of a panel discussion on the Issues faced by women in Chemistry. This is a story of one female chemist's struggles in the lab stemming from her perceived "disinterest" in scientist based on her appearance and outside interests.

SERMACS 524

Pregnancy and parenting in academia

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When is the right time to have a child during an academic career? How do you navigate the job market and assess the family friendliness of a workplace or department while not opening yourself up to discrimination? As a department and a faculty member, how do you convey that you and your colleagues are welcoming and supportive to faculty members with families while staying within legal bounds of topics you can and can't discuss with candidates? This presentation will explore these topics and present my personal take on these concerns. As someone who had a child in graduate school and a second during my postdoc while on the academic job market, I'll share my experiences as well as evidence-based statistics and thoughts for ways we can improve support for female chemists who are or want to be parents.

SERMACS 525

Succeeding in academia: Keep calm and say "no"

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While the number of female chemistry professors has risen significantly over the past 20 years, the representation of women in tenure-track positions remains disproportionate. Those women who do obtain academic positions often continue to experience inequality in the expectations placed on them based on their gender. The purpose of this presentation will be to inform female chemistry faculty about the growing body of literature on gender-specific faculty expectations and empower them to find ways to take action and shift the balance of expectations towards equality in their departments. Disparities in faculty expectation lead to heavier service burdens and increased time spent on emotional labor by women—both factors which contribute to faculty burnout. The burden of "invisible work" may also prevent women from advancing into full professorship or upper administration roles. Therefore, to succeed and persist in academia, modern women must learn to respond to incidents of gender bias in their careers in ways that align with and support their own values and goals. To support female academic chemists in obtaining this essential skill, this presentation will summarize current evidence-based findings on gender bias in academia, with an eye toward those differences most relevant to female chemistry faculty. As a junior female chemistry faculty member, I assert that a faculty member at any stage in their career has the ability to impact the expectations placed on them by others based on their gender. However, I also acknowledge that learning to respond to such incidents requires practice and experimentation. While this may appear high-risk for a pre-tenure faculty member, my presentation will encourage attendees to consider the long-term challenges and professional consequences of not taking action. After discussing the importance of addressing gender bias, we will conclude with a discussion of methods for identifying and responding to inappropriate or gender-motivated requests (i.e. how to say no) sourced from literature, personal experience, and welcome audience participation.

SERMACS 526

My experience as an inexperienced negotiator

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Are you interested in what happens after the job offer? The presentation will navigate through a new faculty's journey of obtaining a faculty position and share tips on negotiating salary and startup packages.

SERMACS 527

Encouraging success and access to opportunities for women and people of color at a primarily white undergraduate institution

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Research suggests that when underrepresented students in STEM are mentored by research advisors, they have a greater chance of completing a STEM degree and pursuing a STEM career. However, underrepresented populations might not know how to navigate their undergraduate career toward research, and therefore miss out on the benefits of mentorship. The important question that arises from these two statements is this: how can faculty and instructional staff best support the needs of women, students of color, and other underrepresented groups in the sciences? With a small internal grant from our university's Office of Multicultural Affairs and Division of Natural Sciences, three faculty members from chemistry, biology, and health & wellness promotion hosted four seminars during the 2018-2019 academic year focused on 1) participating and thriving in undergraduate research, and 2) preparation for life after college via graduate or professional schools. A total of 57 students attended the events, and participants were asked to submit anonymous post-event surveys. Although female students comprised only 44% of the STEM student body, they made up the highest percentage of attendees (67%). Additionally, while there was a high turnout of female attendees at the first event (100% of survey respondents), there were no survey respondents of color. Both the second and third seminars had a higher percentage of racial and ethnic minorities (50% and 44%, respectively) than the campus-wide percentage (22%). We qualitatively assessed that these programs impacted undergraduate women and minority students by welcoming them into a space that has traditionally excluded them.

SERMACS 528

Finding your voice and taking up space

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“Don’t be afraid to take up space” is common advice given to women. How does this advice translate specifically to women in science, in academia and in industry? Combatting imposter syndrome, navigating department and workplace politics, and overcoming years of internalized societal conditioning can be difficult. As a member of the Women in Science panel, I intend to share my experiences finding my voice and taking up space in male-dominated industrial workplaces and later in academia.

SERMACS 529

Empowering undergraduate students through chemical biology research

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Retention of women in STEM fields is linked to a variety of factors including participation in undergraduate research. Students join my lab at the University of Richmond because of their motivation to understand and combat disease states. They use a variety of chemical and biological techniques to answer their research questions. As they grow as researchers, they are encouraged to direct their projects, mentor new students, and contribute to all aspects of manuscript publication. Alumni of my research lab have continued on to medical school, graduate school, and post-baccalaureate programs in STEM fields. I will present stories of the students, the work they have done, and their career paths after graduation.

SERMACS 530

Recent crystallographic studies of fullerenes and endohedral fullerenes

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Obtaining structural information on fullerenes and endohedral fullerenes is difficult because these molecules are generally available in rather miniscule quantities, at least when initially discovered. Additionally, structural characterization becomes increasingly difficult as fullerene size increases because of the number of isomeric structures that can form. For example for $C_{60}$and C_{70}, there is a unique carbon cage structure that obeys the isolated pentagon rule (IPR), which requires every pentagon to be surrounded by 5 hexagons, but for C_{90}there are 46 IPR-obeying isomers, while for C_{100}there are 450 structural isomers. Single crystal X-ray diffraction does allow for collecting definitive, three dimensional structural information on fullerenes and endohedral fullerene, where not only the cage structure but the structure of the contents of the cage can be identified. This talk will focus on some recent crystallographic studies of various endohedral fullerenes.

SERMACS 531

Actinide endohedral metallofullerenes: From cage selection to actinide–actinide interactions

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For almost two decades, intensive work from experimental and theoretical groups has made it possible to advance in the understanding of structural and electronic properties of endohedral metallofullerenes and cluster metal fullerenes. Hence, several groups have proposed diverse rules related with the relative stability of fullerene cages. All of them considered the potential energy when they predict the stability of IPR and non-IPR isomers based on the ionic model, in which the guest transfers usually between three and six electrons to the hosting carbon cage. Those guidelines have explained why the *highly* symmetric $C_{80}(I_h)$ cage is the preferred fullerene when there is a transfer of six electrons, like in the well-known $Sc_3N@C_{80}$, or in many other examples, such as $Lu_3N@C_{80}$, $La_2@C_{80}$, $Y_3@C_{80}$, etc. In endohedral fullerenes with four or less electron transfer between host and guest, there is not a prevalent structure, like $C_{80}(I_h)$, and the diversity of captured carbon cages is larger, the theoretical prediction of the most abundant species to be formed in a K-H reactor being much more difficult. In addition to the relative potential energy, it is also necessary to consider the enthalpic and entropic contributions to the stability of the endohedral fullerenes. A systematic theoretical analysis for a series of $A@C_{2n}$ fullerenes with A = Th and U, in combination with accurate experimental characterization, have allowed us to show that the structures of $A^{4+}@C_{2n}^{4-}$ species are different from those of cluster fullerenes, such as $Sc_2O^{4+}@C_{2n}^{4-}$, $Sc_2S^{4+}@C_{2n}^{4-}$or $Sc_2C_2^{4+}@C_{2n}^{4-}$. Here, we will discuss on the electronic structure and the peculiarities in host-guest interactions and cage selection in actinide endohedral metallofullerenes. We will also analyze the actinide-actinide interactions in dimetallic endohedral metallofullerenes.

SERMACS 532

Actinide-based buckyball maracas: Fullerene cages as nanocontainers that stabilize monometallic and actinide clusters inside

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Monometallic uranium endohedral fullerene compounds with formula $U@C_{2n}$ where 2n = 72, 74, 76, 78, 80, 82, 84 86, 88 and 90 have been prepared in an arc-discharge reactor using U_3O_8 as the starting material. Many of these have been purified using HPLC techniques and have been fully characterized using many techniques, including MALDI MS, UV-Vis, electrochemistry, etc, but more importantly, with single crystal X-Ray diffractometry. Interestingly, the majority of these compounds obey the isolated pentagon rule (IPR) so all five-membered rings are adjacent to five six-membered rings, but there are some exceptions, namely U@C_{76} and U@C_{80}, which possess non-IPR carbon cage structures. The reason for these exceptions is due to strong interactions of U with the cage via the metal 5f orbitals. More interestingly we have observed never-reported U-based clusters with formula U_2X (X = C, N, O, and S) encapsulated inside C_{2n} with 2n = 72, 78 and 80. More recently we have isolated UGd@C72 and UGd@C_{78} and also fully characterized these. The most recent structural and properties on some of these compounds will be presented and discussed.

SERMACS 533

Single-electron lanthanide-lanthanide bonds inside a carbon cage: Towards robust metallofullerene molecular magnets

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Carbon cages known as fullerenes are able to encapsulate various lanthanide atoms and stabilize unusual species within their interior. Protected by the fullerene cage, the endohedral clusters often exhibit unconventional valence and spin state and interesting magnetic properties. Lanthanide-fullerene interactions are usually characterized by a transfer of metal valence electrons to the carbon cage. However, the energy of the σ-type Ln–Ln bonding orbital in Ln_2 dimers encapsulated within the fullerene cage is often quite low, which limits the Ln_2→fullerene transfer to only five electrons. This leads to the appearance of a singly-occupied Ln–Ln bonding orbital. Two air-stable forms of such dimetallofullerenes have been obtained, azafullerenes $Ln_2@C_{79}N$ with one nitrogen atoms replacing the carbon in C_{80} fullerene, or benzyl monoadducts $Ln_2@C_{80}(CH_2Ph)$. Due to the presence of Ln–Ln bonding molecular orbital with one electrons, $Ln_2@C_{79}N$ and $Ln_2@C_{80}(R)$ molecules feature a unique single-electron Ln–Ln bond and unconventional +2.5 oxidation state of lanthanides. The unpaired electron residing on the Ln-Ln bonding MO acts as a radical bridge, leading to giant exchange coupling. Furthermore, fullerene cage and the excess of an electron density between two Ln ions exert a rather strong axial ligand field on lanthanide ion. As a result, $Ln_2@C_{79}N$ and $Ln_2@C_{80}(CH_2Ph)$ compounds exhibit slow relaxation of magnetization and especially high blocking temperatures for Dy and Tb compounds. At low temperatures, $[Ln^{3+}–e–Ln^{3+}]$ fragment behaves as a single giant spin. Furthermore, the Ln–Ln bonding orbital in dimetallofullerenes is redox-active, which allows the changing of its population by electrochemical reactions. The change of the number of electrons residing on the Ln–Ln orbital also affects magnetic structures of the molecule. Thus, the single molecule magnetism in these molecules can be switched by an electron transfer.

SERMACS 534

Isolation of tubular carbon ("fullertubes"): Fullerenes, nanotubes, or neither?

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Since the emergence of buckyballs in the early 1990s, the literature has been full of publications about spheroidal or egg-shaped fullerene structures. Yet, present in a very low abundance (<0.01%) in soot extract, a variety of nanotubular-shaped fullerenes have been hiding for nearly 30 years. Having fullerene endcaps on each side (e.g., C60), these FullerTubes also possess a tube-like belt of hexagons that is similar to nanotubes. The obvious hurdle to overcome is finding a way to isolate them. In this presentation, I will discuss a selective chemical method that reacts and removes spheroidal fullerenes from solution by rendering them hydrophilic. In contrast, the belt-like region of FullerTubes protects them from reacting. Being more chemically inert, Fullertubes tend to remain in solution (e.g. organic solvent). Several purified FullerTubes, pristine and unfunctionalized, are now isolated with this separation approach. These new species will be presented.

SERMACS 535

Nanocarbon reactions for formation of cluster-encapsulated fullerenes

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Fullerenes that encapsulate clusters of atoms represent a fundamental interest in chemistry, materials, and carbon science due to their unique properties and nanoscale structures. Numerous cages that feature a combination of encapsulated carbon, metal, and heteroatom-based clusters have been discovered since, for example, $Sc_3N@C_{80}$ was first reported. Nanocarbon reactions that underlie formation of such compounds, however, are not well understood. Here, we experimentally investigate nanocarbon reactions of metallofullerenes in the gas phase by means of laser-based techniques, analyzed by high magnetic field Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. A variety of structurally defined clusterfullerene cages (e.g., $Sc_3N@C_{68}$, $Sc_3N@C_{78}$, etc.) are probed under energetic conditions to decipher reactions that may lead to encapsulation of C atoms, as well as clusterfullerenes that include metal-loss products. An aim of the present work is to identify mechanistic processes and principles that guide formation of metallofullerenes that entrap carbon, metal, and heteroatom-based clusters.

SERMACS 536

Availability of plastic-associated chemicals to northern fulmar seabirds

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Marine plastic debris is a phenomenon of increasing environmental concern due to its physical impacts on biota via entanglement and ingestion. Seabirds are particularly vulnerable as they can ingest plastic by mistaking it for prey. Recently, there has been a growing interest in plastic-associated chemicals, as plastic formulations are often complex, consisting of small-molecule additives to enhance the production and properties of plastic. Plastic-associated chemicals are rarely measured in marine debris or contaminated organisms. To our knowledge, there has been no investigation of plastic additive compounds in adipose tissue of Northern Fulmars *(Fulmarus glacialis)* from the Bering Sea. This work addresses this gap by measuring the concentration of brominated flame retardants against a baseline of persistent organic pollutants, including legacy and newer contaminants. Northern Fulmar seabirds (n = 43), unintentionally killed by long line fisheries in the Bering Sea, were collected, necropsied, and categorized based on the mass of plastic identified in their stomachs (i.e., no, moderate, high). Fat samples from nine of these seabirds were analyzed for polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), and brominated flame retardants (BFRs). A multi-step extraction and cleanup was performed to isolate the compounds of interest. Gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/tandem mass spectrometry (LC-MS/MS) were used to identify the target compounds. All tissue samples contained PCBs, OCPs, and hexabromocyclododecane (HBCD) BFRs, but polybrominated diphenyl ether (PBDE) BFRs were not readily identifiable.

SERMACS 537

Mapping microplastics in Georgia’s coastal waters: Engaging the citizen scientist

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Citizen science programs offer benefits to research groups, monitoring agencies and policymakers and have shown that they can positively impact communities as participants become more informed and empowered. Microplastics research is a relatively new scientific subject that has caught the interest of the public and this has led to individuals and environmentally-focused groups wanting to volunteer their time to assist with research efforts. Engaging the citizen scientist provides ‘force multipliers’ who can greatly increase the spatial and temporal detail possible in studying microplastics. In addition, citizen scientists gain knowledge and understanding – a valuable asset that will influence larger decisions about science policy. We will highlight how we are using lessons from the past - citizens scientists - to create marine research and education opportunities associated with microplastics research underway along the coast of Georgia.

SERMACS 538

Patterns of microplastic abundances in Georgia estuarine waters

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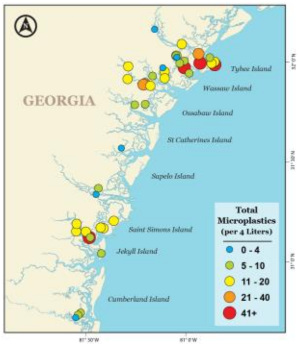
Marine micro-plastic (particles smaller than 5 mm in length) pollution is a recently recognized, and growing, threat to the environment. Microplastic particle estimates number in the trillions and are under-sampled in many ecosystems worldwide. Also, public interest in the issue is high and growing. A primary challenge in mapping microplastic concentrations is collecting and processing samples in a manner that minimizes contamination, and in collecting enough samples to obtain statistically-relevant data. The challenge is especially acute in coastal ecosystems, where the interplay between human activities, tides, currents and ecosystems makes for a very heterogeneous distribution of microplastics. Our initial efforts in mapping microplastics in Georgia’s intercoastal estuaries indicate the presence of a trillion or more microplastic particles in the region, primarily of the micro fiber category. However, spatial heterogeneity was high, with counts ranging from zero to over 80 microplastics per 4 l sample (figure 1). Additional temporal sampling indicates a high level of heterogeneity in this dimension as well. The data suggests rapid cycling (input/removal) from this ecosystem, which further suggests that the primary source for these contaminants is local. Limited riverine sampling from the Savannah, Ogeechee, Satilla and Altamaha Rivers supports this hypothesis as well.



Microplastic abundances (particles per 4 L) observed in surface water samples, June-July 2017.

SERMACS 539

Photochemical degradation of microplastics under aquatic conditions

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Environmental pollution by microplastics (defined as less than 5 mm in length) has become a matter of increasing concern to scientists, regulators, governments and the general public. Inputs of plastics to the oceans were estimated to be 4.8-12 million tons in 2015 and growing rapidly. Estimates of oceanic microplastic abundances have jumped by an order of magnitude within the last 5 years alone. While inputs may be constrained by production and recycling/burial estimates, losses are more difficult to constrain. Studies have shown that plastics have varying degrees of susceptibility to photochemical degradation. However, few studies have been done on photochemical degradation of small size fractions of plastic materials in aquatic environments. We will present a study of photochemical degradation of common plastic materials used in bags and textiles, performed in a solar simulator under temperature and light controlled conditions. Both overall mass loss and conversion to dissolved organic and inorganic carbon will be measured, and FTIR measurements of shifts in the composition of the remaining solid fraction will also be performed. The results will give a constrained estimate of the photochemical degradation of plastics under aquatic conditions that may be used to better understand microplastic cycling in the Oceans.

SERMACS 540

Robust route to multi-functional cellulose-based polymeric bottle-brush cocoons

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Organic nanotubes have been widely studied to show great potential in bioseperation, drug delivery, biosensors, nanofluidics, nanocomposite synthesis, chemical catalysis. Furthermore, they can serve as building blocks to produce nanomaterials and devices with higher order architectures. In this context, in order to impart the functions of hollow interior within organic nanotubes, a robust route to synthesize unimolecular organic bottle-brush cocoons with crosslinked shell were developed where the interior was occupied by judiciously designed polymer chains (polyacrylic acid) to provide preferential anchoring points for organic and inorganic molecules. The azide functionalized outer block of the bottle-brush polymer can be readily crosslinked upon UV irradiation presenting an efficient and robust route for post-loading encapsulation. As a result, the polymeric cocoons showed excellent encapsulation and delivery properties with 3 folds encapsulation amount and total delivery period compared with uncrosslinked bottle-brush polymers. Different from previous approaches for making worm-like bottle-brush polymers, cellulose, which is intrinsically rigid, was used as the backbone giving the cocoons a straight nanorod morphology. This type of bottle-brush cocoons can be directly capitalized as nanoreactors to produce monodisperse inorganic nanorod with controlled size and composition. The crosslinked outer layer on the nanorod provide additional barrier protection to enhance its stability. $CsPbBr_3$ nanorods as a promising perovskite material has been known to have extremely poor stability. However, the $CsPbBr_3$ nanorods synthesized from the polymeric cocoons exhibited much enhanced UV, water, and thermal stability when the outer polymer block was crosslinked after nanorods synthesis, providing them with great potential in application of optoelectronics.

SERMACS 541

Low cost production of xylose from biomass hydrolyzates

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Xylose is the second most abundant sugar in nature. It is a hemicellulose (C5) based sugar and is identified by DOE as one of the top candidates for the production of chemical precursors. A number of extraction processes have been developed to select C5 sugars from biomass. These are developed as pretreatment processes to improve downstream processing of biomass; but, not necessarily, to isolate and utilize xylose. Conn Center at Univeristy of Louisville has developed and demonstrated an integrated C5-based biorefinery for the production of C5-platform of biofuels and biochemicals. One of the key processes of this biorefinery is a precipitation step that delivers D-xylose as a pure starting monosaccharide for its subsequent synthetic transformation to bioproducts. The details of the biorefinery approach and the xylose separation process are discussed during this presentation.

SERMACS 542

Interaction of lignin dimers and derivatives with β-cyclodextrin

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β-cyclodextrin (BCD) is composed of seven D-glucopyranose units linked by α-(1, 4) glycosidic bonds. This cone-shaped oligosaccharide has the remarkable ability to capture guest molecules inside its internal hydrophobic cavity while its hydrophilic exterior improves the water solubility of inclusion complexes and increases their bioavailability and stability. Lignin oligomers have antibacterial properties therefore potential pharmaceutical applications. Interactions between BCD molecules and lignin G-G dimers (coniferyl alcohol) and their derivatives were studied using molecular dynamics (MD) simulations. Potential of mean force calculations show that one end of the commercially available G-G derivatives (G-βO4'-*trunc*G) and natural G-G dimers (G-βO4'-*G*) shows more favorable binding with the BCD interior approaching through the BCD secondary surface. We also simulated two phase systems containing dimers and hydrated BCD molecules. The mole ratio of dimers to BCD was 0.05:1 or 0.15:1. The density profile of the lignin dimers in the water-lignin interface normal direction can be used to estimate the free energy required to dissolve lignin dimers in the water phase. BCD improves the solubility of G-βO4'-*trunc*G dimers, but not significantly. Experimental measurements using ITC (isothermal titration calorimetry), fluorescence assay, and UV-vis spectroscopy show that BCD binds to the G-βO4'-truncG dimer when the dimer is in solution or covalently bound to silica nanoparticles. Preliminary ITC data suggest that the attachment of BCD to G-βO4'-truncG dimers in solution is entropy-driven.

SERMACS 543

Effectiveness of mercury sorbents derived from biomass precursors

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Mercury (Hg) contamination from industrial use, coal-fired power plants and artisanal gold mining is a threat to environmental health globally. Even low levels of Hg contamination in natural environments can lead to the formation of methylmercury (MeHg), which bioaccumulates and biomagnifies up trophic levels and enters the food chain. Engineered and functionalized sorbent materials for the removal of Hg from process streams are routinely used in the petroleum and waste processing industry sectors. However, effective remediation options for the removal of Hg from ecosystems with widespread contamination are limited and frequently cost-prohibitive. Effective, yet inexpensive approaches to remediate large contaminated areas are urgently needed. Sorbents derived from biomass precursors, such as wood, lignin, bone apatite and waste cooking oils copolymerized with sulfur, offer an inexpensive alternative to engineered sorbents. We focus on sorbent materials that can be deployed to treat soils and sediments aiming to minimize Hg flux and limit conversion of Hg(II) to highly neurotoxic MeHg species. We evaluated several biomass-derived sorbent materials in a series of batch experiments examining the role of processing conditions, surface area, sulfur content and other parameters. Furthermore, sorbent performance was compared to a set of engineered sorbents, including SediMite™, Thiol-SAMMS®, and Organoclay™. Natural organic matter (NOM) is ubiquitous in the environment and constitutes a competing ligand for the binding of Hg species by sorbents. Sorption isotherms for Hg(II) at environmentally relevant levels were recorded in the presence of a standardized NOM reference material were compared to unamended controls. The presence of NOM significantly impacted partitioning and sorption capacities. In addition, the release of anions (SO_4^{2-}, NO_3^-, Cl^-) from sorbents was evaluated, as the leaching of solutes can result in changes to the pore water chemistry, which may enhance MeHg production by anaerobic microorganisms. The results advance our understanding of factors impacting the effectiveness sorbents and guide the development of inexpensive biomass-derived materials that can be applied safely to reduce the flux of Hg in contaminated environments.

SERMACS 544

Cellulose and lignin based biocomposites for thermal energy management in buildings

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A substantial portion of the energy produced in the world is consumed by buildings. In 2018, the energy consumption in residential and commercial buildings occupied about 40% (or about 40 quadrillion British thermal units) of total U.S. energy (U.S. Energy Information Administration, 2019). Given rapidly growing global energy demand and the amount of nonrenewable fossil fuels required to meet such energy demand, enhancing the efficiency of energy consumption in buildings has become critically important. In this talk, cellulose and lignin based biocomposites incorporating phase change materials (PCM) are presented. PCM can serve as a source to store and release thermal energy with its latent heat upon phase transition. Specifically, a paraffin based PCM, whose melting temperature is around room temperature, is incorporated in microcapsules consisting of PCM as a core and cellulose nanofibrils as a shell. In another approach, PCM is contained in a lignin-based rigid polyurethane (RPU) foam that serve as a porous template. A sonochemical synthesis method and a vacuum-assisted impregnation method are used for the incorporation of PCM into microcapsules and RPU, respectively. The formation of PCM-containing biocomposites is confirmed by visual inspection, Fourier-transform infrared spectroscopy (FT-IR), and scanning electron microscopy (SEM). Thermogravimetric analysis (TGA) quantifies the level of PCM incorporation in microcapsules and RPU. Differential scanning calorimetry (DSC) is used to estimate the amount of thermal energy that can be stored and released in the temperature range relevant to residential and commercial buildings. With the combined experimental results, I will show that the PCM biocomposites have potential for serving as a energy management component in buildings.

SERMACS 545

Carbon fibers derived from fractionated solvated lignin: Graphitic layers in amorphous matrix?

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In our recent study, the dry-spinning of a fractionated solvated lignin into precursor fibers and their carbonization was discussed. At a carbonization temperature of 1000°C, the tensile strength and modulus of resulting carbon fibers was measured at 1.4 and 98 GPa, respectively, amongst the highest reported to date for carbon fibers derived from lignin precursors. Here we report on the microstructure and properties of carbon fibers produced over a range of temperatures ranging up to 2100°C. As expected, formation of some graphitic crystallinity was observed at the highest temperature with d-spacing decreasing below 0.340 nm, but in an otherwise amorphous carbon matrix. Tensile strength decreased but modulus increased. Ongoing work is investigating material and process improvements to enhance tensile strength.

SERMACS 546

Cellulose-derived bottlebrush-like block copolymers enable the crafting of one-dimensional functional nanorods with unprecedented control over dimensions, compositions, architectures and surface chemistry

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In this talk, I will show a general strategy to craft an exciting, and virtually unlimited, variety of plain nanorods and nanowires, core/shell nanorods, and nanotubes with precisely controlled and targeted dimensions and compositions. The key to this strategy lies in judiciously designing cellulose-derived bottlebrush-like block copolymers (BBCPs) with well-defined structures and narrow

molecular weight distributions as nanoreactors. These cylindrical unimolecular nanoreactors impart a remarkable level of control over the size, shape, architecture, surface chemistry (i.e., organic solvent-soluble or water-soluble), and properties (e.g., metallic, ferroelectric, upconversion, semiconducting, luminescent, thermoelectric, and magnetic, as well as their combinations, for example, metallic/magnetic, metallic/semiconducting, metallic/upconversion, etc.) of the resulting 1D nanocrystals. All these 1D nanocrystals can serve as building blocks for the bottom-up assembly for nanostructured materials and devices with desirable characteristics for use in optics, electronics, photonics, optoelctronics, magnetic technologies, sensory materials and devices, lightweight structural materials, catalysis, drug delivery, biotechnology, and many other emerging fields.

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Biohybrid aerogel from self-assembled nanocellulose and nanochitin as a high-efficiency absorbent for water purification

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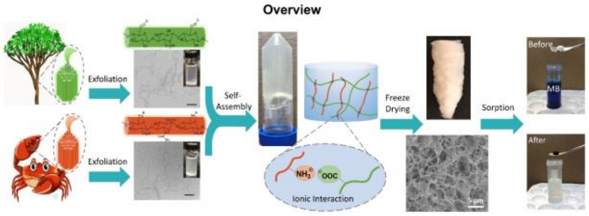
A simple and novel method, self-assembly of nanocellulose and nanochitin, was developed to produce high efficiency and versatile biohybrid aerogel (BHA) for water purification. The self-assembly process was driven by the electrostatic force between one-dimensional (1D) negatively charged TEMPO-oxidized cellulose nanofiber (TOCNF) and positively charged partly deacetylated chitin nanofiber (PDChNF). This results in the three-dimensional (3D) biohybrid hydrogel (BHH) that physically crosslinked *via* both electrostatic interactions and hydrogen bonding between TOCNF and PDChNF. The obtained BHA from lyophilized BHH exhibited highly porous interconnected structure, which guarantees the availability of its internal active site for the absorption of toxic metalloid ions and organic pollutants. Consequently, the BHA displayed super-high absorption capacities of 217 mg/g for As(III) under the neutral pH condition and 531 mg/g for methylene blue (MB) under the alkaline aqueous condition with rapid absorption kinetics, in sharp contrast to conventional biobased absorbents. Our versatile BHA produced via a facile preparation strategy is proven to be promising biodegradable absorbent for water purification, offering simple and green alternatives to the conventional absorbent from synthetic polymers.



Graphical Abstract

SERMACS 548

Nanocellulose based functional textile coatings

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Fibrillated Nanocellulose (NFC) is a non-toxic one-dimensional nanomaterial engineered from abundantly found cellulose sources. NFC has a fibrillar structure, high specific surface area and exists as a stable thixotropic colloidal hydrogel. The hydroxyl groups of the NFC fibrils provide efficient reactive sites for chemical functionalization, physical modifications and post-treatments. Due to such chemical and structural significances, NFC becomes perfect alternative for creating green chemistry for the textile and food packaging industries. Textile industry consumes a massive quantity of water and releases copious volume of hazardous effluents to the environment while food packaging made of synthetic polymers is one of the major sources of plastic pollutions. NFC based sustainable coating technology involves synthesis of functionalized NFC aqueous dispersions. The functional molecules fixed to nanocellulose transform NFC to a fibrous pigment, filler or coating particulates (on the nanoscale). NFC ensures the permanent retention of functional molecules via a combination of strong covalent bonds, hydrogen bonds and fibrillary entanglement mechanisms of adhesion. For example, NFC based sustainable textile dyeing technology promises a greater than 80% dye fixation and excellent dye performance. This technology consumes ten times lower amount of water and dye auxiliaries compared to the traditional exhaust dyeing method. Over the past years, NFC based sustainable textile dyeing technique has been optimized into an industrially applicable technology. Soluble sugars (hemicelluloses) present in NFC hydrogels is another source of functional molecules to play a pivotal role in achieving efficient functionalization with NFC coatings. The developed post-treatment of NFC coatings is involving polycarboxylic acids crosslinking agents to introduce ester crosslinks between NFC fibers and soluble hemicelluloses. This methodology results in improved efficiency of the use of different types of complex carbohydrates and chemical functionalization owing to the combination of chemical reactions in solution and at the interfaces.

SERMACS 549

Facial amphiphilic antimicrobial polymers against gram-negative bacteria

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Drug resistance of pathogenic bacteria is a major global problem leading humanity towards a post-antibiotic era. We have utilized synthetic polymer chemistry to revolutionize cationic polyelectrolytes from facial amphiphilic multicyclic natural products in the hope of discovering new antimicrobial compositions to enhance interactions with bacterial cell membranes. This presentation will cover our efforts in using cholic acid to design antimicrobial polymers for killing multidrug resistant bacteria.

SERMACS 550

Multifunctional polysilsesquioxane nanoparticles for the treatment of cancer

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Multifunctional hybrid nanoparticles are being developed to carry a wide variety of therapeutic and imaging agents for multiple biomedical applications. Polysilsesquioxane (PSilQ) nanoparticles is a promising hybrid platform with numerous advantages to be used as delivery system for photodynamic therapy. In this work, we developed a redox-responsive PSilQ-based platform to transport and deliver simultaneously protoporphyrin IX (PpIX) and curcumin inside human cells. These PSilQ nanoparticles contains a high loading of PpIX and curcumin, and are degraded inside cancer cells due to the high reducing environment. This multimodal delivery system show a synergistic performance for the combined photo- and chemotherapy of the triple-negative breast cancer (TNBC) MDA-MB-231 cells. The safety and phototherapeutic efficacy of this PSilQ-based platform was evaluated in an orthotopic mice model of TNBC. The PSilQ nanoparticles are completely biodegraded and excreted from mice without any side effect. The efficacy data show that the PSilQ nanoparticles efficiently reduce tumor growth in the orthotopic mice model of TNBC. This work demonstrates that PSilQ nanoparticle-based platform is an excellent alternative for the combined photo- and chemotherapy of cancer.

SERMACS 551

Polymer-tetrodotoxin conjugates to induce prolonged duration local anesthesia with minimal toxicity

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There is clinical and scientific interest in developing local anesthetics with prolonged durations of effect from single injections. The need for such is highlighted by the current opioid epidemic. Site 1 sodium channel blockers such as tetrodotoxin (TTX) are extremely potent, and can provide very long nerve blocks but the duration is limited by the associated systemic toxicity. Here we report a system where slow release of TTX conjugated to a biocompatible and biodegradable polymer, poly(triol dicarboxylic acid)-co-poly(ethylene glycol) (TDP), is achieved by hydrolysis of ester linkages. Nerve block by the released TTX is enhanced by administration in a carrier with chemical permeation enhancer (CPE) properties. TTX release can be adjusted by tuning the hydrophilicity of the TDP polymer backbone. In vivo, TTX released from these polymers produced a range of durations of nerve block, from several hours to 3 days, with minimal systemic or local toxicity.

SERMACS 552

Temperature-responsive polymersomes of poly(n-vinyl-2-methylcaprolactam)-*block*-poly(n-vinylpyrrolidone) to dampen drug-induced cardiotoxicity

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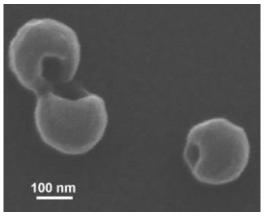
Despite being one of the most potent approved chemotherapeutics, doxorubicin (DOX) can facilitate cardiac toxicity by irreversibly damaging the cardiac muscle and impairing the resolution of cardiac inflammation. Vesicles are promising delivery drug carriers to shield the chemotherapeutics and improve drug efficacy. We report synthesis and assembly of nanosized polymersomes from novel poly(N-vinylpyrrolidone)-block-poly(3-methyl-N-vinylcaprolactam) (PVPON-PMVC) temperature-responsive diblock copolymers and explore their potential to minimize DOX cardiotoxicity compared to liposomal DOX. RAFT polymerization of structurally similar monomers of vinylpyrrolidone and 3-methyl-N-vinylcaprolactam but with drastically different hydrophobicity allowed for decreasing the cloud point of PMVCn-PVPONm copolymers below 20 °C. The LCST of the PMVC58-PVPONm copolymer was varied from 19 to 15 °C by increasing the length of the hydrophilic PVPONm block from m = 20 to 98. The hydrophobic PMVC block facilitates formation of vesicular morphology of the aqueous self-assemblies at room temperature (Figure 1) and highly efficient entrapment of DOX into the aqueous PMVC$_{58}$-PVPON$_{65}$ polymersomal core surrounded with the hydrophobic temperature-sensitive PMVC shell and the hydrophilic PVPON corona. We show that while C57BL/6J mice injected with the lethal dose of DOX at 15 mg/kg did not survived the 14-day treatment resulting in 100% mortality, the DOX-loaded PMVC$_{58}$-PVPON$_{65}$ polymersomes did not cause any mortality in mice indicating successful DOX entrapment. The gravimetric analyses of the animal organs from mice treated with DOX encapsulated into liposomes and polymersomes revealed that the Lipo-DOX injection caused some toxicity compared to Poly-DOX and saline control. Our results provide the evidence for stability of synthetic polymersomes in vivo and show a great promise for development of the next generation of advanced therapeutics carriers with minimal side effects.



SERMACS 553

Promising screening platform to identify oligonucleotide ligands

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Oligonucleotide ligands or aptamers are single-stranded sequences that exhibit high affinity and specificity for a particular nonnucleotide target. Despite the investment in antibody technology for a variety of diagnostic and therapeutic applications, aptamers present an attractive alternative to antibodies due to their relative ease in handling and longer shelf life. For nearly three decades, aptamers for a particular target are typically identified using an evolutionary-based screening approach called "Systematic Evolution of Ligands by EXponential Enrichment" (SELEX); however, SELEX itself is a labor-intensive process with pitfalls such as its propensity to introduce PCR-based sequence bias and contaminants. Here, we have developed a *nonevolutionary* screening approach we call CompELS (Competition Enhanced Ligand Selection) to rapidly and reliably identify single-stranded DNA aptamers for a model target, namely planar {111} gold. Following aptamer selection against our material target, we then evaluated winning sequences to identify base segment consensus as well as any shared and unshared patterns in their predicted secondary structure elements such as hairpins, internal loops, and multi-branched loops. Lastly, in a separate post-screening competition experiment, we ranked our aptamer candidates in terms of their frequency as a bound species using next generation sequencing and identified multiple high affinity aptamers. As aptamers continue to be pursued as potential ligands or capture agents in the biology and bioengineering community, our ongoing and future efforts include adapting our unconventional screening approach to enable faster and easier aptamer identification for challenging biological targets.

SERMACS 554

Fundamental studies and biomaterials application of peptoid polymers

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Peptoid polymers featuring *N*-substituted polyglycine backbones with proteinogenic or synthetic sidechains are structural mimics of polypeptides.[1] Because of *N*-substitution, peptoid polymers lack extensive hydrogen bonding interaction and main chain stereogenic centres. Their backbones are more flexible than those of polypeptides and the main chain conformation can be controlled by judicious choice of *N*-substituent structures, leading to well-defined secondary structures (*e.g.,* PPI helices or S-sheets) reminiscent of those in the polypeptides. In addition, peptoid polymers are backbone degradable, often biocompatible, and thermally processable similarly as conventional thermoplastics. The combination of these attributes makes peptoids an attractive class of peptidomimetic polymers that are potentially useful for various biotechnological applications. This presentation will start with an overview on the synthesis and characterization of peptoid polymers and sequence-defined oligomers by controlled polymerization methods or solid phase synthesis, followed by a discussion of our recent effort towards unravelling the effect of sequence-encoded electrostatic interaction on the solution structure of ionic peptoid diblock oligomers. Examples will also be given on the design, synthesis and characterization of thermoreversible hydrogelators using well-defined peptoid polymers for soft tissue engineering applications.

SERMACS 555

Determination of optimal mild organic solvents for synthesis of PdNPs for carbon-carbon coupling reactions

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The synthesis of nanoparticles is an increasingly popular field of interest. The application of nanoparticles is especially popular in the field of nanocatalysts. Metal nanoparticles (NPs) are favorable for catalysis because of the large surface area to volume ratio, which allows them to catalyze a variety of reactions using lesser amounts of active material. As the field of nanoparticle research expands, efforts are being made to create more sustainable approaches to the synthesis of these particles. This research sought to step away from harsh organic solvents for the synthesis and use of palladium nanoparticles (PdNPs) while recognizing that such organic solvents are a necessary component of a large range of catalytic reactions. PdNPs were synthesized in water, with the use of peptides to mediate the NP formation. The PdNPs were characterized by UV-Vis, hydrodynamic size, and SEM-TED analysis. The effectiveness of these nanoparticles as catalysts was examined through the use of carbon-carbon coupling reactions with aryl halides to yield biphenyl products. The catalytic studies were conducted in matching solvent concentrations as the NP synthesis at room temperature and pressure at a catalyst loading of 0.05 mol%. The results of the carbon-carbon coupling utilizing the PdNPs were quantified using NMR and GC-MS. The overall aim of this research is to determine the optimal conditions to make and use these PdNPs in less harsh organic solvents while maintaining environmentally benign conditions.

SERMACS 556

Synthesis of indolenine and quinoline derived water-soluble squaraine dyes

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Fluorescent dyes have lots of potential biological applications, most notably photodynamic therapy for the treatment of tumors. For this reason, researchers aim to produce compounds that absorb into the bloodstream effectively that also possess ideal optical properties. Our lab synthesized two unique heterocyclic squaraine dyes with varied pendant groups in order to increase solubility in a biological system. The reactions were monitored by UV-Vis spectroscopy and those results were used to obtain fluorimetry data showing absorption and emission profiles of the synthesized dyes. A quaternary-nitrogen appended propyl pendant chain visibly improved solubility in all polar solvents, while still maintaining the dyes' longer wavelength absorbance - promising evidence for future work both in our lab and for in vivo studies by our collaborators.

SERMACS 557

A single-entity method to actively control the nucleation-crystal growth process (I) - basics in lysozyme crystallization

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The ultimate purpose of this project is to establish a controllable method that is capable of synthesizing high-quality single crystals of matter and providing greater insight on the early stages of the nucleation-crystal growth process at unprecedented spatial and temporal resolutions at single entity level. The generalizable methods are developed with a classic macromolecular crystallization system: a quartz pipette with a single nano-sized tip opening is preloaded with NaCl-PEG solution at higher concentration and is inserted into a saturated/metastable lysozyme solution. An external electric field is applied across the nanotip to control the mass/ion transport and thus to tune the extent of supersaturation. During my summer research, it was first discovered that NaCl, alone, was not enough to induce the nucleation-crystal growth process through a nanopipette. Secondly, however, it was discovered that PEG with terminal group COOH did help induce the nucleation-crystal growth process by first forming a dense liquid, domain, inside of nanopipette, followed by the onset of a nano-micro-droplet outside of nanopipette, which eventually transformed into a crystal. We thank the National Science Foundation for their generous support which aided in the development of this research (NSF-REU program Award#: 1757933 and CHE-1610616).

SERMACS 558

A quantum chemical study of enolate, enol, and alkene structures as predictive models for the site of alkylation

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The formation of carbon-carbon bonds via alkylation reactions has a rich history in synthetic organic/medicinal chemistry. The formation of enolates and subsequent alkylation reactions have been studied experimentally and theoretically. Experimental conditions, the use of directing and blocking groups, as well as enolate structures have been used to help predict the position of alkylation. Enolate stability, which in many cases is a reflection of the corresponding alkene stability, has been used as a simple predictive model. We have undertaken a computational study using Spartan with HF, DFT, and MP2 calculations at various basis sets to investigate whether or not simple models of enolate, enol, and alkene stabilities can be used to make predictions about the position of alkylation in ketone and enone systems. Our preliminary computational results and the challenges associated with this investigation will be presented.

SERMACS 559

Biosynthesis of iron oxide nanoparticles by ammonia diffusion

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The use of nanotechnology to synthesize particles has become more common these days. Particles can be synthesized by a variety of methods using nanotechnology but due to recyclability concerns and environmental hazards, using biomolecules is safer and allows us to control size and shape of the nanoparticles in the same way that high partial pressures and temperatures do. Bifunctional peptides were used to make Iron oxide pd nanoparticles under green conditions using a diffusion method. The use of a Bifunctional peptide is significant because it combines magnetite sequence and palladium binding areas. This characteristic makes the Pd nanoparticles recyclable by magnet separation. These materials were used for various surface and carbon carbon coupling reactions where the reactivity and recyclability were explored.

SERMACS 560

Reaction pathway for tetrahedrite synthesized by a modified polyol process

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Thermoelectric compounds convert heat into electricity and vice versa, making them a useful material for generating power or heat. Since the majority of energy produced for use as electricity is lost as waste heat, thermoelectric materials have moved into the spotlight as a solution to the current energy crisis helping to decrease society's reliance on fossil fuels. Tetrahedrite ($Cu_{12}Sb_4S_{13}$) is a compound that demonstrates excellent thermoelectric properties, in part due to its complex crystal structure. It is also comprised of earth abundant elements and thus is inexpensive to produce. Dopants are often added to tetrahedrite to tailor the thermoelectric properties of the compound. Typically, tetrahedrite is made by solid-state methods that are very energy and time intensive, taking over two weeks at temperatures in the regime of ~500°C and above. The Anderson lab has developed modified polyol process that is conducted at lower temperatures for a fraction of the time, taking less than two hours at 220°C. This process makes particles with nanoscale dimensions, which also enhances the thermoelectric properties. With this polyol process, there is a wide range of dopants that can be incorporated with tunable concentrations. Powder x-ray diffraction is used in tandem with energy dispersive x-ray spectroscopy to characterize tetrahedrite's structure and elemental composition. Scanning electron microscopy is used to investigate

the size and shape of the nanoparticles. This research project seeks to determine the growth mechanism associated with this to explore if the addition of dopants follows the same pathway and if not, how they affect it. To further optimize the synthesis, procedural factors have been tested, such as the time it takes to ramp to a given temperature and the time that the maximum temperature is held constant. It is hoped that by understanding the reaction pathway, the synthesis can be optimized to further improve efficiency.

SERMACS 561

Towards the synthesis and complexation of a new Janus-type N-heterocyclic carbene

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This project targets the synthesis and characterization of a new dianionic Janus-type N-heterocyclic carbene capable of supporting zwitterionic transition metal complexes, as well as molecular and supramolecular systems. The corresponding zwitterionic precursor will be synthesized and fully characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography. The target dianionic carbene will be produced by deprotonation of this zwitterionic precursor with a strong base. Details on the chemistry of this carbene with respect to its ability to support catalytically relevant metal complexes will be provided.

SERMACS 562

Influence of ligands and pH on the dissolution of metal oxide nanoparticles

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The increased occurrence of metal-containing engineered nanomaterials (ENMs) in consumer products has generated environmental concerns. The dissolution of zinc oxide nanoparticles (ZnO NPs) and copper oxide nanoparticles (CuO NPs) may introduce bioavailable dissolved metals to waterways and impact ecosystem health. To investigate the effect of aquatic conditions on ZnO and CuO NP dissolution, anodic stripping voltammetry was used for rapid *in situ* measurement of dissolved Zn^{2+} and Cu^{2+} concentrations. CuO NP dissolution was considerably lower for ZnO NPs under the same conditions, and as such CuO experiments were performed in a lower pH range (5.0 – 6.0) than for ZnO (pH = 7.0 – 8.0). In both cases the dissolution of metal oxide NPs occurred more readily at the low pH, consistent with the pH-dependent solubilities of the bulk metal oxides. The role of complexation of Zn^{2+} and Cu^{2+} was also assessed, using ligands with characterized formation constants (K_f) for Zn^{2+} and Cu^{2+} (ammonia, *o*-phenylenediamine, ethylenediamine, citrate and nitrilotriacetic acid). The data show high ligand:metal ratios and high complex formation constants result in greater ZnO and CuO NP dissolution. The availability of ligands capable of forming stable metal complexes increased the equilibrium concentrations of both Zn^{2+} and Cu^{2+}. The results demonstrate the presence of ligands of sufficient concentration and metal ion complexation capacity can control ZnO and CuO NP dissolution even at relatively high pH. Treating NP dissolution as a pseudo-first order reaction, the rate constant of ZnO and CuO NP dissolution increased at higher ligand concentration and complex stability. Although NP dissolution in the environment will occur in more complex systems, these controlled laboratory experiments demonstrate how metal ion complexation may be an important driver of NP dissolution behavior in the environment.

SERMACS 563

*In vivo*UGT isoenzyme glucuronidation of daidzein

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Daidzein is a phytoestrogen primarily found in legumes such as soybeans, which is structurally similar to 17-βestradiol and can bind to estrogen receptor-βdue to its phenol ring. This binding could possibly prevent osteoporosis, reduce atherosclerosis and kill breast, colon ovarian and prostate cancer cells. Daidzein is removed from the body through the metabolic process of glucuronidation which is facilitated in the liver and intestines by UGT enzymes. Daidzein and its glucuronide metabolites were separated using a phenyl column (150 x 2.1mm, 3µm) and 20% water and 80% acetonitrile at 0.4 ml/min. Daidzein and its metabolites were detected at a wavelength of 260 nM. Glucuronidation of daidzein was conducted *in vitro*using isoenzymes UGT 1A1 and UGT 1A9, buffered by tris-HCl at pH 7.5 with alamethicin and the cofactor of UDPGA. The enzyme assays determined an optimal incubation time for the enzyme and daidzein. Calibration curves for daidzein and daidzein 4'-glucuronide were developed accordingly.

SERMACS 564

Ring functionalized D-π-a titanocenes for use in dye-sensitized solar cells

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It has been shown that titanocenes of the form $Cp_2Ti(C_2R)_2$,where R is a ferrocenyl or arylamine substituent, exhibit photo-induced ligand-to-metal charge-transfer (LMCT) from the ethynyl donor ligand to the central titanium. Electrochemical investigation suggests that the resulting excited state has sufficient energy to inject an electron into a substrate of TiO_2. By extension, these compounds present possible implementation in the field of dye sensitized solar cells (DSSC's). In order for electron injection from the titanocene to the TiO_2 to occur, the titanocene must be directly attached to the substrate via a functional group with a high binding affinity for TiO_2. Herein, we discuss the synthetic methodology behind creating anchoring group functionalized cyclopentadienyl complexes.

SERMACS 565

Sulfidation of silver nanoparticles by zinc sulfide

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Silver nanoparticles (Ag NPs) are widely used in consumer products because of their antimicrobial properties. However, the increased use of Ag NPs has raised concerns about the toxicity of Ag NPs when exposed to the aquatic environment. Previous studies have shown an important fate pathway is the sulfidation of Ag NPs to yield a stable silver sulfide (Ag_2S) product, including when it results from the competitive displacement of other metals in metal sulfides by silver. The goal of this study is to examine how both characteristics of the Ag NPs (size and capping agent) and surrounding water conditions (dissolved oxygen and pH) affect the sulfidation of Ag NPs by zinc sulfide (ZnS). UV-Vis spectroscopy was used to measure changes in the surface plasmon resonance of Ag NPs and voltammetry was used to measure the release of zinc ions (Zn^{2+}) that result from the sulfidation of Ag NPs by ZnS. Transmission electron microscopy (TEM) was used to characterize Ag NPs and their reaction product after sulfidation by ZnS. Sulfidation of small Ag NPs happened at a faster rate compared to those with a larger size due to their greater relative surface area. It was also found that the sulfidation of Ag NPs capped by polyvinylpyrrolidone (PVP) was inhibited relative to Ag NPs capped by citrate. These studies not only provide further insight into an important fate of Ag NPs, but also demonstrate how the environmental release of Ag NPs could impact the speciation of other metals.

SERMACS 566

Handheld near-infrared Raman spectrometer

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Raman spectroscopy provides a non-contact, non-destructive means of analysis and identification. The utilization of a handheld device offers the ability to perform analysis in a lab setting or in the field. The handheld spectrometer, equipped with a 1064 nm laser to reduce fluorescence, was used to analyze and correctly identify opioids, pesticides, and cannabinoids. Theoretical spectra were modeled by density functional theory with the aid of Spartan 16 and compared to experimental data. This paper will discuss the utility of handheld Raman systems and the benefits of 1064 nm analysis. Data will be presented on the detection of several classes of compounds including fentanyl, glyphosate, and cannabidiol.

SERMACS 567

Effects of CUBR or AGCL coordination on the photochemistry of arylalkynyltitanocenes

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First row transition metal complexes with ligand-to-metal charge-transfer excited states are of interest as possible photocatalysts. Prior research by our group on titanocenes with the formula $Cp_2Ti(C_2R)_{2,}$where R is a phenyl or arylamine substituent, has demonstrated intense charge-transfer (CT) absorptions associated with CT from the C_2R substituent to Ti(IV). When R is the organic substituent phenyl, dimethylaniline, or triphenylamine, irradiation results in photodecomposition with quantum yields of decomposition between 0.25 and 0.65. Coordinating CuBr or AgCl between the alkynes enhances the photostability of the arylalkynyltitanocenes by two to three orders of magnitude. Herein, we report the photochemical studies of the arylalkynyltitanocenes, and the complexes with CuBr or AgCl coordinated between the alkynes. This research has implications for use of these complexes as photocatalysts.

SERMACS 568

Synthesis of amines by nucleophilic ring opening of aziridines

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Alkylboronic esters react as nucleophiles with aziridines to form amine products in varying yields. The substrate scope with respect to the aziridine is examined. Excellent regioselectivity is observed in this aziridine ring opening reaction with the exception of the reaction with the aziridine derived from styrene.

SERMACS 569

Affordable determination of the elemental composition of quantum dots with portable X-ray fluorescence spectroscopy

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Semiconductor nanocrystal quantum dots possess unique optoelectronic properties dependent on their size, shape, and elemental composition. Current methods used to measure their composition are limited to employing large, expensive instrumentation such as inductively coupled plasma optical emission spectroscopy (ICP-OES) or energy dispersive x-ray spectroscopy. While large, expensive laboratory-scale X-ray fluorescence spectrometers have also been employed to investigate the elemental composition of some nanomaterials, cost-effective portable X-ray fluorescence (pXRF) spectrometers have not yet been demonstrated to have the necessary sensitivity to accurately determine the chemical composition of nanomaterials. We have utilized pXRF spectroscopy, a handheld instrument operated on a simple benchtop under ambient conditions with minimal sample preparation, to experimentally measure the chemical composition of CdSe quantum dots and validated the results with ICP-OES. Additionally, a model was developed to calculate the ratio of cadmium to selenium without the need for a calibration curve by taking into account the depths of analysis and fluorescence efficiencies of each element in the sample matrix. The experimental and modeled results are comparable, consistent, and demonstrate that the compositions of colloidal nanomaterials can be accurately measured with pXRF spectroscopy. This work demonstrates that nanomaterials can be investigated at the atomic level with portable, affordable, and cost-effective chemical instrumentation.

SERMACS 570

Detecting endocrine disrupting compounds: Development of a differential sensing array for use in aqueous media

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Endocrine Disrupting Compounds (EDCs), such as bisphenol A (BPA), have been shown to have negative effects on aquatic wildlife, such as fish and amphibians, female maturation and male reproductive systems, and have been implicated in an increased risk of cancer. Detection methods for EDCs do exist, but are typically highly specific for a given EDC and often require extensive sample preparation and instrumentation. Our research works to address this issue with the construction of a differential sensing array using β-cyclodextrin-based indicator displacement assays (IDAs) that respond to EDCs via patterned colorimetric changes. We have screened and chosen several promising indicators for their changes in absorbance and fluorescence with and without host. We have tested our indicator displacement assay against a selection of EDCs and are currently working to construct our sensing array for use against unknown samples. We plan to employ our array on real-world EDC sources, starting with the detection of BPA from thermal paper and moving toward testing unknowns from real-world aqueous samples.

SERMACS 571

Optimization of reversible-deactivation radical polymerization procedure

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Polymers are crucial to modern society and can be found in everything from plastic bags to clothing fibers. Traditionally polymerization methods (free radical, condensation, etc) are used to produce a wide range of polymers, but there is little control over chain extension, which affects a polymer's molecular weight, properties/functions, and ultimately application. Atom transfer radical polymerization (ATRP) offers an alternate approach and has become a critical method in mass producing polymers. This method is used to synthesize common materials like Pexiglas and Styrofoam. ATRP uses the flipping of high energy radicals from an active form, where the chain can add monomers and grow, to a dormant state, in which the chain is "capped" and does not extend. The cycling equilibrium can be controlled and allows chemists to tune active and dormant states, leading to polymers with specific molecular weights and properties. One of the huge benefits of ATRP is it allows specific sites on a polymer chain to be altered for a desired function. For example, ATRP produced polymers have applications in coatings and sealants. With increased control, polymer chemists can explore more "exotic" polymers such as block copolymers, comb/brush polymers, and branched polymers. For our optimization investigation we have focused on a protocol for block copolymers, which are polymers that contain two different regions derived from two monomers. Since ATRP is a living polymerization method, it can be easily stopped and restarted to accomodate the different monomers. In comparison, standard radical polymerization does not allow such control, leaving the propeties and length of the polymer to chance. My project has focused on optimizing an ATRP protocol for an advanced undergraduate chemistry class. A major consideration for any lab is time, since students only have a set period to work in and cannot necessarily leave a reation. To address this, we were interested in adjusting the temperature of the reaction and monomer concentration in an effort to reduce reaction time while trying to work within the equipment and technical limitations of upper level undergraduate students. Here we report the findings and current optimization protocol along with other nuances we encountered during our investigation. Once the procedure is fully streamlined, research could shift into using various catalysts and monomers to see how widely the procedure can be applied to produce different polymers.

SERMACS 572

Computational study of FXBN spin trap derivatives with hydroxyl radicals

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Spin traps are molecules that may be used to stabilize free radicals, so that the resulting adduct can be characterized using electron paramagnetic resonance spectroscopy. Free radicals, especially small reactive oxygen species, are implicated in diseases such as Alzheimer's, and in the effects of aging. The main spin trap class is nitrones. In this class, 5,5-dimethylpyrroline-N-oxide (DMPO) is the cyclic prototype, and α-phenyl-N-*t*-butylnitrone (PBN) is the linear prototype. In the past, DMPO analogs have been explored, and some include 5-methyl-,5-(trifluoromethyl)pyrroline-N-oxide (TFMPO), 5-acetamide,5-methylpyrroline-N-oxide (MAMPO), and 5-carboxamide,5-methylpyrroline-N-oxide (AMPO). Similarly, one PBN analog that has been found to be particularly effective is α(Z)-(3-methylfuroxan-4-yl)-N-*t*-butylnitrone (FxBN). For this study, the methylfuroxan-4-yl ring from FxBN has been combined with DMPO, TFMPO, MAMPO, and AMPO to create four novel spin traps. Using Hartree-Fock (HF) and Density Functional Theory (DFT), the optimized geometries were calculated for the reactant species, the hydroxyl radical additions at the C-site, at the O-site, and for the diadduct at the HF/6-31G* and DFT/B3LYP/6-31G* levels of theory. The C-site addition is more thermodynamically favorable for all the molecules than the O-site addition. Overall, the diadduct radical addition for the four molecules was the most thermodynamically favorable.

SERMACS 573

Reaction of alkylboronic esters with epoxides

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In a time and temperature sensitive reaction, sec-butyl lithium was added to benzylboronic acid pinacol ester to form a nucleophile. This nucleophile was found to react with epoxides with good regioselectivity. Yields have been promising, but the substrate scope is currently being furthered to expand the depth of this research.

SERMACS 574

Application of evolved tryptophan synthases to encode unnatural tryptophan amino acids into designer peptides

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Unnatural amino acid design strategies have been extensively pursued to expand Nature's molecular toolkit, thereby incorporating new functionalities into proteins and biological catalysts. Many of these applications have relied upon and are limited by the tedious development of evolved amino acyl tRNA/tRNA synthetases to incorporate unnatural amino acids into complex protein systems. Herein, we present a two-step, one-pot strategy using an evolved tryptophan synthase enzyme, developed in the Arnold lab at CalTech, that converts a series of unnatural indole derivatives to corresponding enantiomerically selective L-tryptophan derivatives, which are subsequently converted to their fmoc-protected derivatives for solid-state peptide synthesis. Because tryptophan sidechain is electron rich, it offers an incisive chemical building block from which fluorescence, magnetic resonance, and vibrational spectroscopic as well as thermodynamic probes may be generated. We report on optimized reaction conditions that show near quantitative conversion from indole to purified fmoc-protected L-tryptophan residues. The demonstrative incorporation of these unnatural amino acids into specially designed, structured peptides will be presented.

SERMACS 575

Photoacoustic thermometer: Shift in the photoacoustic signal frequency of ethene due to temperature variation

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Photoacoustic (PA) Spectroscopy has rapidly developed for a wide variety of uses in recent years and continues to do so. This study shows how temperature affects the PA signal produced by ethene in order to develop a PA thermometer. Harmonics of three different length PA cells are examined to show how the shift in signal frequency changes with respect to length. The harmonic number was varied as well to describe how the change in signal frequency changes with respect to harmonic number. A CO_2 laser was used in combination with a chopper to modulate the laser light. The signal was observed within a 65°C range from approximately 5°C to 70°C. A Dewar vacuum flask was used to insulate around the PA cell as the temperature was varied. Ice and thermal strips were used to lower and raise the temperature, respectively. Data was taken from low temperatures to high. The PA signal was seen to increase as the temperature was raised. Preliminary results show that data from graphs of temperature vs. frequency fit 2nd order polynomials. Increasing harmonics of a given cell length have vertices that fit either an exponential function or a 2nd order polynomial.

SERMACS 576

Reaction between benzylboronic esters and alkyl halides

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Benzylboronic acid pinacol ester was found to react with alkyl halides to make new carbon-carbon bonds. A variety of alkyl halides were found to participate in this reaction providing good yields of the products. Other alkylboronic esters were also examined in this reaction.

SERMACS 577

Patterning conjugated polymer growth by microcontact printing

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Conjugated polymers have a wide array of potential uses in fields such as renewable energy through their use in org. electronic devices such as org. photovoltaics. Typically, these devices are fabricated with presynthesized polymers that are cast as films onto a substrate. However, the nature of the film morphol. directly impacts device performance. Being able to grow a conjugated polymer directly from a functionalized surface could lead to higher organization and tighter packing between the mols., therefore creating more effective devices. Self assembled monolayers (SAMs) are used to functionalize surfaces with mols. capable of initiating conjugated polymer growth. We are functionalizing SiO_2 and gold surfaces with a new SAM that initiates polymn., and later can be selectively cleaved to release the polymer. In particular, we are using microcontact printing to nanopattern our substrates so that we can use at. force microscopy to show that polymn. only occurs in the presence of our SAM, and then is removed under our specific conditions.

SERMACS 578

Mechanistic investigation of the platinum-catalyzed acylation of 2-phenoxypyridines

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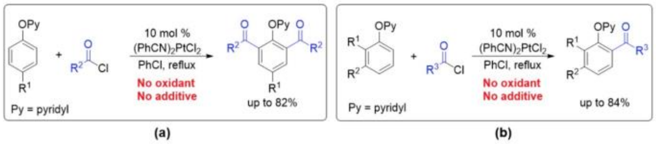
Transition metal-catalyzed, directed C-H acylation offers a way to selectively introduce carbonyls and other important functional groups to aromatic rings. Our group has reported a novel Pt-catalyzed acylation of 2-phenoxypyridines through direct C-H activation that does not require an oxidant or other additives. It is hypothesized that the platinum-catalyzed C-H acylation proceeds through two distinct reactions: cycloplatination of 2-phenoxypyridine (C-H activation) and subsequent regiospecific acylation of the formed cycloplatinated complex. A crucial step to elucidating the mechanism is to carry out the stoichiometric reactions and characterize the related products and intermediates. To our surprise, preliminary results showed that the reaction of the 2-(3-methylphenoxy)pyridine with Pt(PhCN)$_2$Cl$_2$ in chlorobenzene at reflux didn't produce the desired cycloplatinated product, instead, a simple coordination complex was formed. One the other hand, the reaction of 2-(2-methylphenoxy)pyridine produce three different compounds, with the major product being the simple coordination complex. The characterization of the other two compounds is underway. The reaction of 2-(3,5-dimethylpenoxy)pyridine, which does not undergo the Pt-catalyzed C-H acylation reaction, with Pt(PhCN)$_2$Cl$_2$ produce two distinct platinum-phenoxypyridine coordination complexes showing very different chemical shift of the ortho-H of the phenyl group. We are currently investigating these complexes and their implications to the reaction mechanism and the results will be presented at the conference.



Pt-catalyzed acylation of 2-phenoxypyridines through direct C-H activation

SERMACS 579

In vitro glucuronidation of monobenzyl phthalate glucuronidation with UDP-glucuronosyltransferase 2B7

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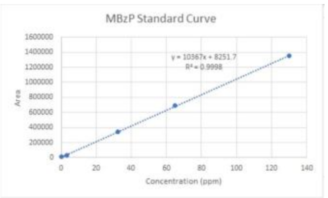
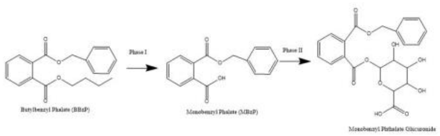
Phthalates are compounds used as plasticizers and industrial solvents in consumer products such as food packaging, personal care products, PVC, and polyvinyl flooring. Exposure to phthalates has been shown to correlate with reduced anogenital distance and testicular weight in developing male fetuses. Metabolism of phthalates diesters begin with phase I metabolism by lipases and esterases in the liver to remove a functional group and yield a more toxic phthalate monoester. Phthalate monoesters are then further metabolized in phase II metabolism by UDP-glucuronosyltransferases (UGTs) to produce a water-soluble phthalate glucuronide to promote urinary excretion. Phthalate glucuronidation has been proven to be inhibited by anti-inflammatory drugs such as diclofenac and could also be inhibited by commonly administered over-the-counter medications. Monobenzyl phthalate (mBzP), active metabolite of butylbenzyl phthalate (BBP), undergoes phase II metabolism primarily by UGT 2B7 in the liver. This study aims to extend the understanding of phthalate metabolism through determining the enzyme kinetics of UGT 2B7 for the substrate mBzP as well as the enzyme kinetics of UGT 2B7 in the presence of ibuprofen to identify inhibition of glucuronidation. Inhibition of UGTs by over-the-counter medications could be linked to abnormal fetal development and understanding phthalate metabolism may present precautions to reduce negative health effects associated with phthalate exposure.





SERMACS 580

Studies into the mutagenic potential of 8-oxo-2'-deoxyguanosine with human polymerase kappa

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8-Oxo-2'-deoxyguanosine (OdG) is a specific DNA lesion that originates from the reaction between reactive oxygen species (ROS) and 2'-deoxyguanosine (dG). Due to the relativley large oxygen at the C8 position, OdG prefers to switch its base conformation from the normal anti conformation to a syn conformation. Additionally, the oxygen at the C8 is in the keto tautomer, causing N7 to have a hydrogen and the ability to hydrogen bond donate. These two changes allow OdG to form stable base pairs not only with dC, as is typical, but also with dA. The latter pair is a mismatch that can lead to a dG to dT transversion mutation in DNA. dG to dT mutations, like those caused by OdG, have been linked to cancer, ageing, and other negative processes. We used human bypass polymerase kappa (polK) to look at how readily it incorporates dATP or dCTP across from OdG and dG. Based on the crystal structure of polK, it has been suggested that it has a rigid insertion site and prefers OdG in the syn conformation. Incorporation of dCTP and dATP opposite various analogues of OdG were tested with polK in order to better understand the effect of the C8 and C2 positions on the mutagenic potential of OdG.

SERMACS 581

Synthesis of a novel perfluoroalkyl(aryl) sulfonylimide (PFSI) monomer as a precursor for PEM fuel cells

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The overall objective of this research is to synthesize novel PFSI monomer for polymerization and use as the electrolyte in Proton Exchange Membrane (PEM) fuel cells. PEM fuel cells offer the advantages, such as operating at relatively low temperatures, and high efficiency and clean exhaust. The expected new PFSI polymers are expected to be more efficient when compared to the traditional Nafion® polymers. We are now focused on exploring the preparation methods for 4-(2-bromotetrafluoroethoxy) Acetanilide, a precursor for the PFSI monomers. The first several steps have been carried out successfully. The purification of the fluoroalkylation products are still in-progress. All the intermediate chemicals were characterized by ^{1}H and ^{19}F NMR.

SERMACS 582

Modular synthesis of fluorescent probes for metal ion detection

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A series of fluorescent probes for the detection of metal ions in biological systems were synthesized via modular design. These compounds were inspired by an unexpected observation of fluorescence of a Zinc complex of a related ligand having a limited pi system. This synthesis utilized click chemistry to simultaneously form both a metal binding pocket and a pi system that might serve as a fluorophore. In the first iteration of the project, a family of more than ten ligands were prepared, and each compound was characterized using ^{13}C-NMR, ^{1}H-NMR, IR, and GC/MS. Upon complexation of these ligands with Zinc ions, spectroscopic measurements showed limited fluorescence. In a second iteration, a fluorophore such as a coumarin or dansyl motif, was attached via an imine linkage on the non-triazole arm of the ligand of each previously prepared ligand. Initial results in our investigation of this second set of compounds indicate that this approach is a viable and efficient route to fluorescent probes for Zinc and other metal ions in solutions or in biological systems.

SERMACS 583

Effects of replacing CP with indenyl on metal-to-metal charge-transfer in $CP_2Ti(C_2FC)_2$ complexes

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Our interest in electron transfer through alkynyl-bridged organometallic frameworks led us to investigate structures with organic bridges between Fe^{II} and Ti^{IV}, specifically $^{R}Cp_2Ti(C_2Fc)_2$, where ^{R}Cp can be a variety of substituted cyclopentadienyl ligands. A specific interest in our group is the effect on redox potentials when the Cp ligands are substituted with indenyl. The $Ti^{IV/III}$ reduction of $Ind_2Ti(C_2Fc)_2$ is shifted anodically compared to that of $Cp_2Ti(C_2Fc)_2$. There is also a red-shift of the Fe^{II} to Ti^{IV} metal-to-metal charge-transfer band observed for the indenyl compounds compared to their cyclopentadienyl counterparts, which is consistent with the anodic shift. $Ind_2Ti(C_2Fc)_2$ possesses several other differences compared to $Cp_2Ti(C_2Fc)_2$. One is the appearance of two irreversible peaks in the anodic scan of $Ind_2Ti(C_2Fc)_2$ compared to one irreversible peak in the anodic scan of the Cp complex. Another is the partial irreversibility of the $Ti^{IV/III}$ reduction. Finally, whereas the $Ti^{IV/III}$ reduction is shifted anodically, the $Fe^{III/II}$ potential is shifted cathodically, hinting that something besides induction is affecting the redox potentials. Herein, we will discuss possible explanations for this unusual behavior.

SERMACS 584

Multi-step electrodeposition of p-type metal chalcogenides as components of water splitting tandems

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Thin films of doped, p-type metal chalcogenides have been cast on transparent conductive oxide substrates by a multi-step electrodeposition method. The films have controllable thicknesses, strong adhesion and good uniformity. Photoelectrochemical analysis confirms p-type behavior and reveals photosensitivity under moderate bias. Under suitable conditions and in the presence of proper co-catalysts, these films show promise as components of tandem solar cells for applications to photoelectochemical water splitting.

SERMACS 585

Coordination chemistry, luminescence, and f-element extraction selectivity of a tripodal carbamoylmethylphosphine oxide-based ligand

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Improving processes used in f-element separations has steadily become more relevant due to numerous applications in rare earth element (REE) mining, nuclear waste remediation, and electronic waste recycling. As a result of the similarities in properties of the f-elements, mixtures containing REEs are often found to contain actinides (An) in small quantities. This is most commonly seen in raw materials such as natural minerals and ores, which is one of the reasons why the pursuit of methods for efficient separation of these An metals from the other REEs is worthwhile. This work examines a phenyl substituted carbamoylmethylphosphine oxide (CMPO)-based tripodal ligand employing a tris(3-aminopropyl)amine (TRPN) capping scaffold. Preliminary results indicate that this TRPN-CMPO-Ph ligand exhibits a high extraction efficiency with respect to the separation of thorium from aqueous solution. This study further investigates the extraction selectivity of TRPN-CMPO-Ph utilizing a mixture containing thorium, uranium, and all of the REEs excluding promethium. Additionally, we probe the extraction efficiency of the ligand by investigating the effect of ligand concentration and stir times used in the extraction protocol. Finally, the luminescence of europium(III) and terbium(III) complexes of the TRPN capped ligand was studied to gain insight into the coordination environment of the metal centers.

SERMACS 586

Incorporation of lignin-coated cellulose nanocrystals (L-CNCS) in poly(hydroxybutyrate) (phb)/poly(lactic acid) (PLA) blends and characterization by DSC and TGA

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In recent years, the clinical potential for biodegradable polymers, such as poly(hydroxybutyrate) (PHB) and poly(lactic acid) (PLA), has increased in the field of biomedical engineering. PHB and PLA are both biocompatible polyesters with favorable physical and mechanical properties. Previous studies have shown that the incorporation of lignin-coated cellulose nanocrystals (L-CNCs) in various grades of PLA by melt mixing led to improved mechanical properties, while incorporation in PHB led to plasticization. We have prepared various PHB/PLA blend ratios and incorporated 0.2 – 2.0 wt.% loading L-CNCs by high torque mixing. By differential scanning calorimetry (DSC) we observe two glass transition temperatures (T_g) and two cold crystallization temperatures (T_{cc}) for the polymer blends; however, in some of the L-CNC nanocomposites exhibit only one T_g and one T_{cc}, suggesting that the L-CNCs have severed to increase the compatibility the polymers. We have also examined thermal and thermal oxidative stability of the nanocomposites by thermosgravimetric analysis (TGA). We will report the results of our studies.

SERMACS 587

Synthesis, characterization, and fluorescence spectroscopy of new ligands and complexes

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A family of ligands was designed and synthesized with the purpose of developing a fluorescent probe for transition metal ions. This approach began with ligands formed from a family of halogen-substituted aromatic cores each with two ligating arms, one of which was functionalization with a known fluorophore moiety: dansyl, resorufin, or coumarin. An azidofluorophore of each of moiety, designed to easily attach to the propargylated ligands via click chemistry, was synthesized in situ. The resulting compounds formed via a Huisgen Reaction featured two components: a ligand pocket for metal complexation and a nearby fluorophore. This allowed for the energy from a photon to be absorbed by metal complexes and subsequently transferred and reemitted by the adjacent fluorophore. Three families of ligands were prepared with corresponding fluorophores and each ligand was characterized via ^{1}H NMR, ^{13}C NMR, FT-IR, and LC/MS. The synthesized ligands fluoresce in the presence of transition metal ions. We anticipate these compounds may be useful in determining concentrations and locations of metal ions present in biological systems or in other analytical applications.

SERMACS 588

Forensic application in determining the age estimation of documents using infrared spectroscopy

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In the field of forensic science, a questioned document will often require its age to be verified to determine the legitimacy of the document. Most research done in the field of questioned document forensics is on ink or handwriting, leaving only 6% of research involving the paper substrate. It is currently accepted that cellulose-based paper can be artificially aged by exposing it to harsh conditions, therefore this project explores the natural aging process of paper to determine the validity of the claim. Known degradation pathways of cellulose involve oxidation and acid-catalyzed hydrolysis, which can be accelerated artificially; however, the potential for alternative pathways that may be independent of conditions exists. Chemical information can be gleaned through use of vibrational infrared spectroscopy such as Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). Both methods are portable and non-destructive, which is of utmost importance in the field of forensic science. Three brands of paper were stored in three different conditions, varying exposure to light, heat, and humidity, some of the most significant variables in document storage. Ten replicates of an individual sample was scanned for each condition and brand combination over the course of multiple months by both ATR-FTIR and DRIFTS. The samples were then normalized and analyzed with principal component analysis (PCA), grouping by date in order to determine their separability. Discrimination was found using PCA with leave-one-out cross-validation, which is an algorithm used to determine the group of best fit.

SERMACS 589

Direct allylation of ketones with trimethylsilyl trifluoromethanesulfonate and triethylamine

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Allyl propionates are readily ionized to provide allyl carbocations in the presence of trimethylsilyl trifluoromethanesulfonate. In the same reaction mixture, ketones can be converted to enol silanes if an amine base is present. In one pot, enol silane formation and

carbocation formation occur, resulting in SN1 reaction to yield the gamma,delta-unsaturated ketone products. Selectivity for unsymmetrical allyl carbocations is influenced by electronic effects.

SERMACS 590

Synthesis of new cinnamaldehyde derivatives as anti-diabetic agents

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Diabetes Mellitus as a disease resulting from high levels of blood glucose due to defects in insulin production and/or action. This disease is common amongst disadvantaged minority groups such as African Americans and Hispanic Americans. Despite a variety of medications available, most of these minority groups seek out more cost efficient and natural therapeutics. Cinnamaldehyde, an agricultural fungicide found in cinnamon, has shown significant anti-diabetic effects by lowering blood glucose. The objective is to alter the structure of the cinnamaldehyde and obtain derivatives which may affect its anti-diabetic properties. The derivatives synthesized via aldol condensation may improve the efficacy and cost of diabetes treatment because of additional functionalization. Three new derivatives were synthesized by the addition of acetaldehyde, sodium hydride, anhydrous solvent tetrahydrofuran (THF), and different substituted benzaldehyde containing methoxy, chloro, and methylene oxide side groups at the para position. These were added in a glove box because the sodium hydride reacts with oxygen and water. An orange solution was the result and it was extracted with ethanol. The solids formed were recrystallized from ethanol to obtain pure compounds. The percent yield of the pure substance was between 20% and 35%. Each of the compounds burned and shrunk at 200°C but did not melt. Once a solid was formed, it was analyzed using 60 MHz Nuclear Magnetic Resonance Spectroscopy where it was dissolved in chloroform to test its purity. The proton NMR analysis showed the C=C double bond signal at 4.8 ppm for each compound. The methyl oxide group was located at 3.9 ppm and the benzyl ring was located between 6.8-7.4 ppm. The piperonal group was found at 5.9 ppm. 2D COSY NMR was also used to analyze coupling and correlations of signals. These new compounds will be tested on live cells to analyze their toxicology effects before testing their anti-diabetic properties.

SERMACS 591

Nitrile aldol reactions mediated by trimethylsilyl trifluoromethanesulfonate

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In the presence of trimethylsilyl trifluoromethanesulfonate, (trimethylsilyl)acetonitrile adds to aldehydes to yield aldol products. Either the aldol addition or aldol condensation product may be observed, dependent upon the electronic properties of the aldehyde. Similarly, acetonitrile itself can be activated in situ with trimethylsilyl trifluoromethanesulfonate and an amine base, leading to a one-pot silyl ketene imine formation-Mukaiyama aldol reaction

SERMACS 592

Binding of cucurbit[5]uril with alkali metal ions via ESI-MS

Jeffery Davison, *jdaviso2@my.westga.edu,* ***Joy Adebajo***, *oadebaj2@my.westga.edu,* ***Anjelina Webb***, *awebb17@my.westga.edu, Farooq A. Khan. Dept of Chemistry, Univ of West Georgia, Carrollton, Georgia, United States*

Cucurbit[n]urils, or CBn, where n = 5, 6, 7, 8 or 10 are "molecular containers" well-suited for binding of a wide array of molecules, and are of immense interest in drug delivery, photochemical reactions and catalysis. Of considerable interest in understanding the fundamental properties of these molecules are their binding properties with metal ions. In our study, we have explored the binding selectivities of CB5 with alkali metal ions via electrospray ionization (ESI) mass spectrometry in aqueous solutions. We find that CB5 binds with one or two alkali metal ions. The relative binding energies for CB5 were determined via collision-induced dissociation (CID) experiments, and found be $Li^+>Na^+>K^+>Rb^+>Cs^+$. Species containing CB5, two metal ions and chloride ions were also observed, which upon CID, result in the loss of a neutral MCl species.

SERMACS 593

Crossed Aldol reactions of aldehydes and subsequent styrene formation promoted by trimethylsilyl trifluoromethanesulfonate

Grant Dixon, *grant.dixon@richmond.edu, Chiles W. Downey. University of Richmond, Richmond, Virginia, United States*

Alpha-branched aldehydes undergo enol silane formation in the presence of trimethylsilyl trifluoromethanesulfonate and and amine base. When a second aldehyde is added to the reaction mixture, crossed aldol addition takes place in high yield. Extended reaction times in the presence of excess base and trimethylsilyl trifluoromethanesulfonate lead to the formation of beta,beta-dialkyl styrenes when aromatic aldehydes act as the desired electrophiles.

SERMACS 594

Synthesis of chiral carboxylic acids from hydrocarboxylation of alkenes

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Carboxylic acids are used as platform chemicals for the synthesis of value-added polymers and chemicals. Carboxylic acids can be used in pharmaceuticals such as ibuprofen and aspirin. Developing a chiral compound could lead to the creation of more medicines and further research into diseases that need cures. Although the carboxylation of olefins using CO_2 has been a great method for synthesizing carboxylic acids, developing its chiral compound has been a great challenge for chemist. Chiral catalysts containing Nickel and Palladium were dissolved in THF in a benchtop glove box and auxillary ligand was added and brought into a fume hood where 4-(Chloromethyl) styrene and excess dry ice were added at room temperature and stirred overnight. Diethylzinc was added the following day as a hydrogen source, stirred for two hours and diluted with 1M HCl. Purification was done by vacuum filtration, extraction with ethyl acetate using a separatory funnel, and vacuum distillation to achieve a pure compound. The pure compound will be characterized using Nuclear Magnetic Resonance spectroscopy and polarimeter to determine optical activity. Proton NMR showed that the carbon double bonds from the substrate were not present supporting carboxylation reaction.

SERMACS 595

One-pot furan synthesis from ketones and propargyl acetates

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Ketones are easily converted to enol silanes in the presence of trimethylsilyl trifluoromethane sulfonate and an amine base, conditions that also result in the ionization of terminally silylated propargyl acetates. When these events occur in a single flask, the intermediates undergo SN1 reaction to generate a beta-propargyl ketone intermediate. Upon concentration in the presence of trace water, the intermediate cyclizes to yield 2-methylfurans in high yield.

SERMACS 596

Binding studies of cucurbit[6]uril with alkali metal ions via ESI-MS

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Cucurbit[n]urils, or CBn, where n = 5, 6, 7, 8 or 10 are “molecular containers” well-suited for binding of a wide array of molecules, and are of immense interest in drug delivery, photochemical reactions and catalysis. Of considerable interest in understanding the fundamental properties of these molecules are their binding properties with metal ions. In our study, we have explored the binding selectivities of CB6 with alkali metal ions via electrospray ionization (ESI) mass spectrometry in aqueous solutions. We find that CB6 binds with one or two alkali metal ions. The relative binding energies for CB5 were determined via collision-induced dissociation (CID) experiments, and found be $Li^+>Na^+>K^+>Rb^+>Cs^+$. Species containing CB6, two metal ions and chloride ions were also observed, which upon CID, result in the loss of a neutral MCl species.

SERMACS 597

Effect of the trifluoropropynyl ligand on emissive platinum complexes

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Alkynyl Pt^{II}complexes of the type $Pt(tbbpy)(C_2R)_2$ have been investigated as phosphors for organic light emitting diodes (OLEDs). The design of blue emitters with high emission quantum yields is an active area of research. In order to observe the effects of the trifluoropropynyl ligand (C_2CF_3) on the photoluminescence of platinum complexes, $Pt(tbbpy)(C_2CF_3)_2$ (tbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine) was synthesized in two steps via a dichloro- precursor. Photophysical properties of the complex were studied using steady-state fluorescence and UV/Vis spectroscopy. The emission of $Pt(tbbpy)(C_2CF_3)_2$ is blue-shifted (λ_{max}= 488 nm) relative to a widely studied analog, $Pt(tbbpy)(CCPh)_2$ (λ_{max}= 536 nm). The strong electron-withdrawing properties of the trifluoropropynyl ligand are thought to be responsible for this shift in emission. Self-quenching of the emission is observed; emission intensity does not increase linearly with concentration. At higher concentrations, an excimer emission (λ_{max}= 613 nm) is also observed in dichloromethane. Consequently, a saturated solution of the chromophore in dichloromethane exhibits white emission as a result of the combination of the luminescence of the excimer and the observed complex. Due to its emissive properties, this molecule could be used in OLED technologies.

SERMACS 598

Identification of the function of protein 3L1W

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The goal of our study was to identify the function of the protein 3L1W, which has a solved structure in the online Protein Database (PDB) but unknown function. The bioinformatics tools PyMOL, ProMOL, BLAST, Pfam, DALI, AutoDock VINA, and PyRx were used in this computational analysis. We found amino acid side chains in 3L1W that had similar structures to those of known enzyme active sites using PyMOL and ProMOL. Then, we used BLAST to compare our amino acid sequence with that of proteins with known functions. In Pfam, we pinpointed the most highly conserved amino acid residues. We used DALI to identify structural similarities between our unknown protein and proteins of known functions and structures. Using PyRx and AutoDock VINA, we were able to identify ligands that are hypothesized to be present in the proposed activation site of our unknown protein. Once the ligands were identified, we uploaded our ligands and unknown protein files onto the Rosetta Online Server that Includes Everyone (ROSIE) to find a more accurate representation of our protein-ligand interaction. By conducting our study, we have evidence that supports our unknown protein, 3L1W, is a member of the Endonuclease Exonuclease Phosphatase Family (EEP). Our protein function is suggested to cleave phosphates through hydrolysis, or the use of water. Results of the docking of specific ligands will be presented.

SERMACS 599

Synthesis of 5'-triphosphate-8-thio-2'-deoxyinosine, an analogue of 5'-triphosphate-8-oxo-2'-deoxyguanosine

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When exposed to reactive oxygen species, such as those formed as byproducts of metabolism, 2’-deoxyguanosine (dG) can undergo oxidation to form 8-oxo-2’-deoxyguanosine (OdG). While still capable of forming stable base pairs to 2’-deoxycytidine (dC), OdG also possess the ability to pair with 2’-deoxyadenosine (dA). Polymerases can recognize both OdG:dC and OdG:dA base pairs, the latter of which can lead to dG to dT transversions during subsequent rounds of replication. Thus, this alternate pairing may explain why OdG has been linked to aging, as well as diseases such as Alzheimer’s and cancer. Study of different OdG analogues can provide insight into the importance of various positions of OdG toward its mutagenic potential. As such, the Hamm lab synthesizes various analogues of OdG including 8-thio-2’-deoxyinosine (SdI). To better understand incorporation of the 5’-triphosphate derivatives of OdG (OdGTP) during replication and other DNA copyinh processes, the 5’-triphosphate derivative of SdI (SdITP) was synthesized. Nucleoside monomers were purified by reverse phase column chromatography and confirmed by NMR. The triphosphate derivative was purified through DEAE ion exchange chromatography and HPLC before characterization by NMR.

SERMACS 600

Wound healing in space: Final frontier and the role of biomimetic polymers

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For several decades, researchershave been trying to produce materials that will mimic tissue environments within the human body. This is of particular interest as it pertains to biomedical care aboard the International Space Station. Due to the lack of medical resources in space, ensuring that there is an absence of complications during the wound healing process is vital to medically safe space travel. Biopolymers like dermatan sulfate, chitosan, and hyaluronic acid promote wound healing and provide a natural inspiration for engineered biomaterials. Through processes like electrospinning, investigators are able to include components such as biomolecules to create nanofiber scaffolds for biomedical applications, such as modern bandages. The biopolymers used are expensive and can prove costly to incorporate into prepared materials. In light of this, the overall goal of this research is to develop cost-effective, biomimetic polymers for use as wound healing materials. In recognition of the elegant designs of natural polymers and the role they play in wound healing, we have added functional groups to a poly(vinyl alcohol) backbone to create a biomimetic polymer for use in the biomedical field. Significant functional moieties found in hyaluronic acid and dermatan sulfate were selected for attachment via organic coupling reactions. The attachment of the functional groups was confirmed through the use of nuclear magnetic resonance. Electrospinning of the synthesized biomimetic polymer yielded novel nanofiber scaffolds and it is anticipated that the inclusion of these functional groups in the scaffold via the biomimetic polymer will allow it to influence wound healing similarly to the original biomolecules. The prepared biomimetic poly(vinyl alcohol) nanofiber constructs will be compared to hyaluronic acid- and dermatan sulfate-containing nanofiber mats to observe differences in the constructs including morphology and *in vitro*cellular responses. We believe that the use of biomimetic scaffolds such as these will lead to a better understanding of wound healing and tissue regeneration.

SERMACS 601

Synthesis of colloidal gold aggregates for speckle patterning of mouse aorta

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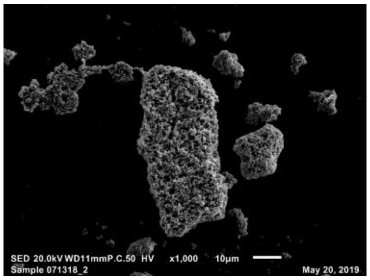
Introduction: Colloidal gold particles are synthesized from chloroauric acid (HAuCl4) and ascorbic acid (C6H8O6). Gum arabic is used as a stabilizer to control the aggregation process after synthesis. Because of the unique surface chemistry interaction between gold particles and sulfhydryl groups in proteins, colloidal gold aggregates can spontaneously bind to create a speckle pattern on the mouse aorta surface. This is an innovative approach to create speckle patterns on soft tissues to measure strain fields using digital image correlation (DIC). Materials and Methods: The concentration of chloroauric acid was optimized in the range of 0.001M-0.0025M. Ascorbic acid was in the range of 0.1M-0.3M. After adding chloroauric acid to ascorbic acid solution, each mixture is vigorously stirred for 15 minutes. This reaction results in the reduction of chloroauric acid and initial rapid production of gold particles in the nanometer range. Then, unit gold nanoparticles start to aggregate to form micron-sized gold aggregates which can be used for speckle patterning of mouse aorta. During the aggregation, gum arabic (0.2 wt %), which serves as a stabilizer, was added to colloidal gold suspensions at different time points (0-72 hours). The purpose is to control the final size of colloidal gold aggregates. Following precipitation, the size of the aggregates was determined by SEM (scanning electron microscopy) and image analysis using ImagePro Plus software. Results: Based on our SEM study, the average particle size increases with the length of time before addition of stabilizer. The particle size can be controlled between the range of 1-10µm. The longer the process continues before addition of the stabilizer, the larger the particle aggregates become. For application in speckle patterning of mouse aortas for DIC, we chose to add stabilizer after 48 hours to produce aggregates with an average size of 5±3.5 microns.



SERMACS 602

Crystal structure of phosphoethanolamine methyltransferase from *Eimeria tenella*

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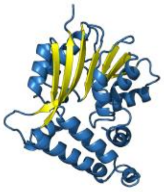
Eimeria tenella is an apicomplexan responsible for coccidiosis in chicken, a disease that can lead to stunted growth and death of the host animal. Recently, it has been reported that host animals and their parasites, including parasitic nematodes and apicomplexans, use different pathways to synthesize Phosphatidylcholine (ptdCho) which is the most abundant phospholipid in the cellular membrane in host animals and many parasites. Many parasites use a pathway called the Phosphobase Methylation Pathway for the conversion of phosphoethanolamine (pEA) to phosphocholine (pCho), an intermediate in the synthesis of ptdCho, through a series of methylation reactions that are catalyzed by phosphoethanolamine N-methyltransferace (PMT). Since this pathway does not exist in host animals, it could potentially be an antiparasitic drug target. Genomic studies show that *Eimeria tenella* contains a type 2 PMT (EtPMT), which is similar to *Plasmodium*. Here, we examine the three-dimensional structure of EtPMT, through x-ray crystallography, to better understand its substrate and cofactor binding sites. The 2.97 Å resolution crystal structure of EtPMT was built and refined using coot and phoenix to an R-free of 0.2649. This structure can be used to verify the contributions of specific active site residues to EtPMT function.

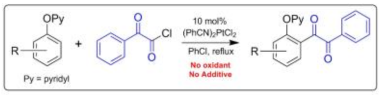


SERMACS 603

Synthesis of 1,2-diketones through platinum-catalyzed C–H functionalization

Justin Neu[1], *neuj16@students.ecu.edu, Avery Hatch*[2]*, Shouquan Huo*[3]*. (1) East Carolina University, Mooresville, North Carolina, United States (2) Chemistry, Elon University, Elon, North Carolina, United States (3) Dept of Chemistry, East Carolina University, Greenville, North Carolina, United States*

1,2-Diketones are important scaffolds found in medicinally or biologically active compounds. In addition, 1,2-diketones are very important precursors to synthesizing other cyclic and acyclic organic molecules. Therefore, the synthesis of 1,2-diketones has attracted a great deal of attention and various methods have been developed. Recently, we have reported a novel Pt-catalyzed acylation of 2-phenoxypyridines through direct C-H activation to make diketones, which does not require an oxidant nor other additives. We hypothesized that 1,2-diketones could be synthesized via the Pt-catalyzed acylation of 2-phenoxypyridines with a-oxoacid chlorides as the acylating reagents, which should provide a straightforward synthetic method for 1,2-diketones. The preliminary results have shown that platinum-catalyzed C-H functionalization reaction, with benzoylformyl chloride as the reagent, produces a diketone compound. It should be also noteworthy that the reaction is free of any additive/oxidant and free of any decarbonylation side reactions. Currently, we are investigating the scope and limitations of this synthesis and the results will presented.



Pt-catalyzed acylation of 2-phenoxypyridines through direct C-H activation to make diketones

SERMACS 604

Investigating the structures and properties of mixed silicon-copper, germanium-copper and germanium-gold clusters

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Doped semiconductor clusters have received recently new attention as novel catalysts in various different reactions. Here, properties of multiple structures of silicon/copper, germanium/copper and germanium/gold clusters (Si_nCu_m, Ge_nCu_m, and Ge_nAu_m) were studied using computational chemistry methods. Global optimization techniques were utilized to locate low-lying isomers. Further optimization was conducted utilizing Density Functional Theory with different spin states. Once global minimum structures were determined, different spectroscopic and bonding properties including infrared spectra, molecular orbital generation, and natural bond analysis of the lowest energy structures were analyzed. We will present these results, compare them to previous investigations, discuss possible use as catalysts, and detail how these calculations complement future matrix-isolation infrared experiments currently being assembled in our research group.

SERMACS 605

Gas chromatography relay: passing the baton from one laboratory student group to the next

Susan Verberne-Sutton, *susan.sutton@vanderbilt.edu. Chemistry, Vanderbilt University, Nashville, Tennessee, United States*

Inquiry-Guided Learning (IGL) in the laboratory is largely difficult in lower-division undergraduate courses due to the lack of laboratory experience the student has had at this point in their education. Teaching students basic concepts while layering problem-solving skill sets as a freshman/sophomore can be particularly difficult. Through the process of active investigation I have created a sophomore-level laboratory experiment for Introduction to Analytical Chemistry called 'Gas-Chromatography Relay' where rather than demonstrating key concepts as the traditional 'sage on the stage' I instead guide the students to discover the instrument for themselves. In this model, students gain a working document from the previous group to move forward in solving an open-ended problem, and they themselves move forward with discovery and update the document for the next group. In this scenario students learn the importance of scientific community through written communication of SOPs, discussion of results, and critical editing of the working document. Student assessment and feedback is gathered as the students are half finished with the senior-level capstone course.

SERMACS 606

Escaping from quant lab: Using competition and teamwork to build critical lab skills

Leslie A. Hiatt, *hiattl@apsu.edu, Hannah B. Musgrove, Will M. Ward. Chemistry Department, Austin Peay State University, Clarksville, Tennessee, United States*

Lab should be a place where students learn freely, make mistakes, and face challenges, but too many labs are cookie cutter exercises that produce results without requiring critical thinking. Commercial escape rooms require players to work as teams to solve tough problems. Other work using games and competition to enhance student understanding in lab has been done, but to the author's knowledge, this lab set-up is the first of its kind, using an escape game as the basis of an entire Quantitative Analysis Lab curriculum. Students begin by learning techniques and improving their skills in preparation for the final challenge. Initial lab sessions end with students questioning how the lab they just performed might help them in the Escape Game mystery. When students begin the Escape Game, they have already invested in improving their lab techniques and understanding how those techniques can help them interpret data about unknowns. In the Escape Game, students were given three bottles of chocolate syrup to analyze. They had four weeks to answers multiple questions about these unknowns. These answers led them to identify a member of APSU's Chemistry Department as "the copper crook" in the final piece of the game. All teams successfully completed the challenge before the time expired. This approach will be repeated and improved in the fall based on student feedback. The students improved in each of the following: experimental design, teamwork, multi-tasking, lab preparation, and data analysis. The approach integrated the classroom and laboratory, particularly in helping students understand selectivity and sensitivity and dealing with error in experimental design. The Escape Game was successful in allowing students freedom to succeed in a challenging environment. These strategic interactions between students allowed them to gain confidence and skills critical to their future endeavors.

SERMACS 607

Study for STARS (self-tracking, assessment and reflection study) in organic chemistry course: Time management project

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The STARS (Self Tracking, Assessment and Reflection Study) project focusses on 5 active learning strategies to help the students analyze and restructure their day-to-day activities to adjust and boost their learning outcomes. Tools such as a minute paper, muddiest point, just-in-time teaching (pop-quizzes), student generated study guide and exam questions are strategically incorporated throughout the semester. The tools are provided in a physical bound paper-back notebook and also on Learning Management System. The minute table and the muddiest point are collected and discussed on a weekly basis. The students have also been provided with a weekly reading chart to keep them on track with the class, and a pop-quiz sheet that would correlate to the weekly reading assignments. The outcome of this research is to see if there is a correlation between effective time management skills and higher and overall test/course grades in organic chemistry I course.

SERMACS 608

POGIL in the physical chemistry lecture and lab

Andrea A. Carter, *aacarter@meredith.edu. Dept of Chemistry, Physics, and Geoscience, Meredith College, Raleigh, North Carolina, United States*

Process Oriented Guided Inquiry Learning (POGIL) is a collaborative, active learning strategy that has a strong basis in the constructivist model of learning. Over several semesters, I have converted a two-semester sequence of physical chemistry courses into predominantly POGIL-style for both lecture and laboratory classwork at a small, primarily undergraduate women's liberal arts college. Almost all POGIL activities implemented in my courses were written by others and are now published. In this presentation, I will share my personal experiences with implementing an upper-level POGIL-style course, including both positives and negatives. I will share my lessons learned, tips for success, and planned future changes, including the use of open educational resources. Finally, student feedback and assessment using ACS standardized exams will be discussed.

SERMACS 609

Computational chemistry applied to interesting problems

George C. Shields, *george.shields@furman.edu, Tyler Ball, Ariel Gale, Tuguldur T. Odbadrakh. Chemistry, Furman University, Greenville, South Carolina, United States*

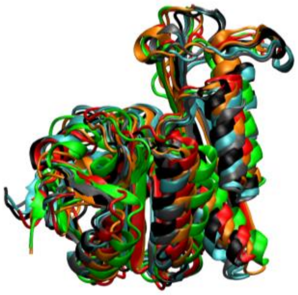
The **M**olecular **E**ducation and **R**esearch **C**onsortium in computational chemist**RY** (**MERCURY**) has been a driving force for increasing the productivity of faculty working with undergraduates at primarily undergraduate institutions, increasing the number of STEM PhDs, and improving diversity and inclusion in chemistry. In this talk I will briefly overview some of the interesting problems tackled by MERCURY faculty, and discuss some of our own work in atmospheric chemistry.

SERMACS 610

Molecular studies of halogen bonding, protein dynamics and combustion

Carol A. Parish, *cparish@richmond.edu. Univ of Richmond, Richmond, Virginia, United States*

Our research is diverse by design – the unifying theme is the careful methodological approach that we employ. We utilize highly correlated multireference quantum chemical techniques to study the structures and energies of di- and poly-radicals, and correlated, single reference methods to study halogen bonding and reaction pathways for pyrolysis and combustion. We also utilize efficient sampling methods to study conformational flexibility, host-guest interactions and protein folding. Results will be presented on our work related to halogen bonding, apo protein dynamics and high temperature combustion of oil shale model compounds.



SERMACS 611

Noncovalent interactions in solution and crystals

Charles D. Sherrill, *sherrill@gatech.edu. School of Chemistry and Biochemistry, Georgia Inst of Technology, Atlanta, Georgia, United States*

Using emerging computational tools, it is becoming possible to obtain a deeper understanding of how noncovalent interactions operate in condensed phases. Regarding solutions, our group's functional-group partitioning of symmetry adapted perturbation theory (F-SAPT) has been employed to understand how intermolecular pi-pi interactions are modulated in an aqueous environment. Results from computational experiments on such systems will be presented and analyzed. Regarding solids, the many-body expansion, which sums up energies in terms of monomer, dimer, trimer, etc., contributions, offers a way to compute lattice energies of molecular crystals in a pleasantly parallel fashion. This talk will discuss our recent progress in developing algorithms and software for such an approach, along with initial applications.

SERMACS 612

New insights into the mechanisms of ubiquitin conjugating and ubiquitin ligase enzymes

Isaiah Sumner, *sumneric@jmu.edu. Department of Chemistry and Biochemistry, James Madison University, Harrisonburg, Virginia, United States*

Cells can rapidly respond to their environments by modifying proteins involved in the relevant regulatory pathways. In one such modification, ubiquitination, the small protein ubiquitin is attached to a lysine sidechain of a target protein. Lysine ubiquitination is important in protein degradation, immune response, and other pathways. It happens in three steps and is catalyzed by a ubiquitin activating enzyme (E1), a ubiquitin conjugating enzyme (E2) and a ubiquitin ligase (E3). In the second step, the ubiquitin is covalently bonded to the E2 enzyme with a thioester linkage. The E2 enzyme catalyzes the rupture of this bond and the formation of an isopeptide bond on the target substrate. A RING-E3 may assist in this transfer but does not affect the chemical steps. Here, we use three computational techniques – Born-Oppenheimer Molecular Dynamics (BOMD), single point Quantum Mechanics/Molecular Mechanics energies (QM/MM), and classical Molecular Dynamics (MD) – to probe the mechanisms used by both the ubiquitin conjugating enzyme, Ubc13, and the RING-E3 domain in RNF4. Our simulations of wild-type and mutant systems contradict the popular assertion that the reaction intermediate is stabilized by a highly conserved asparagine in the E2 enzyme (Asn79 in Ubc13). However, they support the hypothesis that the RING-E3 ligase puts strain on the thioester linkage, allowing it to break more easily.

SERMACS 613

Adventures in DFT designing of organic electronic materials

Aimee L. Tomlinson, *aimee.tomlinson@ung.edu. University of North Georgia, Dahlonega, Georgia, United States*

I will present our work in identifying materials for use in organic light emitting diodes (OLEDs) and electrochromic (those which change color upon potential changes) devices. Through our partnership with the Jeffries-EL group at Boston University, we have generated a number of systems which show promise for use in OLEDs either as a blue-emitter or host-type material. Additionally, I will discuss our recent advances in formulating a high contrast black to transmissive or transmissive to black device through our collaboration with the Reynolds group at Georgia Tech. In particular, we will show the success of our DFT/TDDFT model on both cathodically and anodically coloring electrochromes.

SERMACS 614

Toward a comprehensive predictive model of stacking interactions

Steven E. Wheeler, *swheele2@uga.edu. Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia, United States*

Stacking interactions, which are roughly parallel face-to-face interactions between planar π-systems, play important roles in chemical and biochemical systems. Our ability to predict and rationally tune the strength of these interactions is important in everything from the design of new catalysts to drug design. I will discuss our efforts over the last decade in developing quantitative and qualitative models of various stacking interactions. The focus will be on interactions operative in drug binding sites, and we will introduce a new model of stacking interactions of drug-like heterocycles with the aromatic amino acid side chains Phe, Tyr, and Trp that enables the prediction of the strength of these interactions based solely on the connectivity of the heterocycle.

SERMACS 615

Applications of computational chemistry to engineering problems

Abu Shama Mohammad Miraz[2], *Collin D. Wick*[1], ***Bala Ramachandran***[1], *ramu@latech.edu. (1) Chemistry, Louisiana Tech University, Ruston, Louisiana, United States (2) Engineering, Louisiana Tech University, Ruston, Louisiana, United States*

The most common applications of computational chemistry address the structural and energetic (thermodynamic) aspects of interactions between molecules, clusters of atoms, or chemical reactions. As computing power and the capabilities of software have increased, the range of applications of these methods have also expanded beyond “traditional” chemical problems. In this talk, I will summarize some recent research from our research group in which “first principles” methods of computational chemistry are directed at problems arising from engineering contexts that require understanding the structure, properties, and failure mechanism of metal/ceramic interfaces.

SERMACS 616

Unraveling the mechanism of polyethylene microstructure modulation using a redox-active Ni-based olefin polymerization catalyst

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Redox-switchable catalysis is of great interest in the field of polymer chemistry for its potential to produce tunable structures of functionalized synthetic polymers. Recently, a Ni-based Brookhart-type catalyst has shown a change in the degree of alkyl branching in polyethylene products following reduction of the catalyst. Though such a tunable capability has been shown, neither the mechanism that leads to switchable branch formation nor the structures of the reduced catalyst and resulting active species are completely understood. Here, results of dispersion-corrected TPSSh/cc-PVTZ calculations allow us to not only examine catalyst structure but also to elucidate the nature of this catalytic mechanism to atomistic detail. We find a difference in branching ratios stems from a balance in steric and electronic effects, mainly at the reagent-ethylene addition steps, which is expressed not only in addition-product energies but also in the deviation from square planarity around the Ni center. The changing interplay between steric and electronic factors also affects the selectivity of reagent binding to the catalyst. With larger reagents such as hexene, an additional steric interaction involving the alkyl tail of the reagent, which is imposed by square planarity moreso in the reduced system, leads to a difference in alkene-binding ratios when the catalyst is co-dosed with ethylene and these larger reagents. Finally, we extend our findings to suggest electronic modifications to the catalyst which in concert with redox switchability can enhance the branching-ratio tunability of the catalyst. We hope that these results provide insight into the development of a next-generation redox-switchable catalysts capable of producing a desired ratio of product functionalization.

SERMACS 617

Reproducible, rational, and rigorous QM-cluster enzyme models

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Research using various types of multiscale enzyme simulations has inarguably provided answers to “grand challenge” questions in chemistry and biochemistry, especially using QM/MM, ONIOM, or QM-only cluster models. Despite decades of calibration studies and comparisons of QM and QM/MM results, a dearth of published, algorithmic guidelines or online tutorials exists. The quantitative relationships between composition or size of the active site/QM region and computational accuracy are still poorly understood. Calibration studies of enzyme thermodynamics/kinetics usually employ only 2-15 different enzyme models, and like published applications of QM-cluster models, they frequently lack reproducible structural data. Development of a software toolkit called RINRUS (Residue Interaction Network ResidUe Selector) has allowed calibration of QM-cluster models on an unprecedented, fine-grained scale. By generating hundreds of unique QM-cluster models from 120 – 530 atoms in size, the convergence of thermodynamic and kinetic properties of the Catechol-*O*-methyl transferase (COMT) enzyme is analyzed. Our data will be incorporated into a reproducible and systematic rules-based approach for designing QM and QM/MM mechanistic studies of enzymes.

SERMACS 618

Biochemical mechanistic investigations to enable the synthetic biology of type I polyketide synthases

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Type I Polyketide Synthases (PKSs), pathways primarily found in high GC soil bacteria (such as actinobacteria) present numerous opportunities to engineer a broad range of chemical scaffolds. Due to their modular nature, there is a great ability to predict the structure of the metabolite from sequence, termed the principle of collinearity. We seek to understand how to engineer them for applications in generating small molecules (ranging from medicinal applications, to building blocks, to other valuable fine and specialty chemicals). First, we seek to engineer individual domains through understanding subtle positional changes in the active site introduced via conservative point mutations, with specific focus on the ketoreductase domain. Second, we seek to understand issues of the interacting selectivities of the multiple domains harbored within a module, including understanding the kinetic rate enhancement derived from their substrate being delivered intramolecularly (so-called "thiotemplated natural products), as well as teasing apart gatekeeping interactions among downstream domains when an upstream change is implemented. Finally, we seek to biochemically understand differences in folding, function, and stability when PKSs are expressed in different hosts, or refactored at the genetic level. Using biochemical and biophysical techniques that focus on the characterization of these complex multi-domain proteins enables identifying where some of the key bottlenecks to engineered systems arise.

SERMACS 619

Harnessing actinomycete biosynthetic pathways to expand diketopiperazine chemical diversity

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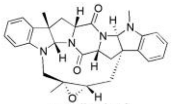
Actinomycetes, a group of gram-positive bacteria, are renowned sources of structurally intriguing natural products that are assembled via specialized biosynthetic pathways. Characterization of these pathways facilitates the development of natural products as pharmaceuticals and agrochemicals, provides tools for chemoenzymatic syntheses, and offers insights into microbial ecology and evolution. My research program aims to understand and expand the biosynthetic potential of actinomycetes. This presentation will highlight our findings for pathways in which cyclodipeptide synthases (CDPSs) catalyze 2,5-diketopiperazine (DKP) assembly from aminoacyl-tRNAs. Although CDPSs are broadly distributed across bacterial phyla, fewer than a dozen multistep biosynthetic pathways that include CDPSs have been experimentally characterized to date. The nocardioazine natural products are uniquely prenylated and methylated indole alkaloid DKPs, and nocardioazine A acts as a non-cytotoxic inhibitor of P-glycoprotein to reverse drug resistance of cancer cell lines. We unveiled the nocardioazine biosynthetic pathway from a marine actinomycete, demonstrating that a CDPS catalyzes *cyclo*(L-Trp-L-Trp) DKP precursor formation followed by tailoring of this DKP via a racemase, prenyltransferase, and methyltransferase to yield nocardioazine B. The nocardioazine pathway was also applied as a model for development of a biosynthetic platform for generating DKPs from unnatural amino acids, extending the utility of CDPS as biocatalysts. Together, our results highlight Nature's aptitude for chemical synthesis and showcase the utility of biosynthetic approaches for expanding the breadth of chemical space provided by natural products.


nocardioazine A


nocardioazine B

SERMACS 620

Investigating the transcript dependence of improved recombinant protein expression in *E. coli* with dynamic metabolic control

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Improving recombinant protein expression in *E. coli* can have a significant impact on lowering manufacturing costs for the growing biologic therapeutics sector. Approximately 30% of recombinant therapeutics are produced in *E. coli*, and several of these top selling therapeutics have expiring patents leading to growth in biosimilars. Since manufacturing costs can be lowered by improving protein titers, we evaluated the use of dynamic metabolic control to improve protein expression. We screened a library of *E. coli* strains with a variety of synthetic metabolic valves (SMVs), for improved GFP expression. SMVs are used to alter levels of key metabolic enzymes either through controlled proteolysis, CRISPR interference, or a combination of the two. Based on this screen, reductions in soluble transhydrogenase can be used to improve GFP expression up to 1.42-fold. This improvement is transcript dependent and when a similar screen was conducted with GFP fused to human hyaluronidase-I, reductions in the soluble transhydrogenase led to over a 2-fold improvement in GFP expression. However, this GFP expression fold-improvement decreases as the hyaluronidase fusion is truncated. We are continuing to investigate the transcript dependence of improved GFP expression to determine if the transcript structure, length, or rich GC content is responsible for the fold-improvement. Ultimately, while dynamic metabolic control can improve protein expression 1.42-fold, there is potential for over 2 fold-improvement with longer or more GC rich transcripts.

SERMACS 621

Analysis and characterization of lanthipeptide gene clusters in *Salinispora*

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Lanthipeptides are ribosomally encoded and post-translationally modified peptides (RiPPs) characterized by the presence of the thioether-containing amino acids lanthionine and methyllanthionine. We analyzed 122 publicly available *Salinispora arenicola*, *tropica*, and *pacifica* genomic sequences for putative lanthipeptide gene clusters and divided the resulting 240 clusters into 8 groups based on sequence similarity. Each cluster was evaluated for the essential components of lanthipeptide formation. Based on sequence analysis, we predicted the structure of the lanthipeptide produced by each of these groups. Intriguingly, none of our predicted structures appear to be closely related to known lanthipeptides. To validate our analysis, we will biosynthesize and characterize the lanthipeptide produced by one of these groups. We have chosen two clusters from the same group that are highly similar (94% sequence identity) and predicted to form the same product; however, the sequence of the leader peptide differs between the two. Comparing *in vitro* activities of dehydratases from each cluster with these two different leader peptides will provide information about the substrate specificity of the dehydratase. To this end, we are currently working to express and purify the pre-peptides and dehydratases from these two clusters. These studies are the first steps toward synthesizing the mature lanthipeptide and creating a library of non-natural analogs.

SERMACS 622

Dihydroxyacid dehydratases containing the [2Fe–2S] cluster are a promising antimicrobial target

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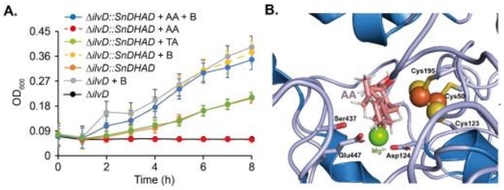
Antimicrobial-resistant infections are a rapidly emerging crisis, while the supply of new antimicrobials is alarmingly declining. Discovery and development of new antimicrobials is significant to address this public health threat. Recent advances of microorganism research indicate that microbes require hundreds of essential proteins for life processes, while only a small subset have been explored previously in the discovery and development of antimicrobial drugs. Branched-chain amino acids (BCAAs, Ile, Leu, and Val) are among the most abundant, essential amino acids and are key players in a wide array of important biological pathways. Bacteria, fungi and plants have evolved their biosynthetic pathways comprising of a common set of three enzymes an acetohydroxyacid synthase, a ketol-acid reductoisomerase, and a dihydroxyacid dehydratase (DHAD). By contrast, animals and humans have to acquire BCAAs from diet or other sources. DHAD belongs to the ilvD/EDD protein family. This oxygen-sensitive enzyme converts (*R*)-2,3-dihydroxyisovalerate into α-ketoisovalerate, the last common step in the biosynthesis of three BCAAs, and inactivation of this gene has resulted in the failed growth and reduced virulence of several bacterial and fungal pathogens in animal models. However, characterization of DHADs has so far limited, preventing the development of its specific inhibitors as new drug leads. Herein, we report the biochemical, genetic, and structural characterization of an oxygen-stable DHAD from one cyanobacterium species. Our studies detail the biochemical properties including an associated [2Fe-2S] cluster and demonstrate new structural features in comparison with other members of the ilvD/EDD protein family. Importantly, we describe the selective growth inhibition of cyanobacterial species and microbial pathogens using selective DHAD inhibitors. Together, our findings provide valuable information for the control and manipulation of microbes via inhibiting their DHADs. This work further suggests the exploration of untapped essential microbial proteins for a wide range of biomedical, biotechnological and environmental applications.



A: Growth inhibition of DHAD inhibitors; B: Active site of DHAD with Fe-S cluster and one inhibitor.

SERMACS 623

Engineered biosynthesis of non-natural polyketides and isoprenoids

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Many clinically used drugs are derived from secondary metabolites that are biosynthesized in a modular fashion by the selection and condensation of small molecule building blocks. Chimeric biosynthetic pathways can be constructed in an attempt to produce analogues for drug discovery. Yet, the scope and utility of this combinatorial approach is limited by the inherent substrate specificity and poor functional modularity of most biosynthetic machinery. Here, we show that biosynthetic pathways are tolerant towards non-natural building blocks. Such promiscuity forms a platform for constructing new biosynthetic parts with substrate specificities orthogonal to those found in Nature. Accordingly, we describe a comprehensive program of enzyme engineering, directed evolution, and synthetic biology aimed at constructing complex natural products that are modified with non-natural chemical functionality. Our approach expands the synthetic capabilities of natural product diversification strategies, and provides an improved understanding of the molecular basis for specificity in complex molecular assemblies.

SERMACS 624

Genetically encoded fluorescent sensors to illuminate cellular chloride signaling

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Living systems have evolved finely tuned mechanisms to coordinate transporters, chaperones, and non-proteinaceous ligands to spatially and temporally position ions for normal physiology. In this context, freely diffusing and protein-bound anions together with anionic protein modifications link to signal transduction, regulation of intracellular pH, and even detoxification. However, a breakdown in cellular homeostasis can lead to anion dysregulation in a wide range of diseases including neuropathic pain, cancer, autism, and cystic fibrosis suggesting that anions could be signals of cellular status. Despite this biological significance, chemical biology approaches to identify the cellular stores, protein targets, and signaling roles of biologically relevant anions, are still underdeveloped, but could provide new insights for the role of anions in human health and disease. Our first goal is to develop and apply turn-on fluorescent tools for the real-time imaging of anions in living systems. Significant advances along these lines for anions, unlike cations, are still lacking because anion-ligand interactions in water are typically weak and can lead to collisional fluorescence quenching or a turn-off response. This results in high background emission and loss of spatial and temporal resolution. To fill this technology gap, we engineer and evolve pigment-containing proteins to generate turn-on fluorescent sensors. In this presentation, I will describe the development and applications of a novel class of genetically encoded fluorescent chloride sensors.

SERMACS 625

Small-molecule poly (ADP-ribose) polymerase (PARP) and PD-L1 inhibitor conjugates as dual-action anticancer agents

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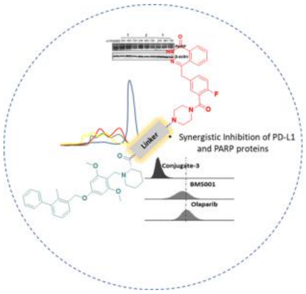
Cancer is one of the leading causes of deaths worldwide. Thus, intense research efforts have been directed towards the search for novel oncological drugs. Key therapeutic regimen include immunotherapy. PD-1/PD-L1 inhibition is an effective immunochemotherapeutic target and has achieved clinical gains in a variety of cancer types. Despite the clinical success, PD-L1 immunochemotherapy possesses drawbacks, including, tumor resistance, low patient response rate, and autoimmune side effects. Hence, combination therapies, which have shown promise, will provide lasting solutions. Dual targeting drug conjugates offer similar profiles, in terms of efficacy and potency, to combination therapy. Additionally, they are amenable to fine-tuning — structure-activity modifications; pharmacokinetics and related ADMET properties. Here, we report the design, synthesis and biological properties of dual-action PARP- PD-L1 inhibitor conjugates. The design of these dual-action conjugates was predicated on Sybyl-based cheminformatics as well as Chou-Talalay combination indices of olaparib, clinically approved PARP1 inhibitor and BMS-001, a small-molecule PD-L1 inhibitor. The conjugates exhibited an enhanced PARP-PD-L1 inhibition profile, as determined by cell viability, FITC Annexin V/PI Apoptosis dead cell assay, cell cycle, cell-surface PD-L1 inhibition, immunoblotting, and T-cell proliferation assays. These dual-action conjugates are 2-20 times cytotoxic than their PARP or PD-L1 inhibitors and induce significant apoptosis in triple negative breast cancer, MDA-MB-231. The compounds induce G1 cell cycle arrest. Most importantly, the conjugates inhibit both PARP- and PD-L1 proteins in cells. We contend that the compounds may serve as a template for the design of more potent small molecule PD-L1 inhibitors. As chemical probes, these conjugates can be used to explore the crosstalk between PARP inhibition and PD-L1 pathway.



SERMACS 626

Pharmacologic modulation of ER protein folding to identify host/flavivirus interactions and inhibit viral propagation

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Approximately 30% of all cellular proteins are routed to the endoplasmic reticulum (ER) during or after translation, where they are folded and processed for trafficking to the cellular surface or extracellular space. ER chaperones and other protein quality control factors regulate protein folding, efficient processing and secretion, or degradation of protein clients. In addition, the ER plays a critical role for propagation and secretion of many pathogenic viruses, including the flavivirus family. Flavivirus proteins are known to interact with many ER quality control factors as they replicate and assemble around the ER membrane; however, the specific dependencies of the virus on these ER host factors are poorly understood. We have probed specific ER quality control dependencies by using recently developed pharmacologic tools designed to perturb ER stress response pathways. We find that treatment with small molecule 147, a preferential activator of the ATF6 signaling branch of the unfolded protein response, leads to a significant decrease in Dengue virus (DENV) propagation. The reduction in viral activity was not dependent on ATF6, but instead required covalent targeting of several ER protein disulfide isomerases by 147. This molecule is known to perturb ER redox processing and using proteomics to look at global host cell proteome remodeling we are currently defining the mechanism of how modulating these redox processes can perturb DENV replication and assembly of new virions. Using biochemical assays to monitor viral RNA, protein, and infectious titer we are able to define the effect of 147 on each stage of the viral life cycle. In addition, we have found that the molecule is effective against multiple strains of DENV and Zika virus, a related flavivirus. Our results highlight that targeting host-centered ER protein quality control pathways could serve as a broad antiviral therapeutic strategy, and could circumvent several known liabilities of current DENV therapeutics, including antibody-dependent enhancement, and rapid evolution of resistance to antiviral drugs that target virus proteins directly.

SERMACS 627

Bioorthogonal probes of protein acetylation

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Acetylation of proteins is one of the most important posttranslational modifications that diversify protein functions. Thousands of acetylated lysine residues have been identified, suggesting that the effects of lysine acetyltransferases (KATs) go far beyond the chromatin kingdom. The outstanding challenge is how to dissect the subacetylomes of individual KATs and address their functions on the proteomic scale. We have explored a bioorthogonal profiling of protein acetylation strategy to label and interrogate substrates of KAT enzymes. In this strategy, a suite of Ac-CoA analogs containing either alkynyl or azido functional group were synthesized as potential cofactor surrogate for selective labeling of KAT substrates. Meanwhile, the active site of the KATs was engineered in order to expand the cofactor binding capability of the enzymes to accommodate the bulkier synthetic cofactors. The acylated substrates can be selectively linked through the copper-catalyzed azide-alkyne cycloaddition reaction with fluorescent reporter or biotin affinity tag for optical imaging or protein enrichment on streptavidin-coated resin. We have successfully used this bioorthogonal technology to profile substrates of Key KAT members in the context of complex cellular proteomes. The discovered proteins are extensively involved in various biological events including gene expression, cell cycle, and cellular metabolism. Our chemical biology strategy provides a powerful enabling technology for activity-based lysine acylation profiling on proteomic scale.

SERMACS 628

Sequestration of gadolinium in sediments of a constructed wetland

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Contaminants of emerging concern are becoming ever more present in the environment and their effect on natural ecosystems as well as human health are not well known. Many of these chemicals enter our environment through wastewater treatment systems, as these waste streams are not designed to retain or remediate these new contaminants. Therefore, they are discharged with wastewater effluents into lakes, streams, rivers, and coastal waters without assessment of their concentrations or effects on aquatic ecosystems. Gadolinium (Gd), a rare earth element used in MRI contrast agents, has recently been identified as an emerging contaminant of concern. The objectives of this study were to determine the occurrence and fate of Gd in the water and sediment of a constructed wetland designed to receive effluent from a single wastewater treatment plant. Anthropogenic Gd concentrations decreased by approximately 24% between the inflow and outfall of the wetland, indicating Gd was sequestered within the wetland system either within the sediments and/or through uptake by plants. Sediment particles within the wetland flow path ranged from sandy to dark muck-like organic biomass. Gd concentrations within the sediment were positively correlated with total organic carbon and were observed to be highest in the dark organic-rich sediments of the wetland suggesting the plants and organic sediment particles were sinks for the emerging contaminant.

SERMACS 629

Environmental occurrence and fate of emerging contaminants from *Lyngbya wollei* blooms

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Lyngbya wollei is a harmful benthic algae that is widespread in the Southeast. The relationship between biomass and toxin concentration in this algae is not well established so control strategies are difficult to plan and execute. In this study, a *Lyngbya wollei* bloom in Lake Wateree, SC was monitored from July 2018 to September 2019 at multiple grab sites. Physical mapping was accompanied with molecular determination of distinctive *Lyngbya wollei*-derived toxins known as LWT 1-6. Algal grab samples were lyophilized, extracted, centrifuged, and analyzed by hydrophilic interaction liquid chromatography along with two complementary mass spectrometry techniques. High resolution mass spectrometry was applied to confirm the structure of the toxins present. The high-resolution fragmentation analysis presented provided an unprecedented range of fragment ions that can be used to conclusively indicate the presence and retention time of LWTs even in the absence of commercial standards. A triple quadrupole instrument was used for quantification of toxins and routine analysis of the samples. High relative standard deviations in the sampling suggested that standard grab sampling were susceptible to interference from inadvertent collection of aquatic vertebrates and invertebrates during sampling as well as harvesting of other members of the microbial community. A 16S rRNA gene sequence assay demonstrated the presence of a diverse community of microbiota present in the grab samples. Application of improved fragmentation schemes, suppression elimination studies, and sample-based correction strategies reduced error in the apparent biomass to LWT ratio, indicating that LWTs are in fact directly correlated with bloom biomass. Its Redfield ratio was determined to better evaluate the use of traditional TMDL strategies as prophylactic control mechanisms. The fate of collected LWTs was determined in model lake water systems to give a better understanding of its half-life and dispersal in the environment.

Lyngbya wollei infestation, Lake Wateree SC, August 2018

SERMACS 630

Uranium immobilization in wetlands varies spatially and temporally in response to hydrogeochemical conditions

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Subsurface contaminants move with groundwater flow and eventually resurface in wetlands. While many contaminants can move readily through aquifers, the movement of most contaminants is strongly attenuated in wetlands because of the presence of geochemistry, microbiology, and hydrology conditions that promote contaminant binding. Between 1966 to 1968, 43.5 metric tons of uranium (U) was released from a nuclear reactor target facility into a stream on the Savannah River Site, Aiken, South Carolina. Early estimates indicate that 70% of the released U, remain in the wetland associated with the stream. In 2019, a detailed mapping of the U contamination was undertaken by systematically traversing the contaminated area with backpacks equipped with NaI gamma detectors, telemetry, and GIS-equipped tablets. The resulting 149,000 gamma spectra, along with satellite images and 1-m LIDAR topographical data were compiled into maps. Preliminary results indicated that the contamination area may be as large as 346 ha, a far greater area than the original estimate of 62 ha based on limited soil sampling of the area. Sediment U depth profile data indicates that as much as 20 cm of sediment have been deposited over the last 40 years on the original contaminated sediment. More detailed studies were undertaken to identify critical processes and areas within the U contaminated wetland that were responsible for U immobilization. Uranium was 15x greater in the rhizosphere (the soil zone near roots) then in the bulk wetland soil. The rhizosphere had elevated C, N, Mn, and Fe concentrations and total bacteria, *Geobacter*, and *Anaeromyxobacter* counts (as identified by qPCR). Furthermore, the rhizosphere contained several organic molecules that were not identified in the non-rhizosphere soil (54% of the >2200 ESI-FTICR-MS identified compounds). Rhizosphere OM contained several unique lipids, unsaturated hydrocarbons, and proteins not found in the non-rhizosphere OM. Stream iron-flocs formed from reoxidation of dissolved ferric iron had extremely high U concentrations, >300 mg U/kg floc. Together these finding suggest that contaminant distribution in wetlands may be controlled by critical zones within the wetland that vary temperally and spatially in response to hydrogeochemical conditions. Understanding the formation of these critical zones are important for the stewardship and long-term management of contaminated wetlands.

SERMACS 631

Role of proton-coupled electron transfers in energy efficient environmental restoration of oxyanion-contaminated waters: Example of chromate reduction

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Freshwater is a critical strategic resource. Decontamination of polluted water sources is a demanding challenge, as is on-site decontamination at the pollution source before release in the environment. In response to global water contamination challenges, our research focuses on energy-efficient remediation of toxic oxyanions (e.g. chromate, arsenate, perchlorate, nitrite, phosphate) from contaminated water as well as industrial waste streams. Oxyanions are central to agriculture and industrial processes. For example, farm water run-offs have high nitrite, nitrates, and phosphate concentrations, which contribute to algae blooms when released in the environment. Industrial processes also contribute to increased oxyanion concentrations of varying toxicity. Here we discuss the use of electrochemical methods for the energy-efficient reduction of highly carcinogenic hexavalent chromium from contaminated waters. Cr(VI) is generated in the waste of a large number of industries from steel to textile. Its reduction faces a high kinetic barrier and significant opportunities exist in the development of new detection and reduction methods. The underlying proton-coupled electron transfer (PCET) processes involved in the mechanism are uncovered and the energy efficiency of the reaction is discussed. We demonstrate that cheap electrodes can be used and highlight the role of acid choice in facilitating the PCET processes. The work contributes to the fundamental understanding of the influence of hydrogen-bonding networks in catalyzing proton-coupled electron transfer processes, thereby contributing to global solutions to the increased pressure on freshwater supplies.

SERMACS 632

Manganese oxide geochemical controls over Tc-99 fate in the environment: TcO_2 oxidative dissolution

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Tc-99 is a by-product of nuclear fission that has found its way into the aquifer and vadose zone due to accidents and past waste management practices. Tc-99 has a veery long half-life (~200,000 years) and shows no reactivity towards mineral phases, making

sparingly soluble TcO_2 to be considered as an immobilization form for the highly mobile Tc-99 in the environment through in situ redox manipulation. The stability of the TcO_2 is considered to be dependent mostly on oxygen concentration which can re-oxidize Tc(IV) to Tc(VII). Manganese oxides are redox reactive minerals which can affect the environmental fate of contaminants thanks to the high redox potential of Mn(IV)/Mn(II) which makes oxidation of reduced metals/species almost always thermodynamically favorable. The current study investigates the role of manganses oxides on TcO_2 oxidative dissolution. Specifically, it investigates the rate of release of Tc-99 in the aqueous phase as a result of solid-solid interface interaction between TcO_2 and common manganese minerals, such as Mn(III/IV) oxide (birnessite) and MnO_2 (pyrolusite) under oxygen restricted conditions. Manganese redox reactions can lead to Mn(III) intermediate solid phases, such as MnO(OH) (manganite) and Mn(II/III) oxide (haussmanite), which in turn can act further as oxidizing agents. Preliminary results indicated that birnessite and haussmanite induce highly oxidizing conditions (Eh~350-400 mV), even when experiments are being conducted under nitrogen atmosphere (<0.1 ppm O_2) and a rapid release of Tc-99 was recorded in the aqueous phase. On the other hand, he rate of TcO_2 oxidative dissolution by manganite was rather slow and the release was limited compared to haussmanite and birnessite. The recorded solubility values of TcO_2 in the presence of manganese minerals were 20-40 times higher compared to the controls not containing manganese minerals ($\sim 1.0\times 10^{-7}$ M). Different physicochemical parameters affecting the dissolution are currently being investigated such as pH and ionic strength, as well as manganese mineral transformations using X-Ray Diffraction, IR, Raman and microscopy.

SERMACS 633

Properties of surfactants in atmospheric aerosol and estuarine waters in coastal Georgia

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Constraining the role of aerosol particles in cloud droplet microphysics remains one of the largest uncertainties in predicting current and future climates. The interactions of aerosol particles with radiation and their ability to grow into cloud droplets depends on both their size and composition. The composition of particles affects their hygroscopicity and surface tension. Recent work has demonstrated the presence of surfactants in atmospheric aerosol particles and the ability of those surfactants to significantly reduce surface tension. One source of surfactants in atmospheric aerosol particles is from the oceans through bubble bursting at the sea surface and emission of primary marine aerosol particles (PMA). In this study, we compare the composition, concentration, and strength of surfactants extracted from estuarine water and atmospheric aerosol particles collected from Skidaway Island, in coastal Georgia to those of surfactants extracted from seawater and model PMA collected during a cruise in the North Atlantic Ocean. We used solid phase extraction to separate the surfactant fraction and characterized the concentrations and compositions using UV-Vis spectroscopy or mass spectrometry. Surfactant strengths were inferred from their critical micelle concentrations (CMCs) and surface tension curves, calculated from surface tensions at a series of dilutions for each surfactant sample. The bulk surface tension of the water samples was measured prior to any extractions. The surface tension depression of estuarine waters was less than that of the seawater from both the productive and oligotrophic seawater regions, consistent with an additional sink or a different mixture of surfactants in the estuarine waters. Properties of surfactants extracted from atmospheric aerosol particles varied as a function of particle size. Surfactant CMCs in biologically productive seawater were lower than those in the oligotrophic seawater suggesting that surfactant mixtures in the two regions were chemically distinct. Surface tension curves indicate that surfactants in model PMA were weaker than those in the corresponding seawater, suggesting preferential partitioning during the bubble bursting process. In both estuarine seawater and biologically productive seawater, surfactant strengths were lower during the day, compared to the night, consistent with photochemical processing.

SERMACS 634

Mechanistic understanding of ozone-assisted oxidation reaction of trans-2-butene in a jet stirred reactor

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Alkenes originating from both biogenic and anthropogenic sources are an important class of volatile organic compounds present in the troposphere. Their reaction with ozone represents the primary removal mechanism of tropospheric alkenes and is recognized to be an important source of atmospheric oxidants, such as HO_x (x = HO and HO_2), peroxy radicals, and Criegee intermediates (carbonyl oxides, CI). In particular, the fate of the CIs is crucial, as they determine the end products of the ozonolysis reaction. An atmospheric pressure jet stirred reactor in conjunction with a high-resolution tunable synchrotron photoionization time-of-flight mass spectrometer offers a unique approach to monitor chemical transformations of key intermediates under well-defined conditions. This experimental arrangement is used to reveal new insights into the ozonolysis of trans-2-butene via identification and quantification of previously elusive intermediate species. A variety of multi-functional peroxide species are identified based on the experimentally measured photoionization spectra and theoretically determined ionization energies. A reaction network of the CIs is also identified, which is described by the addition of CIs to trans-2-butene, water, formic acid, and other molecules containing hydroxy, aldehyde, and hydroperoxyl functional groups. In addition, the experimental evidence for additional oxygenated species such as methanol, ketene, aldehyde, and acetoin suggest multiple active oxidation routes. These findings improve our understanding of the reaction of alkenes with ozone, providing insights relevant to the formation mechanism of tropospheric aerosol building blocks.

SERMACS 635

Post-detonation fate and transport of radioactive debris

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As long as nuclear weapons continue to exist in our world, there will always be a need to prepare and plan for a time when they might be used. A large part of these preparations are to develop and improve models to predict the transport and fallout of radioactive debris, as well as create novel methodologies to characterize the aftermath of a nuclear event that could provide insight into the origin or composition of the weapon materials. In this work, software models are being developed to improve upon the Defense Land Fallout Interpretive Code (DELFIC), originally developed during the Cold War, to predict the growth of the nuclear cloud and distribution of the produced radioactive isotopes post-detonation. Coupled with that effort is the development of a new, three-dimensional modeling paradigm to simulate the fate and transport of radioactive particles in the atmosphere, which will be able to incorporate particle aggregation, air ionization, and topographical effects on fallout patterns. In addition, experiments are being performed to assess the rate at which nuclides may be absorbed into common construction materials such as brick and concrete. Understanding how urban materials absorb various isotopes will aid in the determination of the exposure time and the source isotopes, which have implications into the characterization of the detonated weapon.

SERMACS 636

Influence of aging on the iodine adsorption capacity of reduced silver adsorbents

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Nuclear fuel reprocessing is a significant component of the nuclear fuel cycle that allows for more efficient usage of nuclear fuels and reduces production of nuclear wastes. During reprocessing, a number of radioisotopes including iodine-129 as I_2 and CH_3I, krypton-85, xenon-135, and carbon-14 as CO_2 are released as off-gases. Of these gases, iodine is particularly important as a result of its long half-life and its potential for environmental accumulation. Reduced silver (Ag^0) nanoparticle-based adsorbents are known to have a high affinity for iodine and could offer a potentially more cost-effective means of iodine capture when compared to traditional liquid scrubbers. The iodine capacity of these materials, however, is reduced significantly when exposed to other gas species found in the reprocessing off-gas stream. This loss of capacity, known as aging, occurs as a result of various reactions involving not only those adsorption and oxidation reactions that arise from direct interactions with the nanoparticles but also from interplay with the supporting material. This is particularly important for silver exchanged mordenite, where NO and NO_2 in the off-gas stream likely interact directly with the mordenite crystals. Thus, the goal of this work is to examine the aging mechanisms present in Ag^0 adsorbents and develop reaction pathways that, as accurately as possible, represent these mechanisms. These pathways are then used in the development of predictive models for the simulation of adsorbent performance.

SERMACS 637

Encapsulation of heavy metals from coal-fired generated wastewater

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<p style="margin: 0px; text-align: justify; text-indent: 0.5in;">The treatment of wastewaters containing heavy metals is a critical challenge for coal-fired power generation. In recent years, the USEPA has enacted two new regulations that require the safe disposal of Coal Combustion Residuals (CCRs) and set federal limits on toxic metals in wastewaters discharged from power plants. As electric utilities across the United States improve their processes to meet these regulations, many compliance scenarios require the use of zero-liquid discharge (ZLD) technologies. Meeting the demands for ZLD wastewater management has led to widespread investigation and implementation of heavy metal stabilization/solidification techniques. Stabilization is a process of chemical fixation or adsorption of contaminants to the chemical structure of the solid. Solidification is the physical encapsulation of a contaminants within the solid form. Stabilization/solidification of hazardous waste streams have been conducted within the U.S. for 40 years, but until recently treatment has focused outside the scope of coal-fired generation wastewaters. Comparatively less research and development for stabilization/solidification of coal-fired generation wastewaters has been performed. Here, we propose treatment of coal-fired generation wastewaters using sol-gel encapsulation method. We have developed a novel sol-gel treatment method for the stabilization/solidification of wastewaters using Silane precursor Tetramethyl orthosilicate. The method successfully solidifies wastewater undergoing a massive volume reduction upon drying. Inductive Coupled Plasma-Atomic Emission Spectroscopy, (ICP-AES) measurements indicate 85-95% retention of metals such as chromium, copper, and mercury. We propose that the sol-gel treatment chemically fixates positively charged metals to the negatively charged silicate network leading to strong leaching resistance for transition metals and other positively charged species. </p>

SERMACS 638

Peracetic acid fate and decomposition in poultry processing wastewater streams

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Peracetic acid (PAA) has been an effective antimicrobial agent used in many industries, such as, healthcare, water treatment, and food industry for its wide-spectrum, high disinfection efficiency and absence of mutagenic or persistent toxic disinfection by-products. In

poultry processing plants, PAA is used in chiller tanks as well as for the disinfection of processing equipment. Poultry processing wastewater is commonly treated by dissolved air floatation (DAF) followed by biological processes. The overall goal of this study is to systematically assess the fate of PAA in poultry processing wastewater and its potential effect on biological treatment processes typically used by the poultry industry. Results of this study related to the fate of PAA in poultry processing waste streams, including PAA decomposition kinetics and products will be presented. Poultry processing wastewater samples from the chiller tanks (pre-, main-, and finishing chiller), chiller overflow, DAF influent and effluent were periodically collected from a poultry processing facility and analyzed for conventional wastewater parameters, as well as PAA. The PAA concentration in chiller samples ranged from 100 to 1200 mg/L and from 50 to 80 mg/L in chiller overflow. PAA was not detected in DAF influent and effluent, except during chiller emptying at the end of the processing shift. The decomposition of PAA in poultry wastewater followed one-step ($pH \geq 6$) or two-step ($pH < 6$) pseudo-first order kinetics. The PAA decomposition rate correlated positively with pH, temperature, wastewater strength and organic content, and negatively with initial PAA concentration. Decomposed PAA in DAF effluent resulted in equimolar production of acetic acid.

SERMACS 639

A study on the effect of steric hindrance on the reactivity of phosphinimine NCN-pincer complexes of nickel(II) with dibromomethane

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This research is investigating the effect of steric strain on reactivity and properties of 2,6-bis(phosphiniminomethyl)-1-bromobenzene pincer complexes with electrophilic substrates. We synthesized two ligands, namely 2,6-bis(triphenylphosphiniminomethyl)-1-bromobenzene (L^1) and 2,6-bis(tricyclohexylphosphiniminomethyl)-1-bromobenzene (L^2). We reacted these with bis(1,5-cyclooctadiene)nickel(0) to form the organonickel(II) complexes L^1NiBr and L^2NiBr. The crystal structures showed a greater amount of steric strain in L^2NiBr than L^1NiBr as observed in torsional strain in the pincer ligand. The reactivity of L^1NiBr and L^2NiBr with dibromomethane(DBM) was investigated focusing on the effect of the different steric environments of the complexes. Reaction of L^1NiBr in neat DBM formed intractable mixtures, however, L^2NiBr reacted and was able to promote a redox reaction with DBM to form an iso-indole molecule through C-C and C-N bond forming reactions. The net reaction transferred two electrons from the ligand to DBM forming two equivalents of bromide which transferred to the Ni(II) cation. The methylene moiety of DBM formed a C-C bond between the aryl ring of the ligand and a C-N bond of a phosphinimine. We also studied the reactivity using a variety of solvents in our efforts to establish a pathway for which these compounds were reacting. While there are solvent based differences it was observed that L^2NiBr promoted C-C and C-N bond forming reactions, regardless of solvent, while L^1NiBr was not able to promote this type of reactivity. This study has shown that the unique reactivity of these phosphinimine organonickel (II) compounds seems related to steric strain being placed on the central metal ion coordination sphere.

SERMACS 640

Functionalization of porphyrinic metal organic–framework nanoparticle additives for enhanced reverse osmosis membrane performance

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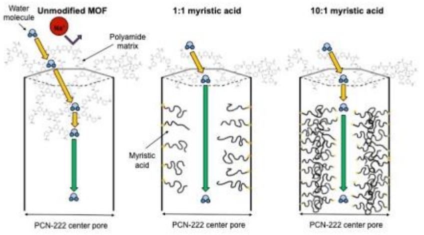
Reverse osmosis (RO) is a process applying thin film composites membranes to filter brackish water for residential, agricultural, and medicinal uses. Over the last several years, thin film nanocomposites (TFNs) for RO methods have enhanced membrane performance through increases in salt rejection, permeation, and anti-fouling properties. We have investigated the effects on RO flux and salt rejection by incorporating a large-pore zirconium-based porphyrinic metal-organic framework (MOF), PCN-222, into a TFN membrane. Functionalization of PCN-222 with myristic acid (MA) modifies channel environment and hydrophobicity. Post-synthetically modified PCN-222 was characterized through powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), Brunauer-Emmett-Teller (BET) gas sorption, and ^{1}H NMR spectroscopy. When incorporated into a TFN RO membrane, enhanced flux of up to 190% and salt rejection within error compared to a control membrane was observed.



SERMACS 641

Synthesis and utilization of polyoxometalate compounds as antimicrobial agents

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This project began with the synthesis of six different polyoxometalate compounds, which were then diluted to lower concentrations of 1, 125, and 256 micrograms per milliliter to find a range for the possible minimum inhibitory concentration each has against two gram positive and two gram negative types of bacteria. Polyoxometalates should demonstrate high specificity for each type of bacteria, and current findings show that they do effect different bacteria with varying ranges of minimum inhibition.

SERMACS 642

Mapping the electronic structure of an iron(II) polypyridine complex with ligand-centered frontier orbitals

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Iron polypyridine complexes are potential cheaper alternatives to ruthenium polypyridines in photovoltaic or photocatalytic solar cells. In order to discover an ideal iron chromophore, we need to first understand the electronic structure of known iron polypyridines. In this study, the photophysical properties of the $Fe(smif)_2$ complex (smif = dipyridylazaallyl) and its derivatives were investigated using B3LYP+D2 density functional theory (DFT) and time-dependent density functional theory (TD-DFT) with the SDD basis set and accompanying ECP on Fe and the 6-311G* basis set on all other atoms. All complexes were optimized in water using the PCM model to implicitly account for solvent effects. The potential energy surfaces for the photophysically relevant states of the $Fe(smif)_2$ along Fe-N bond lengths and N-Fe-N rocking angle were plotted using Smolyak sparse grid interpolation. Unlike other common iron complexes such as Fe(II) bis-terpyridine in which the highest occupied molecular orbitals (HOMOs) are metal-centered, $Fe(smif)_2$ displays a ligand-centered HOMO. Our calculations revealed that the smif rocking motion is critical for spin-state transitions in the $Fe(smif)_2$ complex. The effects of halide substitution of the smif complexes on the ligand rocking motion were also investigated. While the halide substitution restricted the rocking motion according to the substituent size, the electron-withdrawing effect of halides lowered the metal anti-bonding orbital energies, favoring the quintet as the ground state.

SERMACS 643

Tailoring the electronic structure of corannulene-integrated crystalline materials

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Crystalline covalent-organic frameworks (COFs), made entirely out of organic building blocks, offer the unique opportunity for material engineering due to almost no limitations in the choice of organic linker. Taking advantage of COF modularity and tunability, we utilized a self-assembly approach typically used for COF synthesis to prepare the first example of a crystalline (purely organic) donor-acceptor corannulene-based material, which merges the intrinsic properties of COFs and π-bowls. The first example of a crystalline corannulene-COF with the highest surface area among corannulene-based extended structures reported to date. Integration of corannulene inside insulating porous scaffolds provided an opportunity to tune electronic properties resulting in circa 10000-fold conductivity enhancement. Moreover, the porosity of the prepared crystalline hybrids was maintained providing a pathway to re-enforce semi-conducting behavior in typically insulating porous materials (for example, covalent-organic or metal–organic frameworks(COFs/MOFs)). The prepared purely organic corannulene-based material has undergone comprehensive characterization by powder X-ray diffraction, steady-state and time-resolved photoluminescence, X-ray photoelectron spectroscopies, Fourier transform infrared, thermogravimetric, and gas sorption analysis. Upon further advancement, the presented studies not only demonstrate the possibility to merge the intrinsic properties of π-bowls with the versatility of hierarchical scaffolds, but could also foreshadow the engineering of a novel class of crystalline donor-acceptor corannulene-based materials for optoelectronic devices.

SERMACS 644

Versatility and structural functionality of heterometallic metal-organic frameworks (MOFs)

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Metal-organic frameworks (MOFs), well-defined porous structures made up of organic and inorganic building blocks, have been keenly studied due to their porosity, modularity, tunability, crystallinity, flexibility, and long-term stability. The Incorporation of more than one metal into a MOF matrix, resulting in formation of heterometallic systems, have shown numerous advantages in application such as catalysis, separation, gas storage, energy conversion, and storage. Our work in the Shustova group focuses on strategic design, preparation, and extensive studies of actinide- and/or transition metal-containing heterometallic MOFs. We investigate the effect of the incorporation of a second metal on the catalytical proficiency and electronic structure of the heterometallic MOF systems. We performed integration of the second metal through metal node engineering allowing us to preserve the intrinsic MOF porosity. Comprehensive characterization techniques and studies of the heterometallic MOF systems, for example, single crystal and powder X-ray diffraction as well as X-ray photoelectron spectroscopy, reveal not just the structure-property relationship of these systems, but also present valuable insights into the improvement and expansion of MOF applications.

SERMACS 645

Gallium(III) complexes with redox-active quinol-containing ligands as mimics of superoxide dismutase

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Excessive production of reactive oxygen species (ROS) is correlated with oxidative stress which is a marker of cardiovascular, neurological, and inflammatory diseases. Superoxide dismutases (SODs) are metalloenzymes that catalyze the degradation of the ROS superoxide (O_2^-) to hydrogen peroxide (H_2O_2) and dioxygen (O_2). There is significant interest in developing functional small mimics of these enzymes into pharmaceuticals. Our lab has prepared and characterized coordination complexes with polydentate ligands that contain redox-active quinol groups. We initially found that Mn (II) complexes with these ligands could serve as both H_2O_2-responsive MRI contrast agents and SOD mimics. Consequently, we found that a Zn (II) complex with one of these ligands also catalyzes O_2^- degradation. Based on the preliminary data, we find that the SOD activity scales with the positive charge on the metal complex. Therefore, we hypothesize that increasing the charge of the complex through the use of a tricationic metal ion will facilitate the binding of O_2^- and improve catalytic activity with all of the ligands. Here, we describe the syntheses and antioxidant behavior of new Ga(III) complexes with quinol-containing ligands.

SERMACS 646

Electrochemical crystal growth of POM-based complex oxides

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Most polyoxometalate (POM) crystalline materials, if not all, have been synthesized *via* conventional hydrothermal/solvothermal methods. However, the high temperature and pressure required by these methods prove destructive towards thermally sensitive POM anions, resulting in greater uncertainty of the synthesis of crystalline materials based upon these plenary POM structures. We have explored a new approach for the "bench-top" synthesis of POM-containing materials at ambient conditions by employing electrochemical (e-chem) energy as a driving force for new compound formation. We have demonstrated that the e-chem approach allows for convenient synthesis of POM-containing compounds in aqueous solution at room temperature. Compared to conventional hydrothermal/solvothermal synthesis, the new approach offers additional benefits especially towards the synthesis of POM materials that are otherwise subject to thermal decomposition. Furthermore, using e-chem methods for crystal growth facilitates a means for the selective synthesis of compounds with desired frameworks for electrical conductivity. We have had some initial success with e-chem crystal growth in which newly discovered compounds exhibit fascinating structures of one-dimensional (1D), alternating POM anion and transition metal (M) cations, and two-dimensional (2D) frameworks featuring tethered POM clusters on metal-oxide chains have been obtained. In addition to the use of X-ray diffraction methods to investigate crystal structures, we have employed TGA/DSC (Thermogravimetric Analysis /Differential Scanning Calorimetry) methods to examine the thermal behaviors of new compounds, and XPS (X-ray Photoelectron Spectroscopy) to determine the oxidation states of the metal cations and etc. In this presentation, we will discuss new compounds that are otherwise cannot be synthesized by conventional hydrothermal methods. We anticipate new knowledge in chemical bonding of diverse frameworks, as well as applications of new POM-containing compounds discoveries in this research.

SERMACS 647

Zirconium-based metal–organic frameworks as a platform for nuclear waste remediation

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The progress in the nuclear waste management sector is important due to a continuously growing demand in nuclear energy, as well as nuclear weapon decommission. Preparation of novel materials to address current challenges, including but not limited to selective sequestration and separation of radionuclides, followed by their storage, is one of the pathways to address current societal needs. In this regard, metal–organic frameworks (MOFs) are a promising class of materials endowed with porous crystalline structures, a high surface area, unrivaled modularity, and the ability to undergo various postsynthetic modifications. In this work, we will discuss how we can utilize MOFs for the sequestration of radionuclides from solution. In particular, we focus on studying the controllable release kinetics of uranyl species trapped inside porous Zr-based MOF as a function of capping linker installation. Comprehensive analysis of radionuclide@MOFs was carried out using powder X-ray diffraction, induced-coupled plasma mass spectrometry, thermogravimetric analysis, as well as ^{1}H nuclear magnetic resonance, photoluminescence, Fourier-transform infrared, and UV-vis spectroscopies. Moreover, we have tested the stability of prepared Zr-based MOFs under gamma radiation. Thus, leaching kinetics of uranium-containing species from MOFs and gamma irradiation damage studies can foreshadow the understanding of MOFs potential as a viable nuclear wasteform materials.

SERMACS 648

Photophysics and electronic properties of photoswitchable frameworks

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Photoswitchable molecules, which are capable of switching between two discrete colored states upon light irradiation, are the target of applications ranging from "smart" windows and transition lenses, to efficient sensors and drug delivery systems. By utilization of metal-organic frameworks (MOFs) for photoswitch immobilization, we have developed a series of solid-state photochromic systems and elucidated the correlation of electronic and photophysical properties upon photoisomerization. Herein, we present comprehensive characterization of a series of photochromic MOFs, including the photophysical and electronic properties through UV-vis and diffuse reflectance spectroscopies, as well as pressed-pellet conductivity and theoretical calculations. The presented study shows that utilization of a porous MOF in the development of novel photochromic systems can increase their photoresponsive performance and

provide light-modulated control to a MOFs electronic structure, which is a key parameter for their implementation as sensors or devices.

SERMACS 649

Comparative study of the ABTS redox indicator in various solvents

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ABTS [2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonate)] is one of the most commonly used redox indicators in industry and scientific research. It is widely applied in the food and healthcare industries as well as agricultural, environmental and biological research. The colorless ABTS can react with free radicals or other oxidants through one electron oxidation to form a stable green-colored radical ion (ABTS+). ABTS and its radical cation form are soluble in water and a few polar organic solvents, which enables the measurement of both hydrophilic and lipophilic compounds in a variety of environments such as aqueous, organic, and mixed solvents. However, the exact nature of this system and its redox behavior in different media have not been fully understood. Our goal is to understand the exact speciation and redox behavior of ABTS/ABTS+ system in various environments. To this end, we have studied the effect of salt concentration and the nature of buffering agents/electrolytes in aqueous media. Our initial findings have shown that the redox potential of the ABTS/ABTS+ system changes depending on the nature of the electrolyte. We also have prepared a more hydrophobic ABTS salt that can dissolve in less polar organic solvents, including chloroform, acetone and acetonitrile. The preparation and redox behavior of this form of ABTS in different organic solvents will also be discussed.

SERMACS 650

Mitochondrial targeting cyclometallated Au(III) complexes bearing dithiocarbamate ligands: Synthesis, biological evaluation, and mechanistic insights

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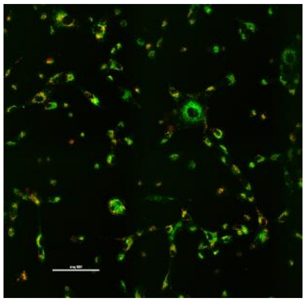
Gold(III) metal complexes have been extensively explored for their chemotherapeutic properties in recent years. Although isoelectronic with Pt(II), the reactivity *in vitro* has given rise to unique biological reactivity. Inherently, the poor stability of these Au(III) complexes in biological media has plagued the use of these complexes in the clinical setting. Cyclometallated Au(III) complexes have been thoroughly studied as alternative chemotherapeutics to platinum due to their innate cytotoxicity. Although a variety of these class of compounds have been proven to be potent, the lack of stability of Au(III) in biological media has inhibited their practical use. In this work, we employed the [C^N] cyclometallated framework in combination with bidentate sulfur ligands; dithiocarbamates, to synthesize ten (10) drug candidates. These compounds were fully characterized by NMR spectroscopy and structurally characterized by X-ray crystallography. Preliminary cell viability assays show cytotoxicity with nanomolar IC_{50} values in cisplatin-resistant breast cancer cells. A further in-depth study revealed mitochondrial targeted damage over the conventional DNA damage pathway seen with platinum-based chemotherapeutics. Examination with JC-1 revealed a drastic change in mitochondrial membrane polarization. Furthermore, analysis using the Seahorse XF mitochondrial stress test alluded to an overall decrease in functionality within 5 minutes of treatment. Overall, this set of cyclometallated Au(III) complexes has shown promising preliminary results *in vitro* and offers a model framework for expansion.



MDA-MB-231 cells were plated at density of 10×10^4 in 35 mm glass bottom dishes and treated with the Au(III) drug candidate at 1 μM for 6 hours.The mitochondrial membrane potential ($\triangle\psi_M$) was monitored using the JC-1 assay; J-aggregates shown in red (exc/em 488/525) and J-monomers shown in green (exc/em 530/590).

SERMACS 651

Porphyrin modified polyhedral oligomeric silsesquioxane molecules for the photodynamic therapy of cancer cells

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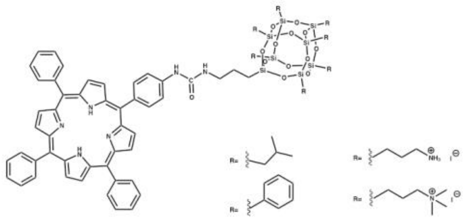
Polyhedral oligomeric silsesquioxane (POSS) molecules are highly ordered organic-inorganic hybrid materials with a cage like core of alternating silicon and oxygen atoms surrounded by eight pedant organic residues. These compounds are well-defined, 3D building blocks that can form hybrid materials with precise control of the nanostructure and properties. POSS molecules are used in a wide variety of medical fields, for example, tissue engineering, drug delivery, or for the oligomerization of bioactive ligands, among them peptides and carbohydrates. In this work, we have taken advantage of the chemical and structural properties of POSS to functionalize this material with porphyrin as a photosensitizer agent. We hypothesize that the differences in surface functionalization on the POSS molecule will have a major impact on the phototoxicity of the POSS-porphyrin compounds against cancer cells. We have carried out a systematic investigation by functionalizing the POSS molecules with either isobutyl or phenyl groups, which render hydrophobic properties to the final POSS-porphyrin compound. We will study also the functionalization of hydrophilic groups such as aminopropyl. POSS-porphyrin molecules functionalized with isobutyl or phenyl groups have been synthesized and characterized using a wide variety of spectroscopic and spectrometric techniques such as ^{1}H, ^{13}C and ^{29}Si Nuclear Magnetic Resonance, FTIR, UV-vis, ESI-MS and MALDI-MS. The phototoxic effects of these POSS-porphyrin molecules have been evaluated *in vitro* using the MDA-MB-231 cell line. Isobutyl POSS-porphyrin molecules were determined to exhibit phototoxic effects on MDA-MB-231 cells 20-fold greater than the porphyrin alone. This is likely explained by the added hydrophobicity allowing for better internalization within cells. It is envisioned that the hydrophilic groups will result in a higher phototoxic effect due to the possession of a positive charge.



SERMACS 652

Extending the ^{3}MlCt state of osmium(II) tris-(2,2’-bipyridine) through encapsulation within zinc(II) trimesic acid metal–organic frameworks

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The Os(II) tris(2,2’-bipyridine) (OsBpy) complex is a member of the transition metal polyimine class of molecules that exhibit robust structural properties and a rich photochemistry. Of particular interest are the long lifetimes and absorption bands in the visible region of the spectrum associated with these complexes making them attractive candidates for solar photochemistry and light harvesting applications. Modifying the photophysics of these complexes can be achieved through encapsulation within metal organic framework (MOF) materials. Here we present the photophysics associated with OsBpy encapsulated within two distinct Zn(II)-trimesic acid MOFs, HKUST-1(Zn) and USF-2. Encapsulation results in a hypsochromatic shift of the steady-state emission band in both frameworks resulting from a destabilization of the metal-to-ligand charge transfer state (^{3}MLCT) attributed to inefficient solvent reorganization within the MOF pores. The encapsulated OsBpy also exhibits extended emission lifetimes in both HKUST-1(Zn) (104 ns in MOF vs. 50 ns in methanol) and USF-2 (80 ns in MOF vs. 50 ns in methanol) arising from a decrease in the radiative and non-radiative decay constant in both systems. By decreasing the energy spacing between the Ψ_{T1} and Ψ_{S0} states the spin-orbit coupling term decreases resulting in the decrease in the non-radiative rate and extension of the excited state lifetime. Destabilization of the Ψ_{T1} state is a consequence of the two different environments imposed on OsBpy by ZnHKUST and USF-2. The cationic nature of USF-2 provides greater stabilization of the encapsulated OsBpy excited dipole moment resulting in observed longer wavelength emission and shorter lifetimes relative to the neutral HKUST-1(Zn) framework.

SERMACS 653

Heme/copper model complexes: Oxidative chemistry and mechanistic studies

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As an integral part of the electron transport chain, cytochrome c oxidase (CcO) reduces dioxygen (O_2) to water (H_2O) through the transfer of four electrons and four protons. This is responsible for the formation of an electrochemical gradient that ultimately enables the synthesis of ATP. The enzyme active site is comprised of two adjacent metal centers, heme-a_3 and Cu_B. Initial attempts at modeling the CcO dioxygen chemistry led to the discovery of an interesting category of heterometallic heme/Cu μ-oxo compounds, [(porphyrinate)Fe^{III}–O–Cu^{II}(L)]$^{+}$. The bridging oxo ligand in heme/Cu μ-oxo model complexes is derived from O_2 reacting with the reduced heme and Cu complexes. These fully oxidized compounds have demonstrated the capacity to oxidize nitric oxide (NO) to nitrite (NO_2^{-}). Here, these heme/Cu μ-oxo complexes are studied for their application in catalytic oxidation of substrates. A second component for discussion will be the viable mechanistic studies for the observation of compound I and II type intermediates that may form during the catalysis.

SERMACS 654

Guest to framework photoinduced electron transfer in a cobalt substituted Kullek type metal-organic framework

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Photoinduced electron transfer (PET) between donors and acceptors in porous materials is a key element in the development of light harvesting applications. Metal org. frameworks (MOFs) are ideal materials for PET processes due to their tunable pore size and diversity of framework building units. Here, PET between excited RuBpy and Co carboxylate clusters composing the metal building blocks of a novel Kullek type metal org. framework is described. The lifetime of the RuBpy decreases from ~600 ns in deaertaed ethanolic soln. to ~8 ns when encapsulated within the CoKullek MOF. The decrease in lifetime is attributed to PET between the triplet MLCT of RuBpy and the Co ion cluster composing the MOF building blocks. The temp. dependence of the electron transfer rates has been used to probe the Marcus parameters for electron transfer and these results will be discussed within the context of guest framework PET in MOFs.

SERMACS 655

Pore modulation of guest photophysics in metal–organic framework: Photophysical studies of meso-tetra (n-methyl-4-pyridyl) porphine encapsulated within MOM-11 and MOM-12

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The ability of metal organic frameworks (MOFs) to modulate the photophysical properties of encapsulated guests is of importance for the applications of these materials in light harvesting and photocatalysis. Here, the photophysical properties of tetra (N-methyl-4-pyridyl)-21H,23H porphine (TMPyP) encapsulated within two Cd-based MOFs (MOM-11 and MOM-12) are reported. The results demonstrate large bathochromic shifts in the Soret band of the porphyrin relative to free-base TMPyP in solution consistent with Cd^{2+} binding to the encapsulated porphyrin in a sit-atop geometry. Bathochromic shift is also observed in the steady-state emission spectra together with spectral broadening that are attributed to porphyrin pyridinium ring conformations. Transient absorbance data reveal porphyrin triplet state lifetimes that are also an order of magnitude longer than that observed in solution ($\tau \approx$ 0.3 ms for CdTMPyP and $\tau \approx$ 1.8 ms and 2.4 ms for CdTMPyP@MOM-11 and CdTMPyP@MOM-12, respectively) that are attributed to planar porphyrin ring conformations for the CdTMPyP enforced by the pore confinement. The planar conformation affects the spin orbit coupling between the non-radiative T_1->S_0 transition.

SERMACS 656

Synthesizing and investigating the catalytic properties of (Cu(II)l)2Mn(II) complexes

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Several novel nonsymmetric heterometallic schiff-base complexes have been synthesized and their catalytic properties have been investigated. This multistep synthetic approach involving the condensation of: salicylaldehyde, 1,3 diaminopropane, and o-hydroxyacetophenone has several possible products including an azide coordination complex and a isothiocyanate coordination complex. With similar coordination complexes showing catalytic activity, the catalytic activity of these novel heterometallic schiff-base ligand complexes was investigated using both cyclic voltammetry and EPR spectroscopy. By mimicking certain biocatalysts, such as catecholase, these nonsymmetric heterometallic schiff-base ligand complexes can offer alternative means of catalyzing reactions to synthetic chemists.

SERMACS 657

Computational study of iron(II)-polypyridines as chromophores for dye sensitized solar cells

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Dye-sensitized solar cells (DSSCs) are one of the ways to convert sunlight to electricity. Light is absorbed by the sensitizer, which is anchored to the surface of a wide band gap semiconductor. Electrons are transferred from the excited dye to the conduction band of the semiconductor via the interfacial electron transfer (IET). IET generally originates from the metal-to-ligand charge transfer (MLCT) excited states of the dyes. Ru(II)-polypyridines have been primarily used as dyes in DSSCs, exhibiting excellent light-harvesting capabilities. However, Ru is rare and expensive. Fe(II)-polypyridines have been considered as a less costly alternative, but their ability to undergo efficient IET is hindered due to competition with intersystem crossing to lower-lying metal-centered (MC) states. In this work, DFT and TD-DFT were used to investigate a series of Fe(II)-polypyridines with extended π-conjugated ligands with the aim of stabilizing the MLCT excited states relative to the MC states, thus improving the IET efficiency. It was found that in addition to stabilizing both ^{1}MLCT and ^{3}MLCT excited states, ligand-centered (LC) excited states are also stabilized over the series of dyes with large extended π-conjugated ligands. These LC excited states show greater stabilization of their relative energies compared to the MLCT states. Overall, our results suggest that extending π conjugation of polypyridine ligands may be a viable strategy to improving the light-harvesting properties of Fe(II) complexes.

SERMACS 658

Using salphenazine-type imidazoles in chemosensing for detection of $[UO_2]^{2+}$ and other metal ions

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As the need for renewable and more carbon neutral energy increases, the need and interest in nuclear power is growing simultaneously. A major concern with nuclear power is the generation of radioactive waste and the possibility of the radioactive material being released into the environment. To combat this issue, fast and in-the-field detection of radioactive material is needed for faster response and clean up if a spill should occur. One method for detecting radioactive by-products is by using a chemical sensor, or chemosensor, that can selectively bind or give a distinct response when bound to uranyl ($UO2^{2+}$), the most biologically relevant species of uranium. The rational design of such a species can be quite challenging. Schiff base ligands with the N-C-C-C-O binding motif have been used previously for this purpose. The Schiff base ligand, 2-(1H-imidazo[4,5b]-phenazin-2-yl) and derivatives thereof, are formed from a condensation reaction followed by an intramolecular cyclization of an array of salicylaldehydes and 2,3-diaminophenazine. These ligands are examined here for their efficiency as chemosensors for uranyl and Copper (II). The shift in UV-

visible spectrum upon metal binding was observed and allows for sensing of these metal ions. Tuning the electronics of the ligand through substituent effects and of the binding affinity to these metal ions is also discussed.

SERMACS 659

Synthesis of novel bismuth containing oxides

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High temperature crystal growth techniques are essential for the synthesis of solid state materials. One such approach is flux crystal growth, which allows one to obtain high quality single crystals in high yield, and phase purity. In order to reveal a structure-directing role of an inert lone pair of heavy elements, such as $Pb^{2+}$and Bi^{3+}, and further expanding this approach to new systems, we attempted synthesis of novel bismuth containing phosphates, germanates, and silicates using molten alkali halide eutectics. The crystal structures of the obtained compounds, which were determined using single crystal X-ray diffraction, show that bismuth incorporation facilitates the channel formation within the structures.

SERMACS 660

Photocatalytic hydrogen production via dual photon absorption pathway

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We have developed a novel photocatalytic system based on dual photon absorption pathway to produce molecular hydrogen by utilizing a molecular Z-scheme. Hydrogen is a sustainable and renewable energy source that is a potential clean alternative to fossil fuel energy sources. In our system, molecular hydrogen is produced from weak acids by utilizing a light absorbing photocatalyst and a light absorbing photoacid. Typically, photocatalytic hydrogen production is achieved through three component systems consisting of light absorbing photocatalyst, a proton source, and proton reduction catalyst. These systems are triggered by single photon absorption by the photocatalyst and electron transfer to the proton reduction catalyst. Alternatively, we have developed a system where simultaneous light absorption by a photocatalyst and a photoacid promotes electron transfer from the photocatalyst to the photoacid with subsequent production of molecular hydrogen. Spectroscopic studies, control reactions, and GC analysis of headspace gas support the dual photon mechanism for hydrogen production

SERMACS 661

Thermodynamic and structural characterization of Cd(II) and Ca(II) binding to EF-hand peptides by isothermal titration calorimetry and circular dichroism spectroscopy

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Calcium-binding EF-hand proteins are ubiquitous in the cell and are essential for many biological functions such as muscle contraction and cell signalling. Divalent cadmium, Cd(II), is a toxic metal that is known to mimic the calcium ion, Ca(II), due to their similar ionic radii (0.99 and 0.97 A respectively). While it is known that Cd(II) can interact with Ca(II) binding proteins, the affinity and structural changes that occur upon binding are not known. In this study, the following EF-hand peptides were made using solid state peptide synthesis: EF-hand V from Calbindin D_{28K} and EF-hands III and IV from human cardiac troponin C (hcTnC). The peptides were purified by reverse phase HPLC and characterized by MALDI-TOF and QTOF mass spectrometry. Ca(II) and Cd(II) binding to these peptides were studied using Circular dichroism (CD) and isothermal titration calorimetry (ITC). CD data show that both Cd(II) and Ca(II) bound peptide display enhanced absorption at 220 nm, which is indicative of alpha-helical formation. ITC data reveal that Cd(II) binding to calbindin EF-hand V is thermodynamically more favored than Ca(II) binding. This confirms that Cd(II) can induce similar structural changes in these three calcium-binding EF hand peptides and that the resulting structures are more thermodynamically favored.

SERMACS 662

Linear Cu^{i}_4 bis(amidinates) as flexible molecular strings

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The excellent luminescence properties of Group 11 metal clusters have received a considerable interest in recent years. This is because of their application potential as powerful building blocks for molecular/organic light-emitting devices/diodes (OLEDs). In particular, copper as a highly abundant and cheap coinage metal resource has become an attractive alternative to silver and gold. Our concept is based on a series of the new ethylene-linked polydentate bis(amidine) ligands with a sterically protected flexible backbone. They undergo a clean conversion with mesitylcopper into neutral, homoleptic, and liner Cu^{I}_4 arrays. This presentation includes the synthesis and structural characterization of two new examples.

SERMACS 663

New hexadentate bis(amidines) as flexible ligands for dichloro-dicopper(I) and -digold(I) complexes

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Since their seminal discovery in the early 1950s, tetradentate bis(amidines) have attracted significant attention as versatile ligands in lanthanide and Group 4 coordination chemistry with related catalytic applications. Only recently it has been demonstrated that these bis(amidines) also serve as scaffolds for multinuclear late transition metal ion assemblies. Herein, we describe the synthesis of five new bis(amidines) and the versatile coordination behavior of the hexadentate bis(amidine) $\mathbf{L}^3H_2$ towards CuCl and $[(Me_2S)AuCl]$.

SERMACS 664

Determination of the binding affinity of Cd(II) to Ca(II) bound human cardiac troponin C using isothermal titration calorimetry: Competition study

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Metals play important roles in biological processes. However, there are some metals ions that are highly toxic such as cadmium, Cd(II), which can cause biological disruption and deleterious health outcomes. Cadmium can cause these toxic effects by mimicking other essential metals, such as Ca(II). However, not much is known about the thermodynamic driving force behind Cd(II) interactions with Ca(II)-binding proteins. The main goal of the Spuches lab is to understand these interactions. Previous studies in the Spuches lab indicate that Cd(II) binding occurs at both the N- and C-domains of human cardiac troponin C (hcTnC), an EF-hand containing protein that is responsible for heart muscle contraction. However, the binding of Cd(II) to Ca(II)-bound protein had not been explored. In this study, we used a competition isothermal titration calorimetry (ITC) method to determine if Cd(II) binds to the protein in the presence of Ca(II). These Cd(II) titrations revealed that the enthalpy of binding to the N-domain is less than the enthalpy of binding to the apo-protein. In addition, Cd(II) binding to the C-domain revealed a lower binding constant than the Cd(II)-apo titrations; both of these results are indicative of metal competition at both the N- and C-domains of the protein. These data have implications for Cd(II) ion toxicity, as Cd(II) may compete for Ca(II) sites on proteins and subsequently alter structure and function.

SERMACS 665

Developing new optical and magnetic materials

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Today, functional crystals are essential for advancements in spectroscopy, communication, and information processing. Therefore, engineers are turning toward bottom-up approaches to design and develop new optical and magnetic materials for these applications that may enhance the performance of these systems. The chemistry approach to this engineering problem requires knowledge of structure-property relationships to predict and exploit unique physical and optical properties. Drawing inspiration from current phosphate and borate crystals used for these applications, this project investigates the potential of transition metal selenates for similar applications. The selenate ion has potential for these applications because of its relation to other oxyanions, such as sulfates, which form many intriguing crystal types. However, the bonding chemistry of selenates is poorly understood. Divalent metal ions including Mn, Fe, Ni, and Co are under consideration due to their interesting electronic properties at the atomic level, which may make them suitable for tunable optical or magnetic applications. After synthesis using simple techniques, the crystals were identified and characterized with single crystal X-ray diffraction. Further analysis connects parameters including composition and reaction environment to crystal type formation. This information could be applied to optimize and predict possible crystal products that display unique optical and magnetic properties.

SERMACS 666

Redox inactive catalysts for aldehyde deformylation

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Two gallium(III) species, $GaCl_3$ and $[Ga(bispicen)Cl_2]Cl$, were found to promote the deformylation of aldehydes using H_2O_2 and base, demonstrating that redox-active transition metals are not strictly required for this sort of reactivity. The two Ga(III) species display different activities and provide two different product distributions. The bispicen complex yields an approximately equimolar mixture of alkenes and ketones. The $GaCl_3$, conversely, transforms an initially generated alkene into an ester under the same conditions when the reactions are run in methanol. In acetone, certain substrates are oxidized exclusively to alkenes. The oxidative stability of $GaCl_3$ and the ability to completely eliminate side-reactivity by switching solvents enables a high level of catalysis.

SERMACS 667

Characterizing the binding of Pb(II), Ca(II), and Cd(II) to EF-hand peptides III and IV of human cardiac troponin C and EF-hand peptide V of calbindin D_{28k} using circular dichroism spectroscopy

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There is much to be seen about heavy metal toxicity in the news today; ranging from the well-known issue of contaminated water in Flint, Michigan, to the presence of Pb found in common household spices. It is known that both divalent lead (Pb(II)) and cadmium (Cd(II)) mimic essential metal ions such as Ca(II), a metal known to be an important secondary messenger in the human body. It is also known that both Pb(II) and Cd(II) can disrupt Ca(II)-binding proteins and pathways; however, there is not much known about metal-protein interactions from a molecular perspective. This project seeks to determine how Pb(II) interacts with Ca(II)-binding EF-hand peptides and what structural changes occur upon binding. These data will then be compared to Ca(II) and Cd(II) binding studies conducted in the Spuches lab. Solid-state peptide synthesis and HPLC were used to synthesize and purify EF-hand V of Calbindin D_{28k} and EF-hands III and IV of human cardiac troponin C (hcTnC), proteins that act as a Ca(II) buffer and regulate heart muscle contraction respectively. MALDI-TOF and Q-TOF were also utilized to accurately characterize the peptides. Circular dichroism (CD) was used to determine the structural changes that occurred upon metal binding. CD data confirmed that Pb(II) was capable of inducing a similar alpha helical structure as Ca(II) and Cd(II) in both Calbindin EF-hand V and EF-hand III of hcTnC, while promoting a beta-sheet structure in EF-hand IV of hcTnC. These changes also occurred at lower Pb(II) concentrations and indicate that Pb(II) may bind more tightly than Ca(II) to these peptides. Cd(II) induced alpha-helical structures similar to Ca(II) when bound to each EF-hand, with these structures being more distinct for hcTnC. These data have very important implications for Pb toxicity and may suggest that Pb(II) can alter the structure and function of Ca(II)-binding proteins.

SERMACS 668

Study of electrocatalytic CO_2 reduction by nickel and copper complexes

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In recent years, chemist have increased their interest in using CO_2 as a feedstock for preparation of value-added compounds, thereby helping to reduce its atmospheric concentration and produce useful chemicals. However, the utilization of CO_2 as a C1 feedstock is very challenging because of its high stability and much effort has been attentive to developing efficient catalytic systems for CO_2 reduction. Electrocatalysis using transition metal complexes has been studied extensively to gain insight into the fundamental aspects of CO_2 conversion. Herein, we report the synthesis and characterization of two molecular complexes of Ni(II) and Cu(II) bearing a BPI ligand [BPI= bis(6-methylpyridin-2-yl)isoindoline-1,3-diimine] to study electrocatalytic CO_2 reduction. Single crystal x-ray diffration reveals that Ni(II) is coordinated with three N-atoms from the BPI ligand in a planar environment and forms a monomer whereas in case of the Cu(II) complex, each Cu(II) is bridged via a hydroxo (-OH) group to form a dimer. Each Cu(II) centre has a distorted tetrahedral geometry via the three N-atoms from the ligand and one µ-OH group. The electrocatalytic properties of these two compounds were measured and compared by cyclic voltammetry in acetonitrile, in the absence and presence of CO_2. The addition of CO_2 shows a large increase in current in case of Cu(II) complex compared to the Ni(II) complex. Molecular geometry and electronic structure are believed to be crucial factors for $[Cu(II)BPI]_2(\mu\text{-}OH)$ complex to acts as a better electrochemical catalyst for CO_2 reduction than the Ni(II)BPI complex.

SERMACS 669

Synthesis and characterization of tri-iron, tri-cobalt, and nickel di-lithio complexes with 2,6-bis(trimethylsilylamino)pyridine

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The investigation of extended metal atom chain complexes (EMAC) of 1st-row transition metals that contain metal-metal covalent interactions has yielded significant insight into the unique physical properties, especially magnetic, and reactivity when compared to their monometallic counterparts. This research entails our attempts to synthesize novel EMAC of 1st-row transition metals supported by 2,6-bis(trimethylsilylamino)pyridine (L) and that contain a linear, trimetallic core. The initial lithiation of L was achieved using *n*-butyl lithium. The subsequent metalation of L with either Fe, Co, or Ni was accomplished via metathesis of the lithium(I) cations with the corresponding chloride salts. While both Fe(II) and Co(II) form linear trimetallic complexes, Fe_3L_3 and Co_3L_3 respectively, the Ni(II) forms a monometallic complex and retains two equivalents of lithium, $(Li\bullet THF)_2NiL_2$. Each complex was characterized by ^1H-NMR, single-crystal X-ray diffraction, electronic absorption spectroscopy, and elemental analysis. The magnetic properties of Fe_3L_3 and Co_3L_3 were investigated by Evans method in benzene and THF showing large degrees of uncompensated spin with both cT values above that expected for non-interacting cations. The redox behavior of all three complexes was investigated through cyclic voltammetry indicating a range of unique behavior across the group. The characterization of Fe_3L_3, Co_3L_3, and $(Li\bullet THF)_2NiL_2$has significantly broadened the knowledge about EMAC. These results show that 2,6-bis(trimethylsilylamino)pyridine is a versatile ligand to support novel EMAC of 1st-row transition metal clusters.

SERMACS 670

Hydrodeoxygenation of vanillyl alcohol by ruthenium pincer complexes

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Biomass can be converted to bio-oil, a more useful form to produce fuel, through pyrolysis. However, bio-oil has problems of thermal instability, affinity for water, corrosivity, high viscosity, and low heating values. This is caused by its high oxygen content. We report a ruthenium CNC pincer complex that is capable of catalyzing the hydrodeoxygenation of vanillyl alcohol efficiently, which is potentially a method to reduce the oxygen content of bio-oil.

SERMACS 671

Isolation of two novel polynuclear Mn 3 and Mn 7 clusters incorporating the anion of 4,5-bis(hydroxymethyl)-2-methylpyridin-3-ol

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The prime focus of the research is to investigate modern coordination chemistry, which has vastly expanded over last few decades particularly in the area of polynuclear metal complexes, often known for their aesthetically pleasing structures, unique supramolecular architectures, and interesting magnetic properties such as single-molecule magnetism (SMM), molecular magnetic refrigeration and quantum computing. An SMM is a nanoscale magnet, consisting of various metal ions. SMMs are discrete, magnetically non-interacting molecular units possessing a potential energy barrier for the reversal of the magnetization vector. To facilitate the formation of such polymetallic structures, alkoxide-based ligands play a crucial role where this functionality act as a bridging group that fosters higher nuclearity product formation. The choice of paramagnetic metals such as iron, manganese, copper in their common oxidation states can often lead to interesting magnetic properties in combination with appropriate ligand. Herein, we are currently exploring the uses of the ligand, 4,5-Bis(hydroxymethyl)-2-methylpyridin-3-ol (PNH_2) with the combination of high-valence manganese ions. The aforementioned ligand has four binding sites through electronegative O and N atoms (O, O, O, N) which will preferentially bind high oxidation state transition metals. Two novel complexes Mn_3 and Mn_7 were isolated and characterized by single-crystal x-ray crystallography, infrared & UV-visible spectroscopies, elemental & thermal gravimetric analysis. Variable temperature, solid-state direct current (dc) magnetization studies were carried out on both complexes and it was found that they have ground state spin values of $S = 5$ or 6 for Mn_3 and $S = 5$ for Mn_7.

SERMACS 672

Towards the synthesis of a metal sensor: Varying reaction conditions in the synthesis of silver nanoparticles with 8-hydroxy-5-quinolinesulfonic acid hydrate

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Nanotechnology is a fast growing and advancing field that continues to introduce new possibilities for the expansion of fields such as sensing, drug delivery materials, and environmental recovery (Irfan, 2014). In particular, metallic nanoparticles that are capped with organic molecules capable of binding other metals are an interesting approach to the detection of heavy metals in water samples due to optical changes that occur upon binding of the second metal. These nanoparticles, therefore, can act as sensors. The work presented focuses on our attempts at synthesizing silver nanoparticles using 8-hydroxyquinoline-5-sulfonic acid for recognition of an array of metallic ions in local and international water samples. (Sang, Gao, Wu, Wan, 2013) Of great importance to the formation of functional nanoparticles are synthesis conditions. For this work varied were the different synthesis conditions such as reagent concentrations, temperature, and order of addition of reagents. Results from UV-Vis suggest the formation of different sized nanoparticles depending on particular synthesis conditions. Further, preliminary results from testing various metal ion solutions (Sn^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}, Fe^{3+}) are reported. Preliminary results on the degradation of pH on the formation of silver nanoparticles are to be reported.

SERMACS 673

Existence of pnictide analogs of small nitrogen and phosphorus compounds: Review

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Since 2003, a research project headed by Dr. John R. Wasson has been investigating the existence of the heavier pnictide (arsenic, antimony, and bismuth) analogs of the lighter nitrogen and phosphor small compounds. The previous studies have included the analogs of HCN, HNCO, HOCN, HN_3, NCX, NCCN, P_4, the III≡V diatomics, N_2P_3, Φ-N_5, $C_3N_3X_3$, $C_3N_3O_3X_3$, HOON, and NOON. The SPARTAN molecular orbital program has been employed to probe the existence and properties of the pnictide-substituted compounds, usually at the semi-empirical PM3 level because of the lack on parameters for the heavier pnictides at the higher levels. As a tribute to Dr. Wasson's lifelong engagement in chemical research, a summary of these studies will be presented with a focus on the most likely candidates for future synthesis.

SERMACS 674

New covalent reactions to tune the optical properties of single-wall carbon nanotubes

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Single-wall carbon nanotubes (SWCNTs) display unique, structure-specific electronic and optical properties. However, it has not been possible to achieve controlled spatial or energetic modulation of those properties. We will describe a simple new method for using chemical reactions with single-stranded DNA (ssDNA) to accomplish this.[1] When aqueous suspensions of SWCNTs coated with ssDNA are exposed to singlet oxygen at ambient temperatures, the nanotubes selectively form covalent bonds to the guanine nucleotides. This locally modulates semiconducting SWCNT energy levels and red-shifts their emission wavelengths by up to 10%. Both the magnitude and spatial pattern of these shifts can be templated by selecting the nucleotide sequence used to coat the nanotubes. Biomedical, optoelectronic, and single-photon emission applications seem possible. We will also describe new non-radical functionalization reactions that have been found to shift and brighten SWCNT fluorescence. [1] Y. Zheng, S. M. Bachilo, and R. B. Weisman, *ACS Nano* **2019**, DOI: 10.1021/acsnano.9b03488.

SERMACS 675

Many faces of carbon

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Carbon, the basis of all life on the Earth, is one of the most fascinating elements in the periodic table. The unique properties of carbon emerge from its ability to form diverse sp^n ($1 < n < 3$) bonds, graphite with sp^2 and diamond with sp^3 bonding being the most common forms. The discovery of zero-dimensional (0D) carbon fullerenes, one-dimensional (1D) chain-like polymer called “carbyne” and carbon nanotube, and two-dimensional (2D) graphene, all with novel properties characteristic of their reduced dimensionality and size, has ushered a new era in carbon science. In recent years many new metastable forms of carbon exhibiting a mixture sp^1, sp^2 and/or sp^3 bonding pattern have also emerged. In this talk I will focus on one of the carbon allotropes that has been studied in our group recently, namely, a Cairo-tilling inspired quasi-2D penta-graphene made only of carbon pentagons. I will also highlight the discovery of a new carbon allotrope that resulted from the synergy between theory and experiment and can be viewed as a cousin of penta-graphene. Interestingly, unlike penta-graphene, this new carbon allotrope, which we name U-carbon, is metallic and magnetic. Theoretical studies were carried out using gradient corrected density functional theory while experiment was conducted using an organic precursor molecule. Thermodynamic stabilities of the above carbon allotropes are confirmed by total energy calculations and *ab initio* molecular dynamics. Potential applications of some of these carbon allotropes will be discussed.

SERMACS 676

Molecular self-assembly on 2D materials studied by STM

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Molecular self-assembly is a powerful tool in nanoscience for bottom-up fabrication of well-defined and ordered molecular nanostructures. Different from traditional flat surfaces of bulk crystals, two-dimensional (2D) materials, such as graphene and atomically thin transition metal dichalcogenides (TMDs), usually exhibit nonplanar aberrations and provide a unique platform to investigate self-assembly. Understanding molecular self-assembly on curved 2D materials is crucial for numerous applications. In this talk, I will discuss self-assembly of a few model molecules on graphene and 2D TMDs. In particular, I will present different self-assembly behaviors of spherical fullerene and planar perylenetetracarboxylic dianhydride (PTCDA) molecules adsorbed on a rippled graphene surface. Our scanning tunneling microscopy (STM) results show that C_{60} molecules form a quasi-hexagonal close packed structure, while PTCDA molecules form a disordered herringbone structure. The density functional theory calculations reveal that the change in the packing pattern of C_{60} and PTCDA molecules is due to competition between the adsorbate-graphene interaction and the intermolecular interaction.

SERMACS 677

Scrolling behavior of nanosheet materials

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The phenomenon of scrolling – the “rolling up” of monolayer or multilayer nanosheets into tubelike structures – is exhibited by graphene, graphene oxide, and a variety of inorganic materials. This contribution aims to highlight the diversity of scroll structures and scrolling mechanisms, as well as their applications related to encapsulation and heterostructure assembly. One example is the spontaneous scrolling of layered graphene oxide-metal heterostructures into freestanding, micron-sized tubes. The driving force for scrolling is generated by stresses from the metal deposition, as well as the weak van der Waals interactions between graphene oxide layers. The inclusion of platinum within these tubes enables microjet activity upon reaction with peroxide. A second example, on a much smaller length scale, begins with a series of topochemical transformations from bulk calcium silicide to calcium fluoride nanosheets and then to lanthanum oxyfluoride nanosheets, which scroll into nanoscale tubes. In this case, the impetus for scrolling is provided by lattice strain generated upon substitution of two fluorides by one oxygen in the atomic lattice. Characterization of the resulting nanoscrolls includes 19F NMR, powder X-ray diffraction, X-ray photoelectron spectroscopy, energy dispersive spectroscopy, and electron microscopy to establish their composition and morphology.

SERMACS 678

Integration of fullerenes as electron-acceptors in 3D graphene networks

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Graphene and fullerenes are examples of carbon nanomaterials with unique electronic structures and related electrochemical properties that have opened the door to many promising applications in the field of energy storage and harvesting. Lawrence Livermore National Laboratory recently reported the integration of the characteristic properties of [60]fullerene in 3D graphene networks. In these systems, graphene provides high electrical conductivity and surface area while fullerenes add high electron affinity. Using molecular design, we optimized the interaction between 3D graphene networks and fullerenes, specifically in the context of stability and charge transfer in an electrochemical environment demonstrating that the capacity of the 3D graphene network was improved 50% upon the addition of C_{60}. Finally, functionalization of C_{60} improved the cycling stability of the hybrid material due to the additional interaction between the addend and graphene and doubled the gravimetric peak current density of the 3D graphene network electrode from 272.2 mA/g to 548.6 mA/g.

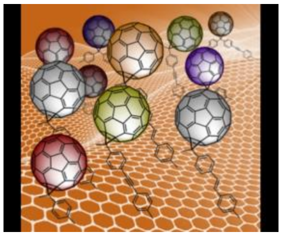

Fig. 1 [60]Fullerene monoadducts in 3D graphene networks

SERMACS 679

Fullerene-based triboelectric nanogenerators

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A triboelectric nanogenerator (TENG) is a viable device that converts waste mechanical energy, e.g., from human motions, into electric power. In a TENG, the waste mechanical energy is used to bring two electrodes with different electron affinities into contact, which results in a voltage across the electrodes. Recently, we reported the triboelectric charging behaviors of TENGs comprised of graphene impregnated PLA[1] and MXenes[2]. Although there has been much progress in identifying several materials (e.g., Teflon, MXenes, polyethylene terephthalate or PET, graphene impregnated polymers, and polyimide or Kapton) for triboelectricity, an important class of carbon, viz., zero-dimensional fullerenes have been largely ignored. In this talk, fullerene-based TENG or F-TENG will be discussed. Lab-scale F-TENGs support both high open-circuit voltages ranging from ~1.0 kV- 1.5 kV and an instantaneous peak power of ~10 mW that is capable of charging a 1 microfarad capacitor up to 180 V under 9 minutes. This study highlights that the triboelectric charging behavior of 0D carbons is more effective compared to that of 2D carbons, when subjected to identical mechanical excitations.

SERMACS 680

Interfacing with nano: Nanoengineering with interfacial chemistry

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Nanograss can be grown from the surface of large pieces of aluminum and silane monolayers can be assembled to create an omniphobic surface. The sidewalls of nanotubes can be covalently functionalized to allow them to integrate with engineering polymers. And by controlling surface chemistry, porous hierarchical structures can be infused with immiscible liquids to create slip planes for fluids to increase heat transfer in microfluidic systems. Nanotechnology is a science dominated by interfaces. Whether it be nanotubes, quantum dots, vapor deposited layers or perhaps a large macroscale surface with nanoscale features, we are often concerned about the translation of properties across the interface of materials. Nanomaterials are wonderful things with properties that are exciting and astounding, but what good are those properties if we cannot integrate them into full scale materials to be used in our everyday lives? In this talk we will discuss materials chemistry and engineering nano-interface for useful applications at the macroscale.

SERMACS 681

X-ray study of the chemistry of lanthanide complexes with heteroaromatic N-oxides

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We have examined the chemistry of lanthanide complexes (Ce, Nd, Sm, and Er) with a series of aromatic N-oxides. The complexes were formed by the reaction of the lanthanide group salts (chlorides, bromides and nitrates) with an equivalent of the N-oxide. The N-oxide compounds are of interest because they can be derivatized with various binding modes, such as monodentate, *bis* bridging, or as a simple oxide bridge between two metals. This talk will present the results of the structural analysis and examine the similarities and differences in the structures.

SERMACS 682

A single-entity method to actively control the nucleation-crystal growth process (II) –electrical and optical signatures during lysozyme crystallization

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Crystallization of biomacromolecules is technically challenging but important for fundamental structure-property studies as well as pharmaceutical and other practical applications. A new method that is capable of synthesizing protein crystals one at a time, i.e., single-entity in contrast to the classic ensemble trial-error approaches, under active control has been developed by our group. Towards better understanding and control of the crystallization behaviors for macromolecules, electroanalytical and optical techniques were combined in the method development with protein lysozyme as the prototype analyte. The enabling mechanism is the active control of mass transport through a single nanopipette that the analyte and precipitant solutions are confined at the interface. The extent of supersaturation at the nanotip is externally tuned by applying an external electric field and monitored both by the electrical current/conductivity and under an optical microscope. From the optical observation, series of phase transitions are resolved including the sequential formation of a micron-sized domain inside the pipette, a nanodroplet outside the pipette, a nucleus with lattice structures and ultimately a single crystal with pristine optical morphology. More quantitative electrical signatures including current decreases in large/small scale, noise level reduction, oscillations and fluctuations are being established as independent feedbacks at the corresponding optically resolved phase transitions for the in-situ controls of the growth kinetics. The growth rate of the (110) face was found to be larger than (101) face at the early stage but decreased during the growth process. Quantification of the growth kinetics and structure confirmation are underway. Financial support by NSF CHE-1610616 is acknowledged.

SERMACS 683

Halogen bonding (XB) consortium in several iodide vs. triiodide cocrystals

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Non-covalent interaction such as halogen bonding are highly directional, making them particularly interesting from a crystal design standpoint. This directionality of the halogen bonding particularly depends on the types of anion involved. Compounds containing triiodide anions display enormous structural diversity and have attracted extensive experimental and theoretical interest. Recently, we began studying the pattern of halogen bonding linking the iodide anion with some organoiodine such as tetraiodoethylene (TIE), 1,2-diiodotetraflurobenzene (o-F$_4$DIB), or 1,4-diiodotetrafluorobenzene (p-F$_4$DIB) etc and compared their halogen bonding motif with systems that involves triiodide anions. A greater variety of interactions can be conveyed by introducing different cations and organoiodines in those triiodide or iodide systems. In this study, a series of cocrystals that involved in creating diverse halogen bonding motif will be discussed. An immense structural diversity has been observed with the choice of cation, organoiodine, and I^- or I_3^-. Here we introduce several new compounds and examine the interactions involving diversified halogen bonding motifs.

SERMACS 684

Halogen bonding as a route to new cocrystals and potential green solvents

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We have been studying cocrystals in multicomponent systems that pair halide salts with organoiodine molecules. These systems are interesting from the standpoint of supramolecular chemistry and crystal engineering in order to understand the formation of different cocrystal compositions and their assembly through halogen bonding. In several of the cocrystal systems, we found the salt and organoiodine components may be present in multiple different ratios, having greatly different halogen bonding motifs. This has led us to further explore these systems to see if some of them also exist as eutectic systems in certain ratios, with potential application as green solvents. Here we report systematic studies varying the identities and ratios of halide salts and organoiodine molecules with characterization by powder X-ray diffraction, single crystal X- ray diffraction and thermal analysis techniques.

SERMACS 685

Advanced structural mass spectrometry strategies in systems, synthetic, and chemical biology

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One of the predominant challenges in systems-wide analyses is the broad-scale characterization of the molecular inventory in cells, tissues, and biological fluids. Advances in computational systems biology rely heavily on the experimental capacity to make omics measurements, i.e. integrated metabolomics, proteomics, lipidomics, glycomics, etc., accompanied with fast minimal sample preparation, fast measurements, high concentration dynamic range, low limits of detection, and high selectivity. This confluence of figures-of-merit place demanding challenges on analytical platforms for such analyses. Ion mobility-mass spectrometry (IM-MS) provides rapid (ms) gas-phase electrophoretic separations on the basis of molecular structure and is well suited for integration with rapid (us) mass spectrometry detection techniques. Furthermore, the timescales of this multi-dimensional separation are well suited for combination with fast condensed-phase separations such as GC, SFC, and UPLC (min) for enhanced separation selectivity as the sample complexity becomes ever more challenging. This report will describe recent advances in IM-MS integrated omics measurement strategies in the analyses of complex biological samples of interest in systems, synthetic, and chemical biology. New advances in bioinformatics and biostatistics will also be described to approach biological queries from an unbiased and untargeted perspective and to quickly mine the data gathered to provide targeted and actionable information. Specific examples of how these high dimensional analysis facilitate analysis in pharmaceutical settings and medical diagnostics are provided.

SERMACS 686

Mapping structural diversity with TIMS-MS: From small molecules to protein complexes

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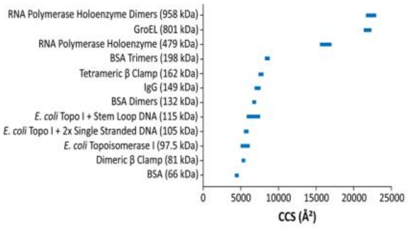
With the advent of trapped ion mobility spectrometry in 2011, a major transformation is occurring in the way mobility separations are performed due to access to high sensitivity (ppt level) and high mobility resolving power (R~150-500) cells coupled to high and ultrahigh resolution mass analyzers (TOF and FT-ICR MS). In TIMS, the mobility separation is currently limited by the trapping and elution strategies, since ions can undergo almost infinite drift lengths (gas velocity x trapping time). In 2018, a new mobility cell design with enhanced sensitivity, resolution and m/z range was introduced allowing studies of native biomolecular complexes in the MDa range. Applications of TIMS-MS will be shown for the analysis of a variety of native proteins, intrinsically disordered proteins, antibodies, and biomolecular complexes. The mobility analysis of native proteins, protein-DNA and protein-protein complexes was successfully extended to 15-20k *m/z* and over a mobility range of 0.3-1.8 cm^{2}V^{-1} s^{-1}. Examples will be shown for native conditions of HMGA2 (MW 12 kDa), BSA$_{n=1-4}$ (MW 66 kDa), CLAMP$_{n=1-4}$ (MW 88 kDa), Topo I (MW 97 kDa); HMGA2-DNA (MW 27kDa); Topo1-DNA (MW 114kDa); IgG (MW 150 kDa), and GroEL$_{n=14}$ (MW 58kDa).



SERMACS 687

Simplified sampling and characterization of THC and CBD using differential mobility spectrometry-mass spectrometry (DMS-MS)

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With initiatives to legalize marijuana, the analyses of tetrahydrocannabinol (THC) and cannabidiol (CBD),two natural extracts obtained from the cannabis plant, face serious scrutiny for the implications of proposed regulatory controls in the past few years. Most importantly, the psychoactive effects of these compounds are widely different such thatCBD's medical benefits arguably outweigh THC's potential for abuse and need for regulatory control. Both CBD and THC have the exact same molecular weight, making it nearly impossible to differentiate and characterize with stand-alone mass spectrometry (MS). Gas chromatography (GC) and liquid chromatography (LC) separation techniques have been coupled to MS to confer the orthogonality for the separation of the pair, but sampling and analysis can be laborious, time consuming, and non-deployable for field analysis. Differential mobility spectrometry (DMS) had been a promising rapid gas-phase separation technique, deployable for field applications. In previous work, we have coupled DMS with MS for the separation of drugs including amphetamine and derivatives. Though THC and CBD possess like molecular weight, their structural difference makes them amenable for ion mobility separation. Herein, DMS-MS system shall be employed for the separation of th pair. A home-built nebulizer was employed to aerosolize liquid sample, introduced from a syringe pump. A plasma-based ambient ionization; Direct analysis in real time (DART) was employed to ionize suspended aerosol containing sample mixture. Sample mixture with transport gas from the ambient environment was allowed to drift through 0.5 mm gap of two DMS electrodes (15 mm × 4 mm) enclosed in a DMS cell, and maintained at 1.2LPM flow rate by a external dry pump (Ionsense Vacuupump). The DMS cell was coupled to a commercial Thermo LTQ XL MS using the commercial DART Vapur interface. RF and DC voltage termed dispersion voltage (DV) and compensation voltage (DV) were supplied and controlled by method set on the commercial Sionex electronics. Initially, 10 µg/mL of Δ^9-THC, CBD and 50:50 mixture in methanol solution was fed into the nebulizer from a syringe pump at 30 µL/min. At fixed DV, CV was scanned from -15 to + 9.5 V for 30 seconds. At each DV; as low as 500V to maximum 1500 V, DMS demonstrated its capability for ion filtration. The result indicates that nebulizer-DART system can be employed for simple and rapid sampling prior to DMS separation and MS detection.

SERMACS 688

Understanding circadian dysfunction in Alzheimer's disease: Cylindrins trigger peptide release in living suprachiasmatic nucleus brain slices

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The amyloid hypothesis has played a prominent role in explaining the etiology and pathogenesis of Alzheimer's disease (AD) for several decades. While high-resolution structures of toxic amyloid oligomers capture the headlines and our imagination, "How" and "Why" the oligomers are toxic to specific cell types remain unanswered. A common strategy to assess the toxicity of amyloid oligomers is to monitor the metabolic activity of embryonic stem-cell-derived neurons in the presence of aggregating proteins via visualization of GFP-labeled cell morphology. This approach is faster and lower-cost than in vivo testing using animal models. Nonetheless, these colorimetric assays are often hypothesis-centric and serve as supporting evidence rather than a starting point for further investigations. A limited set of compounds is traced with traditional solution/fluorescence techniques. Subsequently, invaluable information that potentially bridges the gap between in vivo and in vitro studies will often be overlooked. Importantly, there is evidence for a prion-like propagation of pathology of toxic amyloids. Whether and how these aggregates are internalized by cells and able to cause toxicity are questions that often go beyond the scope of most high-resolution structural studies. In this study, we seek to determine cytotoxicity of an amyloid model termed "cylindrin" on living suprachiasmatic nucleus (SCN) slices isolated from healthy mouse brains. The K11V peptide (KVKVLGDVIEV) is a segment of the amyloid-forming protein αB crystallin, which forms a hexameric complex resembling the shape of a cylindrical barrel. Liquid chromatography ion-mobility mass spectrometry (LC-IMS-MS) is utilized to monitor peptides in tissue media and homogenates after two hours of incubation. Preliminary data uncover that K11V triggered the release of peptides from healthy SCN slices but did not cause significant cell death during the incubation period. We are working on characterizing these peptides in order to unravel the mechanisms leading to circadian dysfunction in Alzheimer's disease.

SERMACS 689

Ozone-based methods for improved differentiation of steroid stereoisomers

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Steroids are involved in numerous biological functions, including sexual differentiation and development. Over the last several decades, they have also become the target of anti-doping regulations due to their performance enhancing capabilities. Despite significant advances in analytical technology for the identification and quantitation of these illicit substances (e.g., gas and liquid chromatography, mass spectrometry, etc.), the threat of introduction of new designer compounds into the athletics community has required the continued development of higher resolution techniques. Of particular concern is the presence of steroid isomers that may be masked by other common, endogenous compounds. Recently, ion mobility-mass spectrometry has shown some promise for separation of steroid structural isomers. However, resolution of many of these compounds, and especially stereoisomers, remains a challenge. Unorthodox approaches (i.e., uncommon cation adducts, multimer formation, etc.) have been utilized, but can be difficult to implement due to the inherently low concentration of these steroids and their metabolites in biological samples. Our approach is to use ozone-based fragmentation and rearrangement of such compounds to create structural differences that can easily be differentiated by ion mobility-mass spectrometry. In this study, we demonstrate separation of testosterone from its structural isomer, dehydroepiandrosterone (DHEA), and its stereoisomer, epitestosterone. Reaction of ozone with the C=C double bond contained within one of the steroid rings leads to ring opening and formation of two new ketone groups. The resulting increased flexibility creates new stable gas-phase conformations that can readily be differentiated. Our approach utilizes both simple, low cost online solution-phase reactions, as well as more efficient gas-phase reactions. We will also introduce these methods for targeted anti-doping measurements of steroid metabolites. All experiments are performed using an Agilent 6560 IM-QTOF coupled to 129 Infinity II UHPLC.

SERMACS 690

Tandem-trapped ion mobility / mass spectrometry: Analysis of protein systems

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Ion mobility spectrometry-mass spectrometry methods offer the potential to correlate protein tertiary and quaternary structures to variations in their amino acid sequences and post-translational modifications. Because ion mobility spectrometry measures cross sections of ions in the gas phase, however, it remains unclear how closely the detected ions resemble the native state present in solution. Here, we apply our recently-developed computational Structure Relaxation Approximation (SRA) method to elucidate detailed protein structures from measurements carried out on our tandem-trapped ion mobility spectrometry / mass spectrometry (TIMS/TIMS-MS) instrument. We discuss the ability of our approach to characterize tertiary and quaternary protein structures from collisional cross sections, but also performing top-down sequencing of mobility-selected protein species.

SERMACS 691

Mechanisms of sequential ion-molecule reactions in protonated methanol using mass spectrometry, *ab initio* methods, and statistical modeling

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We present mass spectrometry results for reactions of protonated methanol clusters, $(CH_3OH)_nH^+$. Mass spectra indicate a preference for association over condensation at our experimental conditions and are used in conjunction with computational methods to probe the reaction mechanisms involved. We find that the reaction for the protonated monomer with neutral methanol consists of two entrance complexes that are in equilibrium due to a very small barrier between them. Statistical modeling indicates that competition between proton transfer, condensation, and association are dictated by the depth of the proton-bound complex and the height of the S_N2 transition state. For the reaction of the protonated dimer we determine condensation is not energetically favorable at thermal energies as a solvation effect raises the S_N2 barrier. Geometries for protonated methanol clusters $(CH_3OH)_nH^+$ up to n=6 are also provided, which allow us to examine the role of entropy and hydrogen bonding in these structures.

SERMACS 692

Exposomic applications of ion mobility-mass spectrometry: Developement of analytical methods for emerging perfluoroalkyl substances (PFAS)

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While advances in analytical instrumentation have promoted explosive growth for discovery approaches in omics' research (*e.g.* proteomics, lipidomics and metabolomics), enviormental and toxicological studies continue to be developed on highly targeted approaches of known analytes of concern. However, as new and emerging data from potential sources of environmental pollution are discovered, it becomes necessary to employ both targeted and untargeted workflows when annotating analytes which may be important to public health. Using recent advances in ion mobility-mass spectrometry, we describe the advantages of using this analytical technique to characterize new and emerging enviromental pollutants, with a particular focus on per and polyfluoroalkyl substances (PFAS).

SERMACS 693

Determining the role of intact proteins on green nanoparticle synthesis using *Verbascum thapsus*

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Green synthesis using nature's biological molecules in nanoparticle (NP) formation is becoming more common. Molecules that reduce metal cations and cap metal NP's include sugars, iridoids, glycosides, reducing amino acids, and proteins. The action of proteins in natural brews are largely unknown and this research focuses on investigating the role of proteins in NP synthesis. *Verbascum thapsus* (Common Mullein) has previously demonstrated its ability to produce NP's when brewed as a tea at 90 degrees C for one hour and mixed with silver nitrate solution. This temperature may denature proteins in this cooked brew. Our research focused on producing a sun tea brewed from *V. thapsus* leaves in direct sunlight for eight hours at a temperature range of 27-32 degrees C. Proteins present were unlikely to be denatured, leaving intact protein in the brew during NP synthesis. A control tea was prepared the same way as the cooked brew. The teas were normalized using UV-Vis spectrophotometry, and NP results were characterized by pH, UV-Vis spectrophotometry, dynamic light scattering (DLS), and atomic force microscopy (AFM). In all trials the sun tea was superior in higher NP production, lower polydispersity, and optimal size. Intense coloration of the cooked brew showed that the extracted components varied from the sun tea brew even after normalization, indicating higher small molecule extraction. This was evident even though the sun tea performed better in all trials. To negate this difference, two sun tea aliquots were obtained. One aliquot was used as a non-denatured brew and the other was cooked to denature proteins contained within the sample. Another series of experiments were conducted where a sun tea aliquot was treated with proteases to denature the proteins to single amino acids. A control (non-denatured sun tea) was inoculated with an equal quantity of self-digested proteases. The denatured sample would be expected to release reducing amino acids from hydrophobic regions where they normally would appear in an intact protein. NP's obtained from non-buffered brews were compared with buffered brews of these denatured and non-denatured teas throughout. Synthesis of NP's were also conducted at temperatures greater than 20 degrees C, but in the normal plant physiological range. Results indicate that intact proteins are significant in both reducing and capping processes of nanoparticle formation.

SERMACS 694

DNA conjugates with molecular silver clusters

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Single-stranded DNA encapsulates silver clusters, and the embedded clusters are chromophores whose spectra are directed by the sequence and structure of the DNA host. We show how these changes are used to detect oligonucleotides. A common type of DNA template has two components: the 3' sequence hybridizes with target oligonucleotides and the 5' sequence forms specific silver clusters. These composite strands exclusively harbor an 10 silver cluster that absorbs at 400 nm with limited emission. When a target hybridizes with these single-stranded conjugates, cluster absorption shifts and strong emission develops. Fluorescence anisotropy, fluorescence correlation spectroscopy, size exclusion chromatography, elemental analysis, and temperature-dependent spectral measurements identify two structural and thermodynamic changes accompanying hybridization. First, the violet cluster folds its single-stranded host and inhibits DNA hybridization. Second, the violet cluster dimerizes its DNA host and forms a near-infrared cluster. Our key conclusion is that silver clusters are both chromophoric reporters and ligands that modulate analyte-sensor interactions.

SERMACS 695

Chalcogenide nanocrystals for energy applications

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The ever-growing need for energy generation and storage applications demands development of low-cost materials with high conversion efficiency and long-term stability. The applications include photovoltaic devices for energy generation and supercapacitors for energy storage. Colloidal suspensions of nanomaterials are attractive for use as inks for low-cost fabrication of thin film solar cells and energy storage photovoltaic devices by simple spin or spray coating techniques. Among different classes of photovoltaic materials, copper-based semiconducting chalcogenides of the I-III-VI_2 and I_2-II-IV-VI_4 family, such as $CuIn_xGa_{1-x}S_2$ and Cu_2ZnSnS_4, are of considerable interest for use in thin film solar cells. Monodisperse $CuIn_xGa_{1-x}S_2$, Cu_2ZnSnS_4, $CuSbS_2$ and other chalcogenide nanocrystals have been synthesized using facile solution-based methods. Depending on the chemical composition and synthesis conditions, the morphology, structure and band gap of the nanocrystals can be controlled. Layer-structured chalcogenide materials are also advantageous for supercapacitor applications owing to their ability to host a variety of atoms or ions, large ionic conductivity and high surface area. $CuSbS_2$ is a layered ternary chalcogenide that is composed of earth-abundant and low toxicity elements. We have developed a simple colloidal method for the synthesis of $CuSbSe_xS_{2-x}$ mesocrystals over the whole composition range ($0 \leq x \leq 2$) by substitution of S with Se. Our approach yields mesocrystals with belt-like morphology for all the compositions. To investigate the suitability of $CuSbSe_xS_{2-x}$ mesocrystals for supercapacitor applications, we have carried out electrochemical measurements by cyclic voltammetry and galvanostatic charge-discharge measurements in KOH, NaOH and LiOH electrolytes. Our investigations reveal that the mesocrystals exhibit promising specific capacitance values with excellent cyclic stability.

SERMACS 696

Morphologically controlled SiO_2 overcoating of Au nanorods and functionalization with Fe_3O_4 nanoparticles

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Silica (SiO_2) overcoatings on nanoparticles (NPs) are important for improving their chemical, thermal, and optical stability, for imparting universal silane functionalization chemistry that does not depend on the core material, and because SiO_2 is biocompatible.

While there has been significant progress in the synthesis of SiO_2-overcoated spherical NPs, overcoating nanorods with SiO_2 presents special challenges for obtaining uniform overcoatings and opportunities for asymmetrical structures. This talk will review our recent efforts in the synthesis and shape control of SiO_2 overcoatings on Au nanorods (GNRs) and binding Fe_3O_4 NPs to their surfaces. We have used cetyltrimethylammonium bromide as a template layer for depositing SiO_2 onto GNRs by adding tetraethoxysilane (TEOS) dissolved in methanol (MeOH) via syringe pump. By adjusting the reaction conditions, shells as thick as ∼20 nm can be obtained. For thin shells (<10 nm), addition of poly(ethylene glycol) silane (PEG-silane) at different times during the overcoating reaction allows facile control over the shell thickness, giving shells as thin as ∼2 nm. The bulky PEG chain terminates further cross-linking and deposition of SiO_2. Varying the amount of MeOH used to dissolve the TEOS determines whether the SiO_2 shell uniformly coats whole GNRs or forms lobes on the ends of the GNRs. The mechanism for forming lobed structures will be discussed. Hydrophobic, oleylamine-stabilized Fe_3O_4 NPs dispersed in hexanes can assemble into dense coatings on the surface of silica-overcoated gold nanorods (SiO_2-GNRs) dispersed in ethanol by mixing. In this nonaqueous heteroaggregation process, Fe_3O_4 NPs are destabilized when ethanol is added, resulting in assembly of core/satellite Fe_3O_4-SiO_2-GNRs. SiO_2 shells and magnetic overcoatings expand the potential applications of GNRs.

SERMACS 697

Out of the furnace: Synthesis and application of cellulose-derived carbon materials containing metallic nanoparticles

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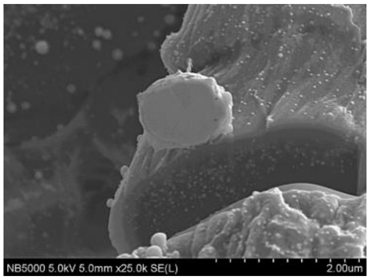
As a viable alternative with respect to carbon-based materials prepared by vapor deposition, the pyrolysis of non-volatile organic precursors has allowed the development of substrates with advantageous properties. Among those substrates, our group has focused on the use of cellulose-derived materials and their applications in various chemical processes. Specifically, the presentation will describe the most critical aspects of the fabrication process, the metallic nanoparticles formed, and the application of the resulting composites as electrodes for oxidation reactions (detection), CO2 reduction reactions, substrates for protein capture, and structures to promote the degradation of chemical warfare agents.



SERMACS 698

Assembling nanoparticles with peptides: From static to dynamic nanoparticle superstructures

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We have developed a peptide-based approach for designing and constructing structurally complex nanoparticle superstructures. In this approach, peptide conjugate molecules bind to inorganic nanoparticles and direct their assembly. This presentation will detail first generation ‘static’ superstructures, including 1-D assemblies such as gold nanoparticle helices and discrete 0-D assemblies such as hollow spherical superstructures. We will discuss the subtle differences between the peptide conjugates which direct the assembly of these morphologically distinct superstructures and suggest design criteria for conjugates that can be used to construct second generation ‘dynamic’ superstructures. As a proof of principle, we design a family of photoresponsive peptide conjugates to control the reversible assembly of gold nanoparticles. The conjugates have different responses to input of UV radiation. We demonstrate that the nanoparticle superstructures constructed from these conjugates can undergo morphological shifts from spheres to 1-D assemblies. These results point toward new methods for dynamically controlling nanoparticle assembly via photo stimulus and new families of structurally complex dynamic nanoparticle superstructures.

SERMACS 699

Rationally-designed iron oxide nanoparticles for biomedical applications

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Material property control and surface engineering are two of the most critically important aspects of nanoparticle design that enables the direct manipulation and control of the chemical and physical properties of nanostructured materials, which in turn lead to innovative applications. In this talk, we will present rationally-designed approach towards the synthesis of iron oxide nanoparticles for specific applications, such as bioimaging, drug screening, and imaging-guided drug delivery. Specific examples include ultrathin iron oxide nanowires as robust positive contrast agents for magnetic resonance imaging (MRI), surface engineering for attaching various molecules onto nanoparticle surfaces for hydrophilicity and desirable functionality. Along with the exploration of the potential of iron oxide nanoparticles as MRI contrast agents, several projects for the use of rationally designed iron oxide nanoparticles will be discussed, including MRI-guided drug delivery, and nanoplatform for drug screening.

SERMACS 700

Designing amphiphilic peptoids for bio-inspired synthesis of hybrid materials

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Inspired by peptide- and protein-controlled formation of hierarchically-structured biominerals (e.g. bones and teeth) in nature, many biomimetic approaches have been developed for the preparation of nanostructured inorganic-organic hybrid materials. These approaches are attractive because they generate complex, functional nanomaterials under mild aqueous synthetic conditions. The unique integration of bio- and inorganic nanomaterials has demonstrated superior performance. Despite the advances in developing biomimetic approaches, the rules of designing sequence-defined molecules that lead to the predictable synthesis of inorganic nanomaterials are unknown. Herein we report the design of sequence-defined peptoids for controlled synthesis of well-defined plasmonic nanomaterials. By engineering peptoid sequences and investigating resulting particle formation mechanisms, we developed a rule of thumb for designing peptoids that predictively enabled the morphological evolution from spherical to nanocoral-shaped metallic nanoparticles. We demonstrate that the individual nanocoral-shaped gold particles exhibit a plasmonic enhancement as high as 10^5 fold. This research significantly advances our ultimate vision of predictive bio-inspired hybrid materials synthesis using sequence-defined synthetic molecules that mimic proteins and peptides.

SERMACS 701

Sustainable fabrication of metal oxide nanomaterials for environmental remediation

***Marc R. Knecht**, knecht@miami.edu. Dept of Chemistry, Univ of Miami, Coral Gables, Florida, United States*

Metal oxide nanoparticles possess unique photocatalytic abilities that could be adapted for environmental remediation applications; however, optimized syntheses for the controlled production of these materials remain elusive. This is especially true for the generation of materials with band gaps in the visible portion of the spectrum, which could prove to be important for solar-based activation. Furthermore, the integration of multiple materials into a single structure is typically required to enhance and optimize the reactivity, where the effect of composite material size, arrangement, composition, etc. remain unclear over the resultant photocatalytic properties of the final structures. Our group has recently advanced a variety of sustainable synthetic approaches for the fabrication of multicomponent nanomaterials composed of metal oxide structures controllably decorated with metallic nanoparticles where the size, shape, arrangement, and composition of the materials can be tuned using facile methods. Many of these approaches employ solution-based chemistries at relatively low temperatures (<70 °C) and in some cases follow biological-inspiration. To generate the composite materials, photo-driven approaches have recently been adapted that employs light to reduce metal ions to generate co-catalysts that optimize their display on the oxide surface. These composite structures demonstrate enhanced photocatalytic reactivity for the degradation of model environmental pollutants under simulated solar light. Furthermore, they are highly reactive in both laboratory water and several environmental media (e.g. water from the Atlantic Ocean), demonstrating their possible use as sustainable catalysts for environmental remediation.

SERMACS 702

Nanotechnology enables hot gold nanorods to kill cancer cells and to stop alive sick cells from migrating to other places in the body

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Cancer kills many people after several years of suffering and after using a great deal of different unsuccessful treatments, like surgery, chemical and/or radiation treatments. The field of Nanotechnology showed us how different materials acquire so many different properties when their size is reduced to the nanometer scale. Gold nanoparticles having rod shape of nanometer size and a length: width ratio of 3:1 can absorb near infrared light (to which our body is transparent) and convert it into heat. If solution containing gold nanorods is injected into a cancer lump and exposed to near infrared light, the hot solution (resulting from the gold nanorods upon absorbing the near infra-red light) melts the cancer cells leading to their death. This was demonstrated by our group in the photo-thermal destruction and destroying cancer cells in solution and in cancer lumps in small and large animals. Normally some of the cancer cells that do not die are able to migrate to other parts of the body away from the location of their initial formation spot until they are located in a sensitive part of the body that leads to the cancer patient death. Thus, most of the cancer patients die from cancer after the cancer cells migrate by a process called metastasis to a more sensitive part of the body. Very recently, however, we discovered that in our photo-thermal treatment, while treating cancer cells in the first cancer location with hot gold nano-rods, the cancer cell legs and arms and the motion proteins are photo-thermally destroyed. This makes it difficult for the cancer cells to migrate to new more important functional locations in the body. This treatment is thus effective in stopping cancer cell migration through the patient body and increases the success rate of the patient recovery.

SERMACS 703

Electrostatic complementarity, a powerful tool for drug design: Optimizing binding and selectivity of protein-ligand complexes

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Electrostatic interactions between small molecules and their respective receptors are essential for molecular recognition and key contributors to the binding free energy. Assessing the electrostatic match of protein-ligand complexes provides important insights into why ligands bind and modifications to improve binding. Ideally, ligand and protein electrostatic potentials at the protein-ligand interaction interface should maximize their complementarity while minimizing desolvation penalties. In this presentation, we discuss a fast and efficient tool to calculate and visualize the electrostatic complementarity (EC) of protein-ligand complexes. Using data from several benchmark examples compiled from mainly electrostatically driven structure-activity relationships, including the protein-protein interaction target, XIAP and the GPCR target, mGLU5, we demonstrate that the EC method can visualize, rationalize, and predict electrostatically driven ligand affinity changes, aid selection of ligand protonation states, and assist with predicting compound selectivity. The methodology presented here for analysis of electrostatic complementarity is a powerful and versatile tool for drug design.

SERMACS 704

Structural selection of immunomodulatory HLA binding small molecules

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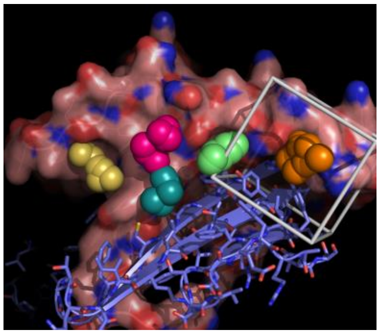
Human Leukocyte Antigen (HLA) class II molecules are strongly associated with many autoimmune disorders. In type 1 diabetes, the HLA-DQ8 molecule is common, confers significant disease risk and is involved in disease pathogenesis. We hypothesized blocking DQ8 antigen presentation would provide therapeutic benefit by preventing recognition of self-peptides by pathogenic T-cells. We used the crystal structure of DQ8 to select drug-like small molecules predicted to bind structural pockets in the MHC antigen-binding cleft. A limited number of the predicted compounds inhibited DQ8 antigen presentation in vitro with one compound preventing insulin autoantibody production and delaying diabetes onset in an animal model of spontaneous autoimmune diabetes. An existing drug of similar structure, methyldopa, specifically blocked DQ8 in recent-onset patients with type 1 diabetes along with reducing inflammatory T-cell responses toward insulin, highlighting the relevance of blocking disease-specific MHC class II antigen presentation to treat autoimmunity.



Targeting specific structural pockets in the antigen binding cleft of HLA molecules associated with disease. Four structural pockets in the antigen binding cleft of HLA-DQ8 are shown as spheres. Large libraries of drug-like compounds were screened by molecular docking, tested in vitro and in vivo, to identify compounds active in modulating autoimmune diabetes.

SERMACS 705

Allosteric modulation of the NMDA receptor: Identifying and exploring novel binding pockets

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The determination of the bioactive binding complex between a protein and ligand is critical for a successful structural-based drug discovery project. High quality protein-ligand complexes can routinely be determined for a range of proteins using protein crystallography and NMR techniques; however, for a large set of proteins, resolving high quality complexes remain extremely challenging. Various modeling techniques have been developed to help determine the bioactive protein-ligand complex inthe absence of a high-quality structure, including docking, induced-fit docking, molecular dynamics, and metadynamics simulations. These methods have a high degree of uncertainty associated with their predictions and could benefit from additional techniques and methods to provide more certainty. We have implemented a methodology that combines the use of phase space sampling, the SAR of a series, and NMR-derived solution conformers to identity the bioactive protein-ligand complex. As a test case, we used a ligand-gated, cation-selective channel, *N*-methyl-d-aspartate receptor (NMDAR), which mediates a slow component of excitatory synaptic transmission. The NMDARs are large tetrameric ion channels consisting of in excess of 3,200 amino acids that can be modulated allosterically at various sites on the receptor in either a positive or negative fashion. Even though numerous crystal and electron microscopy structures have been published for NMDARs, some of the allosteric binding pockets still remain poorly resolved.We use a unique combination of molecular biology, modelling, and NMR-based methods to determine the bioactive binding pose of a pyrrolidinone series to the GluN1/GluN2C di-heteromeric structure.

SERMACS 706

Identification of allosteric exosites on the cannabinoid CB1 receptor using grand canonical Monte Carlo simulated annealing and validation via mutation and SAR

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The cannabinoid CB1 receptor is a Class A G protein-coupled receptor (GPCR) that shares a common architecture with other GPCRs, consisting of seven transmembrane alpha helices (TMHs) connected by intervening intracellular and extracellular loops, an N-terminus outside the cell and C-terminus inside the cell that begins with a short helix (Hx8) that is parallel to the membrane. The TMHs are arranged to form a closed bundle, with individual helices differing in tilt angles and degree of exposure to lipid. Due to this

architecture, distinctive crevices exist on the lipid face of all Class A GPCRs. In the past several years, we have identified several exosites on CB1 that can serve as allosteric modulator sites with surprisingly diverse pharmacological effects. To identify each site, we used the Grand Canonical Monte Carlo Simulated Annealing technique, MMC. [1] This technique has permitted the identification of the binding site of pregnenolone, a CB1 biased negative allosteric modulator.[2] Very recently, we used the technique to identify the sites at which the R stereoisomer of GAT211, GAT229, acts as a CB1 positive allosteric modulator, while the S stereoisomer of GAT211, [3] GAT228, acts as a partial allosteric agonist. In each case, mutation or SAR studies were used to validate the sites. [Support: NIH R01 DA03934] 1. Clark, M et al. Grand canonical Monte Carlo simulation of ligand-protein binding. *J Chem Inf Model* **2006**, *46(1)*, 231-42. 2. Vallee, M. et al. Pregnenolone can protect the brain from cannabis intoxication. *Science* **2014**, *343* (6166), 94-8. 3. Laprairie, R.B. et al., Enantiospecific Allosteric Modulation of Cannabinoid 1 Receptor. *ACS Chemical Neuroscience* **2017**, *8(6)*, 1188-1203.

SERMACS 707

Structure-based drug design: When 3D-docking meets machine learning and dynamic protein-ligand interactions

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Structure-based approaches are quickly evolving from classical 3D docking to multi-step, ensemble protocols involving flexible docking, machine learning and molecular dynamics altogether. The overall goal is to characterize, model, understand, and optimize the dynamic protein-ligand interactions with the target(s) of interest for a given molecular series. As a result, more potent and selective candidates can be virtually designed and prioritized. First, I will present our recent discovery of experimentally-confirmed GalU inhibitors for Listeria using molecular docking and a virtual screening protocol. As these new compounds can attenuate the virulence of Listeria, they could represent alternatives to antibiotics and interesting avenue to treat drug-resistant bacteria. State-of-the-art 3D docking will also be illustrated with the discovery of new Ara h2 binders for combatting peanut allergens. Second, I will describe the Quantitative Structure-Activity Relationships (QSAR) using modern machine learning techniques and chemical descriptors computed for every timestep of molecular dynamics trajectories of protein-inhibitor complexes. We applied this method to a set of 83 ERK2 kinase inhibitors as well as 925 Bcr-Abl tyrosine-kinase inhibitors being analogues of imatinib (Gleevec). The concept of dynamic protein-ligand interactions for ligands' selectivity will also be illustrated with our recent study of WNK inhibitors. Third, I will show how molecular docking can help us predict and better understand adverse drug reactions (ADR). Human leukocyte antigen (HLA) surface proteins are directly involved in idiosyncratic adverse drug reactions. I will present a structure-based analysis of the common HLA-B*57:01 variant known to be responsible for several HLA-linked ADRs. At last, the new pan-HLA virtual predictor will be introduced for the first time.

SERMACS 708

Integrating computational and experimental approaches for neglected disease drug discovery

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Collaborations Pharmaceuticals, Inc. is focused on developing treatments for rare and neglected diseases with many academic collaborators and we have leveraged a broad, collective expertise to identify treatments for parasites (T. Cruzi), bacteria (M. tuberculosis), and viruses (Ebola, HIV etc), progressing to *in vivo* models. Reverse transcriptase (RT) inhibitors are part of the most common therapies for the human immunodeficiency virus (HIV) but are susceptible to drug resistant strains of HIV, and hence alternatives are needed. In addition, there is a need to develop drugs that overcome HIV associated neurological disorders (HAND) that result in problems with memory or severe dementia-like symptoms. We are using a combination of medicinal chemistry, computational drug discovery, *in vitro* assessment against HIV and assessment of BBB entry, absorption, distribution, metabolism and excretion (ADME) properties to develop new RT inhibitors. Chemical enumeration using Sigma-Aldrich fragments was used to create a virtual library and these compounds were assessed via HIV reverse transcriptase docking studies and machine learning models to predict activity. Based on the consensus of these prediction models, 60 compounds were made and experimentally validated, and these data were used to feed back into this pipeline. We will also describe using the NIAID ChemDB HIV, Opportunistic Infection and Tuberculosis Therapeutics Database for machine learning studies which may have utility for virtual screening against HIV targets. Additional current projects which will be described include our efforts to find inhibitors of Mycobacterium tuberculosis (Mtb) targeting KasA. Tuberculosis (TB) or RNA polymerase which have also involved computational approaches.

SERMACS 709

Effective way to apply AI to the design of new drug lead compounds

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Artificial Intelligence can greatly benefit the drug discovery field by lowering the high failure rate, high cost, and finding novel intellectual property. However, the hype surrounding the use of Machine Learning (ML) and Artificial Intelligence (AI) can be found in almost every field today. When AI/ML is applied to drug design, many problems hinder progress. An exciting option is the use of Augmented Intelligence, which is the application of AI methods (such as big data and ML to enhance available information), computational chemistry, and other non-AI algorithms. Augmented Intelligences overcomes several problems encountered in common applications of AI & ML in drug discovery, as we will exemplify here.

SERMACS 710

Establishing a career mentoring network to support women in chemistry

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The chemistry workforce, like a majority of scientific fields, is largely dominated by men, especially at the senior levels. The number of women pursing degrees in chemistry is increasing, however, compared to their male counterparts, their opportunities for promotion are fewer. Furthermore, women are more likely to leave chemistry-based careers. Recent data suggest that the gender gap is closing, however parity remains decades away. This gender disparity is thought to be due to a number of complicated issues including, but not limited to, family obligations, workplace inequality, mental well-being, and others. One way to support, foster inclusiveness, and increase retention of women in chemistry is through the use of career mentoring networks. In this session, we will discuss conventional and virtual ways to build a mentoring support network in order to encourage career retention and advancement, as well as address the current challenges women experience in chemistry professions.

SERMACS 711

Influential and courageous mentorship in STEM

Karelle S. Aiken, *kaiken@georgiasouthern.edu. Chemistry and Biochemistry, Georgia Southern University, Statesboro, Georgia, United States*

My persistence in the chemical field has been fueled by many positive influences. There are many who have provided courageous mentorship including those who were brave enough to do the hard work of trying understand the world as I see it even though they were from very different backgrounds. In doing so, they engaged in thought-provoking conversations and experiences so that they could provide guidance that I, as a young person trying to succeed in science, did not even know I needed. Their actions were transformative and even today, many years since obtaining the Ph.D. degree, the exposure they provided still informs my decisions. This talk will cover key actions taken by influential and courageous mentors in STEM who encourage persistence.

SERMACS 712

Non-traditional careers and mentorship

April Weisbruch, *Aweisbruch@sheppardmullin.com. Sheppard, Mullin, Richter & Hampton LLP, Washington, District of Columbia, United States*

(already submitted)

SERMACS 713

Mind the gap: Underrepresentation of women in chemistry and the impact of networking and mentorship in a woman’s career

Sharon K. Hamilton, *sharon.k.hamilton@gmail.com. Chemistry and Physics, Ouachita Baptist University, Arkadelphia, Arkansas, United States*

According to the National Center for Science and Engineering Statistics, women currently represent almost half of the Chemistry undergraduate degrees awarded in the United States. However, in 2016, females only constituted 41 percent of all chemists employed at the bachelor’s level. Likewise, approximately 36 percent of the 2006 Chemistry doctorates were awarded to women but, as of 2016, only 19 percent of all employed Chemistry Ph.D.’s were women. Why is there such a discrepancy between female chemists earning degrees vs. female chemists using these degrees in the workplace? One cause could be a lack of individual support networks amongst women chemists including formal or informal mentors. A good network provides opportunities to learn about possibilities for advancement as well as expectations and nuances of the workplace. Mentoring has been identified as an important factor that impacts faculty retention and tenure rates. Without mentors and role-models, it can be difficult for some women to feel they “belong” in specific careers. In this presentation, I will highlight the role my support network has played in my education and career thus far and how women chemists and engineers played a significant role in that network.

SERMACS 714

Supporting female graduate students in STEM: Role of doctoral career training programs

Cora E. MacBeth, *cmacbet@emory.edu. Department of Chemistry, Atlanta, Georgia, United States*

Female students pursuing graduate degrees in STEM disciplines face a number of challenges. Implicit bias and exclusive workplace environmental factors can negatively impact a student's graduate education. These issues can also influence long term-career choices and job search strategies. This presentation will explore the role that PhD career training programs play in equipping students with strategies and resources to prepare for a broad job market (non-academic). Programs designed to specifically support the needs of female graduate students and post docs will also be described.

SERMACS 715

Strategies for dealing with gender bias in STEM fields

Julia L. Brumaghim, *brumagh@clemson.edu. Chemistry, Clemson University, Clemson, South Carolina, United States*

Gender bias in STEM is well-documented and is increasingly a focal point for reports on higher education. Often, these reports cite grim statistics in hopes of raising awareness of this issue, but understanding the negative impact of gender bias (especially combined with racial or other types of bias) without offering tools to mitigate these impacts can be overwhelming and depressing for women. Describing effective strategies to deal with gender bias in STEM is less common, but equally important. This presentation will outline strategies that can be implemented at the personal, departmental, and institutional levels to directly address gender bias in STEM fields.

SERMACS 716

Raising the profile of women in chemistry

Dorea Reeser[1], *D_Reeser@acs.org, Amanda T. Yarnell*[2]. *(1) C&EN, American Chemical Society, Washington, District of Columbia, United States (2) American Chemical Society, Somerville, Massachusetts, United States*

How many amazing women in chemistry do you know? Chemical & Engineering News's Audience Engagement Editor Dorea Reeser will describe how ACS's flagship magazine is raising the profile of women in chemistry and inspiring generations to come. Plus, learn about her atypical career path from an environmental chemistry PhD at the University of Toronto to working with C&EN.

SERMACS 717

Women in chemistry in the United States: From the past to the future

Dabney W. Dixon, *ddixon@gsu.edu. Dept of Chem, Georgia State Univ, Atlanta, Georgia, United States*

The United States is almost at the century and a half mark for women in chemistry, with Ellen Swallow Richards being the first women admitted a scientific school when she started at MIT in 1871. In 1887, Rachel Holloway Lloyd would become the first American woman to earn a doctoral degree in chemistry, graduating from the University of Zurich. A century and a quarter later, in 2015, women earned 1,206 Ph.D. degrees in chemistry in the United States, up 156% from a decade earlier. However, women represent less than 20% of tenured and tenure-track faculty at the top 50 chemistry schools. In addition, the median overall base salaries of men continue to be much higher than those of women. In this presentation, we will look at statistics on the rise of women in chemistry in the United States. We will turn to success stories as a way to encourage the next generation of women. We will look at ways in which various academic institutions have sought to support their female faculty. Finally, chemical genealogies offer a way to create a sense of belonging for our chemistry majors.

SERMACS 718

National science foundation programs that support undergraduate chemistry education

Jennifer E. Lewis[2,1], *jennifer@usf.edu. (1) National Science Foundation, Alexandria, Virginia, United States (2) Department of Chemistry, University of South Florida, Temple Terrace, Florida, United States*

This presentation will provide a brief overview of National Science Foundation (NSF) programs that support projects focused on undergraduate chemistry education research and practice, as well as scholarships for students, emphasizing diversity and inclusion themes. Within NSF's Division of Undergraduate Education, these programs include Improving Undergraduate STEM Education (IUSE) and IUSE for Hispanic-Serving Institutions (IUSE:HSI); Advanced Technological Education (ATE); Scholarships in Science, Technology, Engineering, and Mathematics Education (S-STEM); and the Robert Noyce Teacher Scholarship programs. Additional programs that support undergraduate chemistry education research include the Directorate for Education and Human Resources (EHR) Core Research program, and the NSF-wide Research Experiences for Undergraduates (REU) and Faculty Early Career Development (CAREER) programs.

SERMACS 719

Opportunities as a Florida Georgia Louis Stokes Alliance for Minority Participation (FGLSAMP) fellow

Guizella Rocabado, *grocabado@mail.usf.edu. Chemistry, University of South Florida, Temple Terrace, Florida, United States*

As a Hispanic female scientist, I have found it difficult to go through the leaky academic pipeline unscathed. Opportunities such as participation in the Florida-Georgia Louis Stokes Alliance for Minority Participation (FGLSAMP) Bridge to Doctorate program at the University of South Florida not only affords financial support to continue my doctoral studies, but also provides a strong social network of brilliant scholars in academic, industry and public sectors in which I can rely for extra support. Research shows that Hispanic female students' attitude toward science is low despite of their level of academic performance, which can lead to lower retention rates. I have gone through several periods of doubt about my academic choices; yet, I have been fortunate to have found support and encouragement at every turn. One of the greatest opportunities I have been awarded by the FGLSAMP program, is to be part of the effort to broaden participation and retention of students in STEM fields. These opportunities and support networks have made a strong impact in my life, to which I owe the career path I am currently pursuing.

SERMACS 720

NOGLSTP scholarship funds: Advancing LGBTQ+ students in STEM careers

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The National Organization of Gay and Lesbian Scientists and Technical Professionals (NOGLSTP) empowers lesbian, gay, bisexual, transgender, and queer individuals in science, technology, engineering and mathematics (STEM) by providing education, mentoring, advocacy, professional development, networking, and peer support. NOGLSTP grew out of a grassroots network to organize events and meetings known as the National Organization of Lesbian and Gay Scientists (NOLGS). It was founded in 1983 and incorporated in 1991 as a non-profit educational organization, 501(c)(3). NOGLSTP established its *Out to Innovate*® scholarships for LGBTQ+ students in STEM in 2013 through the generous support of the Motorola Solutions Foundation's Innovative Generation Grant. Now in its 7th year, NOGLSTP awarded $15,000 in merit-based scholarships to two undergraduate and two graduate students in 2019. This presentation will describe the history of these scholarships, application process, selection criteria, and successful awardee profiles.

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SERMACS 721

Joining forces: McNair Scholars Program and National Science Foundation research experiences for undergraduates

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With similar objectives for broadening participation among PhD degree holders, the Georgia Southern (GS) McNair Scholars Program (MSP) and the Chemistry and Biochemistry National Science Foundation Research Experiences for Undergraduates (NSF-REU) Program, CEMITURE, joined forces for the 2019 Summer Research Institute (SRI). The result was a dynamic and extensive network of undergraduate researchers who shared a common goal, the determination to excel in their respective fields. While CEMITURE was focused on Chemistry- and Biochemistry-related disciplines, GS-MSP participants' research spanned a wider range of areas, biology, chemistry, physics, history, sociology, and mathematics. The programs created a framework where both groups of scholars worked side-by-side in professional development workshops and in many cases, McNair and CEMITURE students were members of the same research group. As a result, the scholars had numerous opportunities to interact and they, in tandem with workshop leaders, graduate assistants (GA's) and faculty mentors, actively encouraged and mentored each other in the development of their technical and soft skills. Through their full-time commitment to research during the SRI and working with GA's, the scholars also gained valuable insight into the expectations of graduate programs. Together, CEMITURE and GS-MSP achieved their common goal of promoting student success.

SERMACS 722

Peptide nucleic acids with backbone modifications to control binding and applications

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Peptide Nucleic Acids (PNAs) are synthetic mimics of nucleic acids that have the nucleobases of oligonucleotides attached to a peptidic backbone. PNAs bind to complementary oligonucleotides with the standard Watson-Crick hydrogen bond pairing rules. In many cases, PNA-oligonucleotide duplexes are more stable that the corresponding duplex of two oligonucleotides. Because PNAs are synthetic, they also are completely resistant to degradation by enzymes. Our lab has developed a chemical method to further enhance the stability of PNA-oligonucleotide duplexes by incorporation of cyclopentane rings into the peptidic backbone of regular PNA. The cyclopentane PNAs we study are conformationally preorganized for binding to oligonucleotides and can significantly enhance the stability of PNA-oligonucleotide duplexes. Our lab uses the ehanced stability of cyclopentane PNAs to develop biomedical applications in the area of nucleic acid diagnostics.

SERMACS 723

Smart-responsive nucleic acid nanoparticles designed to modulate immune behavior

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The integration of nanotechnology into modern therapeutics provides additional control of unique physicochemical properties including size, surface charge, hydrophobicity, and the addition of moieties for biomedical applications. The ability to fine-tune these properties subsequently allows for the improved efficacy of therapeutic treatments and has implications for the future of personalized medicine. Nucleic acids, including both DNA and RNA, are natural biopolymers which offer a biocompatible and programmable therapeutic approach. Beyond its traditionally known roles as a carrier and regulator of genetic information, nucleic acids have emerged as a building material for versatile biological drugs, called therapeutic nucleic acids, which can take advantage of cellular pathways for the sensing, targeting, and silencing of various diseases. This talk will highlight how rationally designed nucleic acid nanoparticles can be used to communicate with our immune system and conditionally activate the response in cancer cells.

SERMACS 724

Fluorescence imaging reagents based on RNA aptamers, synthetic polymers and fluorogenic cyanine dyes

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Fluorescent labeling technologies are essential to providing insight into fundamental cellular biology and new diagnostic tools. Our lab works on two different types of labels. The first technology relies on an RNA aptamer that binds to and activates fluorogenic cyanine dyes, giving either blue or red fluorescence, depending on the structure of the dye. The utility of this promiscuous aptamer is demonstrated by experiments in which it is fused to a separate aptamer that recognizes a cell-surface receptor protein, leading to fluorescent labeling. Internalized and cell-surface receptor can be distinguished temporally based on two successive labeling steps in which either blue or red fluorogen is applied to the sample. The second technology involves fluorescent DNA-polymer hybrid materials that exhibit improved brightness compared to conventional labels. Whereas most fluorescent reagents (e.g. antibodies) are labeled with a few dyes, we have developed a hybrid material consisting of a polymeric scaffold from which is grafted double-helical DNA that acts as a host for fluorescent intercalating dyes. The resulting *nanotags* host >1000 dyes with minimal quenching and can be attached to antibodies for use in fluorescence microscopy, flow cytometry and dot blotting applications.

SERMACS 725

Investigating a disulfide linkage in the backbone of peptide nucleic acid

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Peptide nucleic acid (PNA) as well as a host of other non-natural DNA mimics, have been developed and adapted to fulfill roles where endogenous oligomers perform poorly or not at all. Central tenents to all of the mimics are 1) high affinity and selectivity for the target strand, 2) resistance to nucleases and degradation pathways, 3) cellular delivery, 4) low toxicity and binding of proteins, 5) synthetically accessible for large scale production, and 6) clinical relevance. While PNA oligomers satisfy many of these criteria, they lack the ability to cross cell membranes, thus hindering its capacity to act as an antigene or antisense agent. The overall goal of this project is to development a robust and facile means to transport antisense PNA oligomers across cell membranes using a “transporting PNA”. Currently, we have synthesized a new Fmoc-base disulfide monomer and incorporated it into the backbone of a PNA oligomer using standard coupling techniques. Here we report our findings related to duplex stability, cleavage efficiency, and ultimately a proof of concept release assay.

SERMACS 726

Enhanced nucleic acid recognition by small molecule-oligonucleotide conjugates

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DNA and RNA polymers and oligomers can be sequence-specifically recognized by other oligonucleotides. Small molecules on the other hand are much better at shape and sequence recognition of shorter sequences. In this presentation, I will present our recent results in the exploration of covalent complexes of small molecules with oligonucleotides and their potential synergy in enhanced recognition of DNA and RNA. Specific examples will include the use of benzimidazole-oligonucleotide conjugates that can bind AT rich sequences and can be effectively delivered in cells.

SERMACS 727

Examination of RNA-privileged small molecule chemical space and elucidation of important recognition properties

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Small molecules have been proven to be a viable avenue to study disease-driving RNAs; however, the development of RNA-targeted chemical probes has been hindered due in part to a lack of guiding principles for achieving specific RNA:small molecule interactions. To elucidate these guiding principles, our laboratory has analyzed cheminformatic and shape-based descriptors of bioactive RNA-targeted ligands and identified statistically significant trends that support the existence of a privileged chemical space for targeting RNA. Consequently, this work aims to validate the existence and examine the boundaries of RNA-privileged chemical space through rapid evaluation of small molecules against various RNA targets and analysis of physicochemical, structural, and spatial properties that lead to specific recognition. Towards these goals, we have rationally designed and purchased an RNA-focused small molecule library that encompasses the putative RNA-privileged chemical space identified by our laboratory. A fluorescent indicator displacement assay has been set up and validated as a reliable high-throughput screening tool to identify small molecule interactions with four biologically relevant and diverse RNA targets. Current work is focused on screening the library and employing computational methods to analyze small molecule leads as well as distinguishing molecular properties that are important for specific RNA binding. In parallel, we are evaluating specific RNA-binding of a general, drug-like small molecule library that has been extensively screened against protein targets. Binding profiles of focused and general screening libraries will be compared to identify distinct recognition properties of specific RNA-binding small molecules which in turn will serve as input to refine algorithms and apply machine-based learning for the prediction of RNA-targeting ligands. This work will help to define the RNA binding preferences of thousands of small molecules and elucidate the chemical properties and molecular shapes that contribute to specific RNA recognition. Additionally, the screening of small molecules that encompass RNA-privileged chemical space will result in the identification of new RNA-binding scaffolds and leads for targeting therapeutically-relevant RNAs. Altogether, these efforts will further guiding principles for the rational targeting of RNA with small molecules and potentially lead to specific chemical probes for the study of disease-driving RNAs.

SERMACS 728

G-Quadruplexes in both subunits of the human ribosome

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Metazoan ribosomes are nearly twice as large as those of bacteria mainly due to extraordinary rRNA expansion in the form of double-stranded tentacles that link to the solvent-accessible regions of the ribosome and protrude from the ribosomal core. Some of longest tentacles known in nature are found in specific rRNA expansion segments of the human ribosome. These long tentacles are not well resolved in current three-dimensional structures and have been assumed to adopt static Watson-Crick duplex helices. However, we have recently discovered that both the large and small subunits of the human ribosomes contain tentacles capable of forming G-quadruplexes. We have extensively characterized several RNA oligomers derived from the tentacles of the human LSU and SSU rRNAs, as well as the intact LSU and SSU rRNAs, and found they form highly stable G-quadruplexes *in vitro*. Our results indicate that the surface of the human ribosome can form G-quadruplexes through numerous tentacles located in both ribosomal subunits. Our recent findings suggest human ribosomes can also form G-quadruplexes *in vivo*. The surface localization of these regions suggests they associate with proteins and/or cellular factors. In addition to identifying the proteins that bind to these regions we have also discovered that intact human LSU and SSU rRNAs bind heme through its G-quadruplex regions. To our knowledge, ribosomes have not been previously reported to form G-quadruplexes or to bind heme. Because rRNA is the most abundant RNA in cells, these results could indicate that the “G-quadruplexome” is ribosome-centered. The changes in structural conformation might allow metazoan ribosomes to bind to specific proteins/factors under certain cellular conditions, making them direct participants of processes other than protein synthesis.

SERMACS 729

Theranostic microcapsules for imaging and ultrasound-triggered drug delivery

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The ability to track drug carriers in their administered environment in real time and to release the drug in a controlled, minimally invasive manner are hallmarks of an advanced drug delivery system. This talk focuses on ultrasound-sensitive multilayer capsules as efficient contrast-enhanced imaging agents utilizing ultrasound, magnetic resonance imaging (MRI), and positron emission tomography (PET) imaging modalities. These capsules are composed of hydrogen-bonded polymers and capable of delivering biological and synthetic molecules upon low-power (~100 mW/cm^2) diagnostic or high-power (>10 W/cm^2) therapeutic ultrasound irradiation. We will also discuss the capsule efficacy in modulating the redox state that can influence immune responses for prolong circulation in the blood. The ability of this material to conjugate metalloporphyrin to further enhance immunomodulatory potential by dissipation of free radicals will be also presented. Owing to the active contrast, long circulation, customizable size, shape, composition, and precise delivery of high payload concentrations, these materials present a powerful and safe platform for imaging-guided precision drug delivery.

SERMACS 730

Polymer-functionalized optical nanosensors for diagnostics

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Biomolecular sensing technologies facilitate accurate diagnosis and treatment of diseases. Optical nanosensors based on single-walled carbon nanotubes exhibit stable photoluminescence in the tissue-penetrating near-infrared region and electro-optical sensitivity to their molecular environment. The surface chemistry of nanotubes plays a critical role in modulating their interactions with biological systems both *in vitro* and *in vivo*. We designed and synthesized new polymers to functionalize carbon nanotubes and mediate their interactions with biomolecules. These sensor materials are tunable and could be applied to engineer devices such as portable, wearable, and implantable sensors for diagnostics and health monitoring.

SERMACS 731

Electrosynthesis and characterization of isoindigo based copolymers for use as NIR-II imaging agents

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Research has been focused on finding alternative approaches to bioimaging. Most of these attempts have resulted in materials that operate in the near infrared-I (NIR-I) region (700-1000 nm). However, these attempts have yielded materials with wavelengths of radiation exhibiting poor penetration depth and when paired with autofluorescence from tissue in the human body, results in poor image quality. To counteract these issues, studies have begun to create materials that access the NIR-II region, which ranges from 1000-1700 nm. In order to perform this task, strategies have employed the donor-acceptor motif, where compounds allow for the control of the LUMO of an electron deficient acceptor and the HOMO of an electron rich donor. While the modes of synthesis have been mostly relegated to chemical methods and polymerization, the inclusion of electro-synthesis has its advantages. Herein, we have taken the electro-chemical approach for forming conjugated polymers using different monomeric units so that they can be used to form conjugated polymeric nanoparticles (CPNs) as NIR-II imaging agents. We electrochemically synthesize block copolymers consisting of functionalized isoindigo (Iso), terthiophene (T3), and thienothiadiazole (TTD). Analysis of the resulting polymers in both solution and solid state reveal unique electronic properties of the polymers, allowing for absorption and emission of NIR-II radiation. Formulations yield CPNs with sizes ranging from 126 to 278 nm via analysis by dynamic light scattering (DLS) and

microscopy. The CPNs are then subjected to UV-vis and fluorescence studies to ensure that the desired electronic properties have been retained. Results indicate potential applications as efficient NIR-II imaging agents.

SERMACS 732

Polymer modified magnetic colloids: Surface binding, colloidal stability, and added functionality

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Over the past decade there has been extended interest in the use of magnetic nanoparticles for both imaging and therapeutic applications in medicine, as well as assessing the environmental impact of metal oxides. Key to the success of these opportunities is the preparation of well-characterized materials with tailored magnetic, thermal, colloidal, and bio-interaction properties. To address these issues, we have focused our efforts on three distinct areas in this problem: 1.) Surface-ligand interfaces, 2.) Controlling interparticle interactions through polymeric brushes, and 3.) Specialized surface moieties for additional imaging, therapy, and targeting. This talk will describe radioanalytical techniques to quantify the surface functionality, calculations of interparticle potential based on molecular weight considerations, and the addition of functional groups for therapeutic applications. These includes the creation of alternatives for antibiotics, multimodal MRI contrast agents, drug delivery for the treatment of hyperplasia, and detection of markers for Alzheimer’s and diabetes.

SERMACS 733

Coating orthopedic implants with a polymer based pH sensitive layer to noninvasively image pH changes on the implant surface using X-ray excited luminescence chemical imaging

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We are developing a polymer based pH sensor to noninvasively image pH changes on the surface of orthopedic devices using X-ray Excited Luminescence Chemical Imaging (XELCI) to detect implant-associated infection. Implant-associated infection is a leading cause of fixation failures and is often challenging to detect due to lack of symptoms and specific tests to detect localized infection. Low pH is believed to be associated with infection as bacteria and inflammatory responses cause a pH drop in the affected area. To detect the pH changes that occur at the nidus of infection, we cover the orthopedic implant with a hydrogel based pH sensitive coating consisting of scintillator particles embedded in polydimethylsiloxane (PDMS) followed by a layer of biocompatible hydrogel containing a pH dye. The scintillators act as an in situ light source emitting 620 and 700 nm light intensities upon irradiation by x-rays. The pH doped polymer layer differentially absorbs the scintillator emission depending on the pH with higher absorption values during neutral and basic conditions and less absorption under acidic pH. These changes in pH are noninvasively imaged using X-ray Excited Luminescence Chemical Imaging through the tissue. We evaluated the pH sensor response in vitro through chicken tissue, ex vivo through human cadaveric tissue and in vivo through live rabbit tissue. We characterized the effect of tissue thickness on signal intensity at a series of pH and constructed a calibration curve. In future, we plan to study the pH changes on the device surface during infection and antibiotic treatment in animal models.

SERMACS 734

Development of a high-temperature multi-composite reactor: Monodisperse nanoscintillators for noninvasive optogenetics

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Optogenetics is a technique that combines optics and biology to control living tissues via light-sensitive proteins (opsins) and radiative energy. Traditionally, an optical fiber waveguide is used to introduce light to the targeted tissues, typically neurons; consequently, this has negative side effects such as localized heating and surgical scars. Here a noninvasive technique is proposed utilizing a high penetrating x-ray excitation source and sub 100 nm scintillators to deliver radiative energy to opsins. Scintillators are a class of materials that can experience an extreme down conversion of electrons from a high energy excitation source, such as x-rays. The ideal scintillators utilized in radiation detection have a high atomic number, high density, inert, and have discrete emission behaviors suitable for its end use. Typical non-toxic and high light output scintillators (e.g. Lu_2SiO_5:Ce) that can be applied in the biomedical field are silicate materials which are synthesized at temperatures above 1000°C; as such the synthesis of sub 100 nm scintillators is a challenge not fully explored yet due to the difficulties from sintering. Two polymorphs of the $Re_2Si_2O_7$ (Re = Y^{3+} or Lu^{3+}) were crystallized at the nanoscale above 1000°C while remaining monodisperse particulates. A core bishell architecture was used as a size and chemical template composed of a SiO_2 core and a Re_2O_3 shell through sol-gel and seed-mediated growth, followed by a secondary poly(divinylbenzene) shell through free radical polymerization on the inorganic core-shell particulates. At temperatures above 1000°C, the organic coating was able to carbonize to amorphous carbon at conventional sintering temperatures preventing particle-particle contact, while the inorganic particulate recrystallizes to a new phase. A series of single, co-, and tri- doped systems (Ce^{3+}, Tb^{3+}, and Eu^{3+}) were incorporated into the particulates with emission behavior that span the entire visible spectrum and can couple to different opsins. The sacrificial amorphous carbon process demonstrated control over structure-luminescent properties that can potentially be used for non-invasive optogenetics. The two atypical fields of organic and inorganic chemistry provided complementary abilities that were instrumental into the development of the high-temperature nanoreactor and has the potential to be expanded upon to different crystals.

SERMACS 735

Discrimination of seawater contaminants using conjugated polymers

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This project outlines the design of a four-year collaborative enterprise to design new sensing technologies for deployment in the marine environment for detection of pollutants (phosphates, polycyclic aromatic hydrocarbons (PAHs), and heavy metals). New modular receptor-analyte interactions capable of transducing an analyte-binding event into a useable signal were designed and evaluated. The reported approaches span a wide range of disciplines including synthetic chemistry, polymer science, analytical chemistry, and statistics. Modular synthetic approaches, thiol-ene click chemistry, linear discriminant analysis, and the inner filter effect were leveraged to detect marine pollutants using conjugated polymer-based sensors. Inorganic phosphate was detected at parts-per-billion concentrations (+/- 6 nM) in seawater conditions, a mixture of 16 PAHs was detected and discriminated, and a complex mixture of heavy metals was detected and discriminated in aqueous solution at parts-per-billion concentrations. The comprehensive set of approaches outlined should offer valuable insight toward future sensing technologies utilizing conjugated polymers.

SERMACS 736

New strategies for the C–H functionalization of amines

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This lecture will cover our recent efforts in the development of reaction cascades for the rapid buildup of molecular complexity via the α- and β-C–H bond functionalization of amines. Mechanistically distinct approaches will be discussed.

SERMACS 737

Search for narrow-spectrum antibacterials & ways to access fluorinated molecules

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Drug-resistant infections present a global health risk that needs urgent scientific interventions. In the United States alone, two million people become infected with antibiotic-resistant bacteria leading to 23,000 deaths each year. Since the discovery of penicillin, bacterial populations have naturally evolved to confer resistance. In the modern era, the misuse of antimicrobials spurred the growth and spread of resistance. Unfortunately, our arsenal of new drugs is insufficient to combat the multi-drug resistant and extreme-drug resistance bacteria. Narrow-spectrum antibacterials need to be developed to overcome the growing challenge of antibacterial resistance. Targeting MraY (phosphor-MurNAc-pentapeptide translocase or translocase I), a membrane-bound protein that plays a vital role in the peptidoglycan biosynthesis, by using a structure-based drug discovery strategy could be an effective approach towards narrow-spectrum antibacterials. This presentation will outline our ongoing structure-based efforts using (a) hybridization of pharmacophores from MraY and *Mycobacterium tuberculosis* (Mtb) inhibitors and (b) target based virtual screening protocols to identify new $\mathrm{MraY_{Mtb}}$ inhibitors and will establish a new strategy for tuberculosis therapy. Fluorinated compounds make up ~25% of all pharmaceuticals and 30% of all agrochemicals with anti-depressant fluoxetine (Prozac), cholesterol-lowering Lipitor, and antibacterial ciprofloxacin being the top-selling fluorinated pharmaceuticals. Despite the recent advancements in organofluorine chemistry, there are limited methods to synthesize fluorinated heterocycles directly. Fluorinated building blocks with F directly attached to the sp2 or sp centers will be of paramount interest to meet the increasing demands for fluorine-containing small molecules in academia and industry. This presentation will highlight our ongoing efforts to generate and use C_{sp}—F and C_{sp2}—F containing building blocks for various chemical transformations and their applications in biomedical research.

SERMACS 738

Azetidine functionalization by transition metal and electrochemical methods

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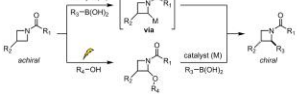
Azetidines are 4-membered, nitrogen-containing rings that are important pharmacophores and currently underutilized intermediates in synthesis. Azetidines appear in several natural products with biological activity ranging from pain relief to cancer cell cytotoxicity. Recent applications in the pharmaceutical industry have focused on the incorporation of azetidines as bioisosteres, since they are generally stable despite strained bond angles that provide altered physiological properties. Our group is investigating novel methods to expand the availability of azetidines as single enantiomers to the chemical industry. Studies on the nucleophilic ring opening of azetidines will also be discussed.



SERMACS 739

Synthetic methodologies inspired by complex dimeric natural products

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Complex secondary metabolites isolated from natural sources (i.e. natural products) provide a wealth of diverse chemical space which often serve as the basis for drug development. Furthermore, the synthesis of these compounds serves to test current reaction methodologies in complex environments as well as provide inspiration for developing new reactions. An active goal of the Hill group is to develop new reactions to access complex dimeric natural products. To this end, we have developed a new adiponitrile lynchpin reagent, (i.e. bis(1-chloroacrylonitirile)), and have shown that this compound reacts with a variety of nucleophiles such as secondary amines and malonate derivatives affording value-added products which could be used as the starting point for accessing dimeric natural products from truncated monomeric units.

SERMACS 740

Photoredox catalysis in the undergraduate research laboratory: Synthesis, characterization, and application of carbazoles as single-electron reductants

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Photoredox catalysis has gained considerable attention in recent years due to the ability to perform selective single-electron transformations under mild conditions. While the field has been predominantly focused on the use of transition metal photosensitizers, the use of organic molecules as photocatalysts has been gaining interest due to being metal-free alternatives and exhibiting unique reactivities. Carbazoles are nitrogen-containing heteroarenes with desirable characteristics as single-electron reductants. However, the current carbazoles used as photosensitizers require low wavelengths of light for excitation and some derivatives exhibit irreversible oxidation. This presentation will discuss the design, synthesis, and characterization of various carbazole derivatives that address these issues and their current applications as photocatalysts in the dehalogenation of aryl halides and direct C–H arylation of five-membered heteroarenes. In addition, the presentation will also discuss how this project has been tailored towards performing research at a primarily undergraduate institution and how the undergraduates immersed in the research program are exposed to multiple techniques that tie together fields of electrochemistry and photochemistry with organic chemistry.

SERMACS 741

Make allylation great again

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Homoallylic alcohols are highly valuable intermediates in organic synthesis, particularly in the syntheses of polyketide natural products. Traditionally, homoallylic alcohols are prepared through the addition of an allyl or crotylmetal reagent to carbonyl compounds. However, the vast majority of prior studies on allylation chemistry only produce homoallylic alcohols with a terminal olefin group, which often requires a multiple-step manipulation to enable subsequent C-C bond formation reactions. Therefore, the development of novel methods that allow the access to homoallylic alcohols with a functionalized olefin group remains an important goal in organic synthesis. Toward this end, we developed several 1,1-bifunctional allylmetal reagents to address this challenge. Synthetic applications in the context of complex molecule synthesis will also be discussed.

SERMACS 742

Semisynthesis: Unexpected pathway to novel methodology development

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Our group has collaborated with natural products chemists to directly modify natural products in an effort to identify non-natural medicinal leads. During our efforts to fluorinate secondary metabolites, we discovered a novel palladium-catalyzed method to dehydrate primary amides and generate nitriles. This process proceeds under very mild reaction conditions and is compatible with many funcitonal groups. The utility of the dehydration was exemplified by dehydration of different glutamine residues in a peptaibol to obtain interesting structure-activity relationships.

SERMACS 743

Quantification of 11 amino acids in human plasma using LC-MS/MS: Applications in the prediction of prediabetes

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Although prediabetes and type 2 diabetes affect many individuals worldwide, current diagnostic tests may only detect diabetes after irreversible negative effects have taken root. Previous results suggest that free amino acids circulating in plasma, such as the branched chain and aromatic amino acids, serve as promising alternative biomarkers, as they have been shown to be in a state of imbalance in prediabetic individuals. Therefore, this work focuses on developing a plasma based free amino acid indicator with low limits of detection to robustly predict trends toward a prediabetic state earlier than current methods. Using hydrophilic interaction liquid chromatography-tandem mass spectrometry (HILIC-MS/MS), a novel method was developed for the separation and quantitation of the amino acids alanine, L-glutamic acid, glycine, L-isoleucine, L-leucine, L-methionine, L-phenylalanine, L-threonine, L-tryptophan, L-tyrosine, and L-valine. Samples were extracted by protein precipitation using methanol and analyzed underivatized. This eliminates the need for lengthy sample preparation steps common in amino acid analysis that can affect reproducibility. In addition, separation of the isobars (same mass species) L-leucine and L-isoleucine was achieved. Included in this study are method validation experiments to assess linearity, carryover, precision and accuracy, autosampler stability, freeze/thaw stability, recovery, and matrix effect, as recommended by the Food and Drug Administration's (FDA) 2018 Bioanalytical Method Validation Guidelines and the Clinical and Laboratory Standards Institute's (CLSI) C62-A: Guidelines for Liquid Chromatography-Mass Spectrometry Methods. Upon validation, amino acids will be quantitated in samples from patients without diabetes, with well-controlled diabetes, or with uncontrolled diabetes. Amino acid profiles will be assessed to determine which specific amino acids correlate with diabetes state and could be predictive of prediabetes. In addition to the application of earlier assessment of prediabetes, this method also has utility in other areas requiring amino acid quantitation due to its minimal sample handling steps, reproducible separation, and nonderivatized analysis.

SERMACS 744

Enhanced protonation upon addition of chromium(III) during matrix-assisted laser desorption ionization mass spectrometry

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Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI/TOF MS) provides high-throughput analysis for proteomic research. In automated processes (such as MALDI-TOF MS), the correct identification of peptides greatly depends on the ability to efficiently isolate precursor ions and interpret product ions formed from tandem mass spectrometry techniques. In cases like this, high signal-to-noise (S/N) ratios are important to reduce the likelihood of false-positive identification. In previous reports, our group has shown that addition of trivalent chromium, Cr(III), can enhance the protonation of peptides by electrospray ionization (ESI) and increase the charge state formed. The goals of this work are to study the ability of Cr(III) to enhance protonate peptides in MALDI/TOF MS and to determine the best conditions for enhanced protonation with Cr(III). As an example of the peptides studied, bradykinin(1-7), with sequence RPPGFSP, has a molecular mass of 756.9 Da and produces only $[M + H]^+$ in MALDI. Preliminary data has shown that Cr(III) has the ability to enhance formation of the singly charged ion. With DHB matrix and $Cr(NO_3)_3$ additive, a 4 times (4x) increase in absolute signal intensity of $[M + H]^+$ is observed for bradykinin(1-7). The method in which the sample is deposited on the target plate was studied using two methods: the dried-droplet and the thin-layer method. In the dried-droplet method, the peptide, matrix, and Cr(III) were first mixed in solution and then deposited onto the target plate. The thin-layer method involves layering the different components and allowing the different layers to dry in-between. All variations in the layering of peptide, Cr(III), and matrix were studied. Enhanced protonation with Cr(III) using ESI has shown that the presence of a carboxylic acid group is important to the mechanism. The common matrices 2,5-dihydroxybenzoic acid (DHB) and a-cyano-4-hydroxycinnamic acid (CHCA) both contain a carboxylic acid functional group. In order to determine whether the carboxylic acid group present in the matrix can influence enhanced protonation in MALDI, the matrix 1,5-diaminonaphtalene (DAN) which does not contain a carboxylic acid functional group, will be studied. Other conditions left to be studied include different neutral, basic, and acidic peptides (i.e., amino acid composition of the peptide), matrices, target plates, and the matrix to sample ratio.

SERMACS 745

Glucuronidation of Bisphenol A by UGT2B15 and possible inhibition by over-the-counter drugs

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Bisphenol A (2,2-bis(4-hydroxyphenyl)propane, or BPA), an industrial compound used in the production of many plastics causing near ubiquitous exposure, acts as a xenoestrogen in humans. Metabolism of BPA occurs primarily through glucuronidation, catalyzed by UDP-glucuronosyltransferase (UGT) enzymes. UGT isoenzyme 2B15 acts as the predominant enzyme for this process in both the liver and intestines, producing BPA-glucuronide (BPA-G). BPA has a longer half-life in the body if UGT enzymes are inhibited, which may produce toxic effects such as diabetes, obesity, and birth defects. This study examined BPA glucuronidation by UGT2B15. BPA and BPA-G were quantified using liquid chromatography-mass spectrometry. Enzyme assays were performed with an assay mixture containing BPA, recombinant UGT2B15, Tris-HCl Buffer (pH=7.5), MgCl2, alamethicin, and a UDPGA cofactor. Reaction products were examined over time to determine the incubation time using LC-MS/MS methods to measure glucuronidation activity. A concentration-dependent enzyme assay was performed using UGT2B15. Future enzyme assays will be performed to determine the kinetic parameters of BPA glucuronidation by UGT2B15 and examine the possible inhibitory effect of over-the-counter drugs on BPA glucuronidation.

SERMACS 746

Enhanced protonation due to chromium(III) during liquid chromatography–electrospray ionization mass spectrometry

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Trivalent chromium, Cr(III), has previously been shown to enhance the protonation of peptides and other biological molecules during electrospray ionization (ESI). Enhanced protonation includes an observed increase in ion intensity and often charge state. Liquid chromatography (LC) is a commonly used separation technique that is frequently coupled with mass spectrometry to enable mixtures to be separated and individual species in the sample detected and identified. All previous studies with Cr(III) have been conducted using direct infusion to ESI. The present study focuses on the use of Cr(III) to enhance protonation in the context of LC-MS. Cr(III) has been added to the LC mobile phase for the analysis of model peptides. All experiments were performed on an Aglient 1200 Series LC and a Bruker HCTultra QIT PTM Discovery System mass spectrometer. Model peptides investigated include A7 and A2IA4 which are neutral peptides with one basic site at the N-terminus. The mobile phase consists of acetonitrile and water. The samples were subjected to LC-ESI MS and the resulting ions were observed with no additive, 0.1% formic acid, 0.1% trifluoroacetic acid, 0.1% acetic acid, and Cr(III) salts present at a 10:1 metal to peptide molar ratio. The peptides studied produce $[M + H]^+$ via ESI without Cr(III) present in solution. The peptides are being studied individually under isocratic conditions. The investigation will proceed to a mixture that will be separated under gradient elution. When Cr(III) is absent, no $[M + 2H]^{2+}$ is observed. Both peptides produce $[M + 2H]^{2+}$ when Cr(III) is added to the mobile phase, but was absent in the presence of the weak acid additives. The 2+/1+ ratio is 0.1 when Cr(III) is present. However, suppression of the absolute ion signal is observed when Cr(III) is added to the mobile phase. Also under investigation is the method of delivering Cr(III); for example, the addition of Cr(III) after chromatographic elution.

SERMACS 747

Temporal monitoring of MVOCs from *Macrophomina phaseolina* using HS-SPME GC/MS

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Microbial volatile compounds (MVOCs) reveal specific metabolomics pathways of microbes and, hence can be used for species identification. The focus of our study was the fungi-*Macrophomina phaseolina* which belongs to botryosphaeriaceae. There are two different morphological types belonging to this fungus, flat and fluffy. The phenotype-flat is considered as more pathogenic than the fluffy. Early identification of this fungi is very important because it can cause a huge economic impact on commercial crops by causing charcoal rot disease. In this study, MVOCs were temporarily monitored using PDMS/Car fibers for the head space solid phase micro extraction (HS-SPME) followed by gas chromatography mass spectrometry. The evolved chemicals are significantly different with different fungal growth stages throughout the studied time period. The main object of the temporal study is to identify the greatest MVOC emission fungal growth stage and then optimize the biomarker discovery pathway of this fungi. Multivariate statistics can be used to identify MVOCs which belong to different chemical classes, such as aldehydes, ketones, esters, terpenes, organic acids, and hydrocarbons. The relative levels of the above chemical classes are related to fungal physiochemistry and pathogenicity, hence the specific MVOC profile will provide insight into the pathogenicity of *Macrophomina Phaseolina*.

SERMACS 748

Determination of pesticide residues in vegetable samples

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Pesticides are described as a substance used to kill, repel, or control any plant or animal life considered to be a pest. Pesticides used in the agricultural industry offer many immediate benefits such as increasing crop production and controlling insect infestations. However, the long-term damage to human health due to constant exposure to volatile organic compounds from pesticide residues in foods is still unknown. Many people are unaware of what they are consuming when they pick up a piece of produce from the store. This presentation describes the experimental design used to isolate and identify the volatile organic compounds in various vegatables using gas chromatography/mass spectroscopy (GC/MS) coupled with a purge-n-trap concentrator. The procedures, preliminary results and future work will be highlighted in the presentation.

SERMACS 749

Synthesis of immune modulating benzofuran-2-carboxylic acid derivatives

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The National Aeronautics and Space Administration (NASA) has worked hard to maintain the well-being of astronauts during planned long-term space flights. Studies have shown that long term exposure to microgravity and radiation during space flights can compromise the immune system with debilitating effects including cancer. A significant imbalance in the body’s immuno-modulatory system, affecting cells such as CD4+ (helper) T cells, B cells, monocytes/macrophages/dendritic cells, NK cells, hematopoietic stem cells and cytokine networks can occur. In this research, 3-methyl-benzofuran-2-carboxamide were synthesized in order to augment the immune system, restore immune cell function in astronauts involved in long-term space flight missions and inhibit the initiation and development of cancer. Our initial results obtained after two-weeks at the International Space Station (ISS) indicate that carboxamide such as, 5,6-Dimethoxy-3-methylbenzofuran-2-yl)(piperidin-1-yl) methanone (KMEG), exhibit significant potential in the prevention of immune dysfunction associated with long-term space flights. Our continued investigations involve the synthesis of additional novel benzofuran-2-carboxylic acids derivatives via Perkin rearrangement reaction of 3-halocoumarins involving initial base catalyzed ring fission, in which the resulting phenoxide anion attacks the vinyl bromide to produce the final benzofuran moiety. The corresponding carboxamides are then produced by reacting an amine with the benzofuran-2-carboxylic acid in the presence of DCC/DMAP at room temperature.

SERMACS 750

Utilizing α-aminocycloalkylcopper reagents to synthesize 1,2,3,4-tetrahydroquinoline alkaloids and derivatives

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The 1,2,3,4-tetrahydroquinoline alkaloids, angustureine, cuspareine, galipeine and galipinine, are isolated from the bark of the Venezuelan angostura tree. These purified alkaloids have demonstrated anti-malaria activity, analgesic properties, and a range of enzyme inhibitory activity. There are reported syntheses of these four alkaloids; however, the are no reported approaches that utilize α-aminocycloalkylcopper reagents derived from inexpensive 1,2,3,4-tetrahydroquinoline. We will present our preliminary results of our methodology to prepare these targeted 1,2,3,4-tetrahydroquinoline alkaloids via α-aminoalkylcopper/cuprate chemistry.

SERMACS 751

Enantioselective rhodium-catalyzed dearomative addition of boronic acids to aromatic nitrogen heterocycles

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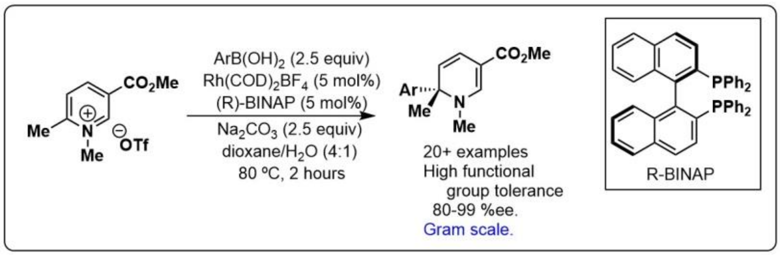
Nitrogen-containing heterocycles are among the most common structural motifs in FDA-approved therapeutics. Specifically, the piperidine ring is the most common heterocycle and accessing highly-substituted piperidine rings is of utmost importance to the pharmaceutical community. We have shown that boronic acid nucleophiles can be added to the N-alkyl salts of aromatic nitrogen heterocycles such as pyridines and quinoxalines to yield dihydropyridines and dihydroquinoxalines in an enantioselective manner using a Rhodium bis-phosphine catalyst. These addition reactions have demonstrated high yield and enantioselectivity and tolerated broad range of functional groups. In case of pyridinium salts, dihydropyridines that contain fully substituted stereocenter can be synthesized using this approach. Dearomatization reaction products, can be further derivatized to form substituted pipiridine and tetrahydroquinoxaline rings. We will also discuss factors that influence the yield and enantioselectivity of these reactions and current limitations of the method.



SERMACS 752

Identification and characterization of biocatalysts for synthesis of the Wieland-Miescher ketone

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The world of synthetic chemistry has been revolutionized and dominated by transition-metal based catalysts, which allow scientists to perform complex chemical reactions with control of stereochemistry. However, these catalysts have several drawbacks including high cost, toxicity, and adverse environmental effects. As a result, chemists are currently exploring the benefits of using biocatalysts for carbon-carbon bond forming reactions. Biocatalysts are derived from biological molecules such as proteins, RNA, and DNA, and can be obtained from a wide variety of sources including plant, mammalian, fungal, and bacterial species. Lipases, a versatile class of biocatalysts, have been studied extensively over the past few decades. They have been shown to function in non-aqueous media/organic solvents, possess catalytic activity for a wide range of organic transformations, and can be recycled via various immobilization strategies. In this study, we explore the catalytic properties of commercially available lipases by screening them for catalysis of the Robinson Annulation, a synthetically important carbon-carbon bond forming reaction. Specifically, we screen our lipase library for synthesis of the Wieland-Miescher Ketone, an important intermediate in the synthesis of biologically active compounds such as steroids and terpenoids, from methyl vinyl ketone and 2-methyl-1,3-cyclohexanedione. Although commercially available lipases are generally crude preparations, containing many different enzymes, they are used by many researchers without further purification. Therefore, we describe methodology to isolate and characterize the active component(s) of these lipase preparations.

SERMACS 753

Synthesis of novel diazonium N-(perfluoroalkyl) benzenesulfonimide polymer for use in proton exchange membrane fuel cells

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The purpose of our research was to synthesize a new diazonium N-(perfluoroalkyl) benzenesulfonimide polymer, which is expected to replace traditional used Nafion® polymer as the electrolyte for proton exchange membrane fuel cells. From the perfluoro (4-methyl-3,6-dioxaoct-7-ene) sulfonyl fluoride monomer, the free radical homopolymerization was carried out with perfluorobenzoyl peroxide as initiator. Upon polymerization, the Nafion® polymer will be subjected to a series of chemical modification, such as coupling reaction, N-deactylation, and diazotization to yield the novel diazonium N-(perfluoroalkyl) benzenesulfonimide polymer. Characterization of the polymer and the intermediates was accomplished using IR and $^{19}F/^{1}H$ NMR spectroscopy, Thermogravimetric analysis **(**TGA), Differential scanning calorimetry (DSC), as well as gel permeation chromatography (GPC).

SERMACS 754

Exploration of silicon phthalocyanines as viable photocatalysts for organic transformations

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Photocatalysis has increasingly become a major focus as a sustainable pathway for chemical reactions with visible light photocatalysts performing a large range of reactions such as redox reactions, cyclization reactions, and energy transfer reactions. Silicon phthalocyanines (SiPcs) have been largely ignored as photosensitizers in photocatalytic reactions, despite their low energy excitation, long triplet lifetimes, and their ability to form singlet oxygen. By incorporating alkyl, aryl, and silicon protecting groups as axial

ligands on the silicon center, three SiPcs have been generated by the Wiskur research group with the goal of developing three novel photocatalysts for organic synthesis. Using cyclic voltammetry and Stern Volmer quenching studies, we have shown SiPcs are capable of acting as electron donors or acceptors with appropriate substrates, including Hünig's base, maleic anhydride, and benzoquinone, with varying redox potentials. We have also successfully used a SiPc catalyst in a reductive quenching reaction where Hünig's base served as a sacrificial electron donor in the reaction. In addition to being redox-active, our preliminary data also shows SiPcs are capable of performing energy transfer reactions, by performing a reaction that utilizes singlet oxygen as a reactant under visible light conditons. This reaction, in combination with cyclic voltammetry studies, has also served as a model to understand how axial substitution on the silicon center seems to influence the photostability of these species. These results, as well as the photophysical and electrochemical experiments for each SiPc, will be presented.

SERMACS 755

Synthesis and conformational analysis of aza-peptide β-hairpin analogs

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β-sheets are common secondary structures implicated in protein-protein interactions and protein aggregation. Characterization of these motifs has been aided by development of simple and well-folded β-hairpin peptides, consisting of two antiparallel strands and a short turn region. These systems provide a tool for the in-depth study of sequence dependence and folding characteristics of β-sheets, and allow the impact of unnatural amino acid substitutions to be quantified. Peptidomimetics are non-natural peptide derivatives that closely mimic the secondary structure of peptides while providing increased protease stability. Aza-amino acids, where the α-carbon has been substituted to a nitrogen, have been shown to induce turns; however, incorporation within an extended strand region have not been conducted. We envisioned that the increased acidity and basicity along one face of the aza-amino acid would reinforce favorable cross-strand interactions through hydrogen bonding while inhibiting aggregation. Herein, we report the synthesis of two aza-peptide analogs of a β-hairpin model system, where a valine residue situated in the middle of the β-strand region was substituted for aza-valine and aza-glycine. Additionally, quantification of the percent folding of each analog was conducted using 1D and 2D ^{1}H-NMR analyses.

SERMACS 756

Investigation of the reaction of monochloramine and 2,6-dichlorophenol as a model for the purification process of drinking water

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The goal of the water purification process is to minimize the amount of toxic chemicals formed while maximizing public safety by eliminating bacterial and fungal growth. Chlorine is added during the process for an antibacterial effect, but it is also what causes the formation of toxic chemicals, such as chloroform. When monochloramine is used as the primary chlorinating agent it significantly reduces the amounts of toxic chemicals formed when compared to bleach. The primary organic components present in unpurified water are the humic and fulvic acids, which are a series of complex polyphenolic compounds. Phenols can act as a simplified substitute for studying the complex reactions that ultimately lead to the formation of toxic byproducts such as chloroform and other polychlorinated organic compounds. 2,6-Dichlorophenol is of particular interest as it is an intermediate between phenol and 2,4,6-trichlorophenol in the chlorination of phenol and retains an open para position. While monochloramine generally acts as a chlorinating agent on phenolic compounds, there are a number of potential alternate reactions that may occur at the para position. This makes 2,6-dichlorophenol a particularly interesting model compound to study the various types of intermediate compounds that may be formed during the drinking water purification process. Using Gas Chromatography Mass Spectrometry, High-Performance Liquid Chromatography, and Ultraviolet-Visible Spectroscopy we aim to identify and quantify the minor products and the colored compounds formed during the reaction between 2,6-dichlorophenol and monochloramine under aqueous conditions at moderate and high pH.

SERMACS 757

Extensive alignments of atomic orbitals in the substrate-binding strands of HIV-1 protease mutant ASP25ASN

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This presentation describes part of an ongoing conformational analysis of HIV-1 protease complexes. It begins with a review of extensive orbital alignments identified previously in several complexes of an HIV-1 protease mutant, Asp25Asn. The crystal structures of those complexes were reported by Schiffer et al. as stable models of corresponding enzyme/substrate complexes. The orbital alignments are housed specifically in the mean conformations of the enzyme-bound oligopeptide ligands and the active-site Asp-bearing strands. Those alignments intersect at the scissile substrate linkage, like similar alignments in trypsin and subtilisin complexes, implying an involvement of through-strand electronics in the enzyme and substrate during proteolysis. Additional extensive orbital alignments have now been identified in the substrate-binding strands. The mean conformations of the binding strands were calculated from the crystal structure data. The corresponding alignments of atomic orbitals will be described and possible mechanistic roles considered.

SERMACS 758

Repurposing nTZDpa: Antimicrobial effective against growing and persistent *Staphylococcus aureus*

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Because conventional antibiotics struggle to treat resistant or persistent bacteria, we need new antimicrobials that can affect these pathogens. Identified in a high-throughput screen, non-thiazolidinedione peroxisome proliferator-activated receptor gamma partial agonist (nTZDpa), an antidiabetic, kills both growing and persistent *Staphylococcus aureus* through membrane perturbation. Furthermore, nTZDpa works synergistically with the aminoglycosides, restores gentamicin activity against persister cells, and exhibits low probabilities of resistance development. However, because nTZDpa lyses red blood cells, we utilized rational design in combination with molecular dynamics to develop nTZDpa-inspired analogs that are potent and do not induce hemolysis. Further synthetic efforts are toward designing informed nTZDpa analogs that maintain potency against both growing and persistent *S. aureus* while reducing renal toxicity.

SERMACS 759

C–H functionalization of five-membered heteroarenes with aryl halides using carbazole as photocatalysts

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Photoredox catalysis enables chemists to perform radical reactions under mild conditions by utilizing light absorbing photocatalysts as opposed to toxic radical promoting reagents such as tributyltin hydride. Common photocatalysts are metal complexes. While these complexes offer many advantages, complexes used for single electron reductions are typically expensive and can lead to metal contamination. Organic photocatalysts are more favorable because they do not contain metals and can be relatively inexpensive for single electron reductions. Carbazoles are nitrogen-containing heterocycles and strong reductants upon excitation. Our group has previously synthesized several carbazole derivatives with the ability to absorb light at 365 nm and demonstrated their ability as photocatalysts in the dehalogenation of substituted benzenes. We are now expanding the use of the carbazole derivatives as photocatalysts in the C–H arylation of five-membered heteroarenes using aryl bromides and chlorides. The redox potentials of the carbazole derivatives should be beneficial for this reaction compared to previous photocatalysts by eliminating the need for a sacrificial electron donor. By removing the sacrificial electron donor, unwanted side reactions can be prevented.

SERMACS 760

Substituted [3]-radialene dianions as catholytes for energy storage

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Substituted [3]radialenes are promising molecules for energy storage due to their ease of preparation, stability, and reversible redox behavior. However, little work has been done to probe their stability and electrochemical behavior in water. Four water-soluble [3]radialene disodium salts have been synthesized via simple two-step procedures. Compounds **1**-**4** were structurally and electrochemically characterized. Cyclic voltammetry reveals that each derivative exhibits a reversible single-electron redox process in aqueous solutions, to yield the radical anion. Galvanostatic cyclic charge-discharge studies were performed to probe the stability and the potential use of these materials as an active species in aqueous redox flow batteries. Solubility for each derivative was also measured using UV/Vis spectroscopy. Derivatives with enhanced solubility are obtained upon interruption of molecular symmetry. Stability studies indicate that compounds **1**-**4** are stable in solutions of water for over 5 days.

SERMACS 761

Synthesis and complexation of boronic acid derivatives with N-oxides

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The synthesis of molecular machines have attracted considerable attention since Jean-Pierre Sauvage, James Fraser Stoddart, and Bernard Feringa were awarded the 2016 Nobel Prize in chemistry. These “machines” are specially designed molecules with parts that produce controlled movements when energy is added. These complexes could potentially be used to form a molecular machine. Boronic acids contain only six valence electrons on the boron and have an empty p-orbital which is used to complex with the n-oxide. Lewis acidity of boronic acids is found to be dependent on atomic size and the electronegativity of the substituent. As the substituents become more electronegative, boron’s valence become more deficient in electrons, leading to it becoming a stronger Lewis acid. Phenylboronic acids containing a variety of functional groups were used to synthesize a boroxine by using three equivalences of the boronic acid or a boronate by using one equivalent of the boronic acid and one equivalent of a catechol. These molecules were prepared using a microwave-assisted synthesis and then analyzed using Nuclear Magnetic Resonance, Infrared Spectroscopy, and Gas Chromatography-Mass Spectrometry. The resulting boroxines and boronates were then complexed with picoline n-oxide to form a dative bond between the oxygen and the boron. The degree of complexation was determined by H^1NMR by comparing the chemical shifts of the hydrogens located near the complexation site. There is a significant shift in the H^1NMR spectra in the aromatic region that appears when complexing the boronic acid derivative with an n-oxide. There is an increase in the melting points between the uncomplexed and complexed boronic acid derivatives. We report the one-pot, microwave-enhanced synthesis of several unique amine N-oxide/boron complexes in high yield. The next steps would be to look into the ability of boron atoms to coordinate with a variety of Lewis bases in simpler boron-containing systems.

SERMACS 762

Synthesis and characterization of new albuterol double salt ionic compounds

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The field of study regarding ionic liquids (ILs), has grown its size as the benefits of ILs have been realized by virtually every world industry. Although the application of ILs in the pharmaceutical industry is relatively new, the research has proved promising with IL active pharmaceutical ingredients (APIs) having superior chemical and physical properties than their HCl counterparts. For society to benefit from pharmaceutical ILs, various methods must be developed to transform different APIs into the corresponding ILs and successively studying their physical and chemical characteristics. Only once the fundamental chemical aspects of these compounds have been thoroughly studied and documented, will the continuation of these enhanced pharmaceutical ILs into clinical trials occur. Although the list of pharmaceutical ILs currently being studied is growing, albuterol has yet to be analyzed as its ionic counterpart. The typical treatment for asthma and chronic obstructive pulmonary disease is the administration of albuterol along with corticosteroids to treat bronchospasm and bronchial inflammation. Although albuterol is a relatively safe drug, corticosteroids present with a variety of adverse side effects, including headaches, sore throat, reflex cough, adrenal suppression in children, and weight gain. Due to this list of side effects, it is common for medical providers to administer non-steroidal anti-inflammatory drugs prior to prescribing a corticosteroid. To circumvent these drawbacks, we have chosen to prepare new double ionic liquids by pairing ionic albuterol with salicylate and docusate in their ionic states. Combining albuterol cation, an NSAID anion, and docusate anion in various molar ratios to form new DSILs will allow the use of a single drug administration instead of multiple administrations, as well as improved efficacy, and controlled properties. This presentation focuses on the synthesis and spectroscopic characterization of three new albuterol double salt ionic liquids with potential analgesic and enhanced transdermal properties.

SERMACS 763

Epoxy isonitriles, a unique class of antibiotics: Synthesis of their metabolites and biological investigations

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Epoxy isonitrile containing natural products isolated from various bacteria species often possess specific and potent antibacterial activity against Gram-positive bacteria. Epoxy isonitriles, however, are extremely labile under acidic and basic conditions, undergoing a Payne rearrangement to produce stable epoxy ketone metabolites and releasing hydrogen cyanide. Due to the toxicity associated with hydrogen cyanide, we synthesized and performed biological assays with the corresponding epoxy ketone containing metabolites. We identified that the epoxy isonitrile moiety is pertinent for potent and selective biological activity against Gram-positive bacteria. Serendipitously, we discovered an α,β-unsaturated epoxy ketone analogue that exhibited activity against both Gram-negative and Gram-positive baceteria possessing a similar chemotype to known fatty acid biosynthesis inhibitor cerulenin.

SERMACS 764

Increased organoid nutrition using TPG as a dynamic natural collagen analogue

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Organoids consist of different tissue cells from parts of the body and are used by scientists as a simplified organ. The use of organoids can change the way of how we look at developmental diseases. Hence, there is a need to promote nutritional flow in organoids so that full experimentation can be optimized. Dynamic networks (a prime subject of matter in the relatively new field of systems chemistry) in living organisms bridge the gap between chemical and physical networks, allowing for organisms to promptly adapt to external stimuli. Collagen, the most abundant protein in our body, plays a major role in the extracellular matrix. Despite the assortment, all collagens share a common structure known as the collagen triple helix. This project aims to create a dynamic network of self-assembling monomers into a collagen fiber structure that can create a triple helix strand. Results have shown that the amino acid pairing of Asparagine, Proline, and Glycine (NPG) along with the synthesized protection group of Fluorenylmethyloxycarbonyl chloride (Fmoc) promotes cell survival and prevents apoptosis and promotes neurogenisis in organoids. NPG has been demonstrated to polymerize reversibly through N,N acetal linkages. Unlike peptide bonds, acetal formation proceeds via a Schiff base intermediate and is readily reversible allowing for a more dynamic structural protein. With the introduction of a new amino acid that will replace Asparagine in the collagen fiber synthesis, Threonine (making Fmoc-TPG), the TPG N,O acetal is more susceptible to hydrolysis because of the leaving ability of the oxygen on the 5-membered ring when protonated. This would allow the TPG system to be even more dynamic than that of NPG because TPG is chemically less stable. Different ratio mixtures of TPG to NPG might allow us to optimize dynamic nature while maintaining stability in the organoids. However, it remains to be determined whether TPG polymerizes to any significant extent or forms strands like those observed in collagen. Results from MALDI mass spectroscopy show that TPG coupling has been successful. Further research is being conducted to see if solid state synthesis will yield more TPG, which will help determine the dynamic self-assembly structure so it can react with organoid stem cells to promote nutrition flow. Thus, here is a new method of increasing organoid nutrition through creating an alternative self-assembling collagen fiber using new concepts from systems chemistry.

SERMACS 765

Improving student knowledge of GC-MS through analysis of electronic cigarettes in organic chemistry

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Organic chemistry students were exposed to the analysis of electronic cigarettes in a two-week laboratory experiment. Most college students are familiar with the usage of e-cigs and this real-life application of organic chemistry was used to teach students about gas chromatography-mass spectrometry (GC-MS). The students constructed smoking machines in order to collect nicotine vapors on a glass fiber filters. The contents of the filter were then mixed with methanol and syringe filtered prior to GC-MS analysis. One week was spent in the lab on the extraction of e-cig components and one week was spent analyzing chromatograms and mass spectrometry data. The students were surveyed and quizzed to determine knowledge gains and proficiency increases before and after the lab experiment. The students had a 56.8 % increase in quiz grades, and they showed an improvement in their chromatography and mass spectrometry knowledge. Primarily, the students responded favorably to this lab experiment that provides a realistic connection between lecture and lab material.

SERMACS 766

Adsorption of juglone free acid and its tetrabutylammonium derivative on hydrophilic mesoporous silica

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Juglone, an organic compound found in significant amounts in black walnuts, has longstanding status as a source of pigmentation and medicinal properties. The allelopathic effects of juglone have been underused in agricultural applications. Juglone is a less attractive option for current herbicidal delivery methods in its free acid form because it is somewhat soluble in water, is highly volatile (it exposes workers during application), and has potential to drift to non-target areas. These issues can be reduced by synthesizing ionic compounds composed of the anionic form of juglone and ammonium cationic surfactants that reduce the movement in water, increase the movement across the fatty membranes of unwanted plant species, and minimize the leaching of juglone to undesired locations. A controlled leaching of the compound can be attained by adsorption on mesoporous silica materials of different pore sizes. Our presentation focuses on synthesis and characterization of new silica materials obtained by adhering juglone as well as its tetrabutylammonium derivative on silica gel with pore size of 90 Å (SiO_2-90). Three wt/wt% loadings, namely 10%, 20%, and 50%, were synthesized by using the adsorption from solution loading procedure and characterized using infrared spectroscopy.

SERMACS 767

Drug delivery of naringenin to adipocytes using ultrasmall superparamagnetic iron oxide nanoparticles (USPIO)

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According to the CDC, obesity is one of the main risk factor for cardiovascular disease and type-2-diabetes. Biologically active phytochemicals such as Naringenin (NG) have shown potential for promoting benefits again type-2-diabetes and obesity. Infact, NG has already showed to decrease adipose tissue mass, however, their bioavailability has remained controversial. Hence there is a need to develop targeted therapy, which will increase the concentration of NG in the adipose tissue. Currently, nanoparticles are used for drug delivery where conventional therapies have proven to be less effective. Among various types of nanoparticles, USPIO have found considerable attention in drug delivery as they are easy to synthesize, inert, and are biocompatible. However, to use them for drug delivery system, the USPIO need to be surface functionalized by ligands such as aminotripropyl ethoxysilane. The use of aminotripropyl ethoxysilane provides an amine functional group on the surface of USPIO. Once amine functionalized, the USPIO-NH_2will be conjugated to a NG *via* dicarboxylic tetraethylene glycol (TEG) linker (HOOC-TEG-COOH) to yield USPIO-TEG-NG. However, to increase the specificity of the nanoparticles to the white adipose tissue (WAT), a WAT specific peptide, P3 (CKGGRAKDC) will be conjugated onto USPIO-TEG-NG to yield a final product USPIO-TEG-NG-P3. The P3 peptide has been reported to bind specifically to WAT vasculature through the membrane protein prohibitin, hence the presence of P3 onto the nanoparticle will increase the specificity and selectivity of the nanoparticle to the adipose tissue. USPIO was synthesized using Fe(II) and Fe(III) chloride in presence of NaOH. USPIO obtained was later aminated in the presence of aminotripropyl ethoxysilane. The presence of amine functional groups on the surface of nanoparticles was confirmed *via* FTIR and quantified using ninhydrin Assay. The ninhydrin assay revealed the presence of 4.5micromolar of amine groups per mg of the USPIO. TEM analysis showed that the USPIO and USPIO-NH_2, particles were all spherical in shape with the average particle size of 20 and 25 nm, respectively. Once developed, the bioavailability of USPIO-PEG-NG-P3 will be evaluated both *in vitro* and *in vivo.*

SERMACS 768

Dual red and near infrared emitting charge transfer probe for detection of serum albumin

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Small molecule fluorophores with strong intramolecular charge transfer properties in the red and near infrared (NIR) region of the spectrum are very important in biological applications. Herein, we have designed, developed and assessed the efficacy of a double-wavelength emitting probe for potential diagnostic application of microalbuminuria. The probe was synthesized in two easy synthetic steps from commercially available reagents. Functional groups were carefully selected to tune the optical properties of the probe in the visible and NIR windows of the electromagnetic spectrum. Structure-optical properties of the probe were investigated in various chemical environments of solvents and aqueous buffers, including with other proteins and enzymes. The optical properties of the probe was highly sensitive to the micro-environment. Both pH and rigidity of the solution controlled the light emitting properties of the probe. Hence, the visible as well as the NIR-I emission dramatically changed in presence of human serum albumin. The intensity of the lights was linear to the amount of serum albumin, resulting quantitative detection of the protein in aqueous solution. The probe specifically recognized serum albumin over other proteins and enzymes with a limit of detection of 10 mg/L and 20 mg/L in synthetic urine samples at red and NIR-I emission window of the spectrum, respectively. Molecular modeling and experimental drug displacement assays suggest that the specific response of the probe toward human serum albumin originated from the tight supramolecular complexation between the probe and the protein at subdomain IA.

SERMACS 769

Enantioselective ring opening of epoxides with anilines

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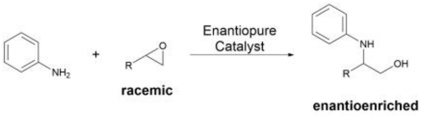
Amino alcohol derivatives are important intermediates for the synthesis of nitrogen-containing molecules. Anilines can be used as nucleophiles for the enantioselective ring opening of epoxides, but substrate limits exist for known procedures. Our laboratory is developing the enantioselective ring opening of commercially available epoxides with various anilines under Lewis acid catalysis. A wide range of β-amino alcohols were synthesized with high yield and moderate to high enantioselectivity. Efforts to extend the method to alternative nitrogen nucleophiles and preliminary mechanistic insight will also be presented.



SERMACS 770

Developing biocompatible thiol-ene coupling conditions

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The thiol-ene coupling (TEC) is a widely applied methodology in materials and polymer chemistry to photoinitiate polymerization. However, transferring the methodology of this click reaction to aqueous and functional-group rich environments found in conditions that mimic biological settings is not straightforward. Our work to find and develop protocols that allow efficient TEC in these demanding reaction conditions will facilitate the study of disulfide bonds using the thioether bond. One example of a biocompatible TEC methodology has been developed to help study signaling systems by successfully installing a model thioether bond between an alkene and a small-cysteine containing peptide without the use of harsh UV light or inorganic photoinitiators.

SERMACS 771

Oxidation reaction screening of tricyclic ketones towards the synthesis of furan-bridged medium-sized rings

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Many promising therapeutics, such as the sarcodictyins, cladiellins, and briarellins, bear a furan-bridged ten-membered ring. This project seeks to rapidly access this core ring skeleton via the Baeyer-Villiger oxidation of a tricyclic eneones or similar substrates. The reaction products were analyzed via GCMS and NMR.

SERMACS 772

Application of a visible light-catalyzed [2+2] photocycloaddition to the synthesis of natural products containing medium-sized rings

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The synthesis of natural products containing medium-sized rings has been a constant pursuit in organic chemistry. Laurencin, a marine natural product containing an eight-membered cyclic ether, is a classical target for demonstrating advances in synthetic methodology. We are developing an intermolecular [2+2] dioxenone photocycloaddition using visible light photocatalysis for the synthesis of these eight-membered cyclic ethers. Methods include Stern-Volmer analysis of phosphorescence quenching and cyclic voltammetry. Progress towards a carbocyclic model system will be discussed.

SERMACS 773

Quantitative study of Van der Waals interactions in organic solvents using N-arylimide molecular balance

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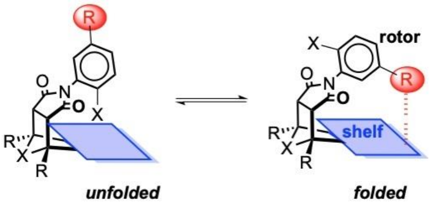
Knowledge of van der Waals (vdw) interactions is an important component toward the understanding of the stability and conformational preferences of proteins. In this work, seven molecular balances were synthesized using a modular process to systematically examine the vdw interactions between an alkyl group on the 5-position of the *N*-phenyl rotor and the aromatic shelf. In these molecular balances, restricted rotation about the C_{aryl}-N_{imide} bond yields distinct *folded* and *unfolded* conformations allowing the *folded/unfolded* ratios in solution to be readily assessable via ^{1}H NMR. Change in strength of the alkyl-arene interactions was quantitatively analyzed by comparing the *folded/unfolded* ratios and the folding energies of the corresponding balances. The strength of vdw interactions between the alkyl and arene surfaces appears to be correlated with the polarizability of the alkyl group as well as with the change in accessible surface area of the molecule. The stabilizing term in the alkyl-arene vdw interactions is hypothesized to arise from a combination of dispersion and solvophobic effects, which is further examined in a series of solvent studies.



SERMACS 774

Metal catalyzed coupling in the synthesis of bis-*para*-anisyl alkanes

***Andrew Pampu**, pampud@g.cofc.edu. Chemistry and Biochemistry, College of Charleston, Charleston, South Carolina, United States*

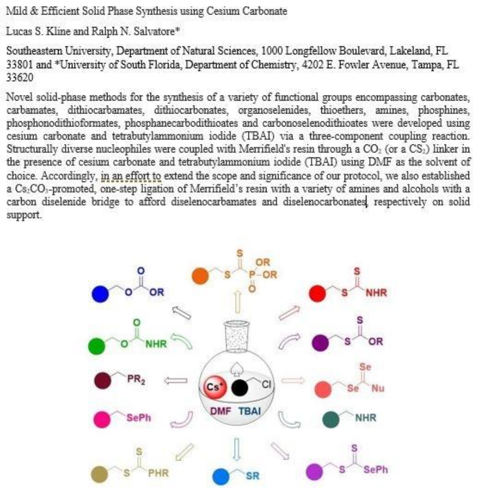
A method developed by Weix for metal-catalyzed coupling between an aryl bromide and mono-bromo alkanes was tested to determine if it could be used to couple aryl bromides and alkyl di-bromides. Developmental efforts proved the method to be successful at the milligram scale and then was scaled up. The goal was to synthesize gram quantities of the desired product using this modified Weix method. The results of the scale up and the purification process will be presented.

SERMACS 775

Mild & efficient solid phase synthesis using cesium carbonate

***Lucas Kline**, lucaskline11@gmail.com. Southeastern University, Silver Springs, Florida, United States*

Novel solid-phase methods for the synthesis of a variety of functional groups encompassing carbonates, carbamates, dithiocarbamates, dithiocarbonates, organoselenides, thioethers, amines, phosphines, phosphonodithioformates, phosphanecarbodithioates and carbonoselenodithioates were developed using cesium carbonate and tetrabutylammonium iodide (TBAI) via a three-component coupling reaction. Structurally diverse nucleophiles were coupled with Merrifield's resin through a CO2 (or a CS2) linker in the presence of cesium carbonate and tetrabutylammonium iodide (TBAI) using DMF as the solvent of choice. Accordingly, in an effort to extend the scope and significance of our protocol, we also established a Cs2CO3-promoted, one-step ligation of Merrifield's resin with a variety of amines and alcohols with a carbon diselenide bridge to afford diselenocarbamates and diselenocarbonates, respectively on solid support.



Mild & Efficient Solid Phase Synthesis using Cesium Carbonate

Lucas S. Kline and Ralph N. Salvatore*

Southeastern University, Department of Natural Sciences, 1000 Longfellow Boulevard, Lakeland, FL 33801 and *University of South Florida, Department of Chemistry, 4202 E. Fowler Avenue, Tampa, FL 33620

Novel solid-phase methods for the synthesis of a variety of functional groups encompassing carbonates, carbamates, dithiocarbamates, dithiocarbonates, organoselenides, thioethers, amines, phosphines, phosphonodithioformates, phosphanecarbodithioates and carbonoselenodithioates were developed using cesium carbonate and tetrabutylammonium iodide (TBAI) via a three-component coupling reaction. Structurally diverse nucleophiles were coupled with Merrifield's resin through a CO_2 (or a CS_2) linker in the presence of cesium carbonate and tetrabutylammonium iodide (TBAI) using DMF as the solvent of choice. Accordingly, in an effort to extend the scope and significance of our protocol, we also established a Cs_2CO_3-promoted, one-step ligation of Merrifield's resin with a variety of amines and alcohols with a carbon diselenide bridge to afford diselenocarbamates and diselenocarbonates, respectively on solid support.

SERMACS 776

D-γ-tocotrienol: Promising radioprotective agent isolated from palm oil

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The health consequences sustained from ionizing radiation contact are known to claim a lot of life recently. Many efforts have been directed towards discovering a proficient radioprotective agent for acute radiation syndrome (ARS) without any success. The United States Food and Drug Administration (FDA) has not accepted any effective and harmless radioprotector for alleviating ARS. However, current studies have shown that an isomer of vitamin E (γ-tocotrienol, GT-3) mostly found in palm oil, has radioprotective abilities in non-human primate (NHP) and murine models. Even though GT-3 is an outstanding promising counteracting agent revealed; the separation and purification from its matrix or different E vitamers are challenging. This has placed a limitation on its characterization, derivatization, and its addition to new products such as functional foods, supplements, and pharmaceuticals, as well as biomedical application. We have therefore generated new chromatographic and fractional distillation methods to optimize isolation and enhance the purity and stability of GT-3. Thin layer chromatography (TLC) was used to establish the finest solvent system for the large column chromatography (CC). Gradient elution with ethyl acetate (EA) in petroleum ether (PE) resulted in a certain degree of purity based on the ^{1}H NMR and GC-MS analysis. Outcomes obtained so far have revealed the precise structure and a purity of ≥95% of the compound. Hence, some traces of impurities, specifically β-tocotrienol (BT-3), in the GT-3 distillate tend to compromise its stability and solubility to some extent. It is anticipated that this work will support the development of new medications for ARS.

SERMACS 777

Synthesis and virtual screening of novel acridone derivatives as potential topoisomerase II α catalytic inhibitors

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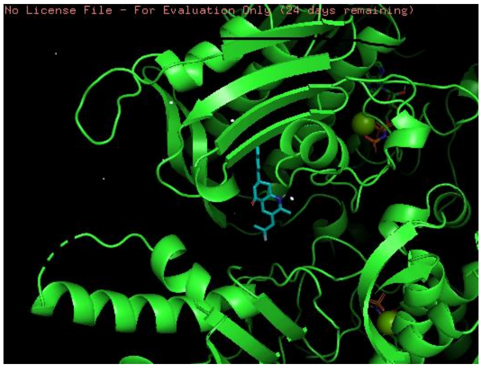
We report on the synthesis of a novel series of fluorinated acridones from 5-trifluoromethyl, and 5-phenyl-1,3-cyclohexanediones, respectively. The products **(3a-3j)** were characterized by spectroscopic methods (NMR, IR, MS) to confirm their structures. The compounds were further subjected to virtual screening using Autodock Vina, a computational program software. Several of the molecules displayed good binding affinities to human topoisomerase IIα ATPase. We hypothesize that the acridone derivatives of the above series are catalytic inhibitors of Topo IIα. The synthesis, binding affinities, and molecular properties of compounds **(3a-3j)** will be presented.



SERMACS 778

Search for highly selective and potent CB1 and CB2 inhibitors: Synthesis and characterization of (s,e)-11-[2-(thionylmethylene)hydrazono]-pbd

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Pyrrolo [2,1-c] [1,4] benzodiazepine (PBD) is a class of natural products originally obtained from various actinomycetes which have selective binding to the cannabinoid receptors. The cannabinoid receptors, CB1 and CB2 are members of the G protein-coupled receptors group and can be involved in modulating several functions in the CNS (memory, cognition and pain control), and in the immune system which is of pharmacological interest. This research focuses on the synthesis of novel 11-hydrazinyl PBD derivatives using a multi step synthesis. PBD-dilactam was initially produced using isotaic anhydride and (L)-proline which was then converted to the PBD-thiolactam using Lawesson's reagent. Reaction of thiolactam with hydrazine in ethanol afforded 11-hydrazinyl PBD in good yield. Condensation of PBD-11-hydrazinyl with 2-thiophenecarboxaldehyde was performed to generate (S,E)-11-[2-(thionylmethylene)hydrazono]-1,2,3,10,11,11a-hexahydro-5H-benzo[e]pyrrolo[1,2-a][1,4]diazepin-5-one. 1H-NMR, 13C-NMR, DEPT, GC-MS were used to characterize the products. Binding efficacy towards cannabinoid receptors will also be tested.

SERMACS 779

Investigating the importance of binding pocket size for nerve gas binding to rhodamine-b derivatives

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Nerve gas agents are colorless, odorless toxic compounds. Detection of these compounds at low concentrations is very important. Here, we have synthesized three rhodamine-B derivatives with varying sizes of binding pockets to study the mechanistic aspect of nerve gas binding with rhodamine-B based sensor molecules. Rhodamine-B derivatives are good candidates for chemosensors due to their high quantum yield and high molar extinction coefficients. The equilibrium between the non-fluorescent colorless form and the highly fluorescent pink form of rhodamine-B derivatives provides a better model for the development of turn-on sensors for various analytes. The binding of nerve gas mimics (diethyl chlorophosphate, dimethyl methylphosphonate and demeton-S) with these sensors was studied using UV-Vis, fluorescence and ^{1}H NMR spectroscopic techniques. All sensor molecules bind selectively with diethyl chlorophosphate. The binding of diethyl chlorophosphate caused the appearance of a new absorbance band at 555 nm confirming the formation of ring open form of rhodamine-B derivatives. The ^{1}H NMR studies confirmed the formation of a phosphoester bond between the sensor and analyte. Computational studies on binding between the sensors and diethyl chlorophosphate also confirmed the formation of a phosphorester bond compared to other forms of sensor-analyte assemblies. The effect of binding pocket size will be further discussed.

SERMACS 780

Synthesis of ionic liquids

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The following project is an investigation of syntheses of heterocycles, using newer methodologies such as greener solvents or microwave heating. Recently, the new Ionic Liquid (IL) class of fuels and propellants were recognized as contemporary materials with advantages in environmental friendliness and a highly designable temperature range surpassing previous limitations. Given its additional retention of important properties in extreme conditions, this class is potentially useful as artificial, chemical media capable of supporting exoplanet exploration. The prospect of microwave synthesis for this class is a more ecologically sustainable and efficient synthesis of this unique, organic resource.

SERMACS 781

Synthesis of cyclopropane aminoisoquinolines as highly selective kinase inhibitors

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Rho kinases (ROCKs) are key effectors involved in the phosphorylation of myosin light chain kinase. ROCKs are involved in the regulation of calcium ion intake and are regulators for stress fiber formation and cell contraction. Programs to inhibit these kinases are prevalent in cardiac, respiratory, diabetes and ocular indications. Janus Kinases (JAKs) are a family of tyrosine kinases that activate cytokine receptors via their signal transduction pathways. JAKs are key facilitators in the activation of the STAT protein family, responsible for many facets of the immune response, cellular growth, apoptosis, and differentiation. Programs to affect immune response pathways at Aerie Pharmaceuticals include the development of novel, biologically active small molecules that target members of the JAK family (JAK1, JAK2, JAK3, or TYK2). Of interest to our group is the synthesis of derivatized cyclopropanes bearing modulated aminoisoquinolines, which allows a range of both activity and selectivity for JAKs and/or ROCKs as new classes of inhibitors targeting various ophthalmic diseases.

SERMACS 782

Design, synthesis and biological evaluation of imidazo[2,1-*b*]oxazole derivatives as ^{V600E} BRAF kinase inhibitors acting as melanoma therapy

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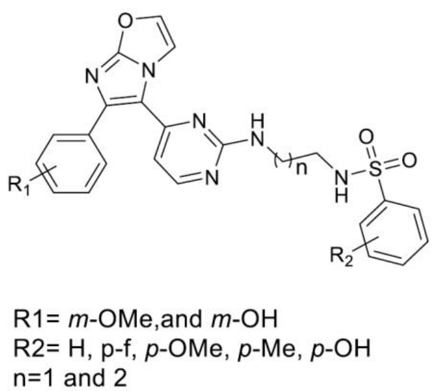
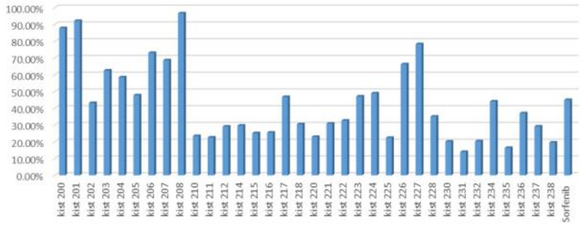
A new series of imidazo[2,1-*b*]oxazol derivatives was synthesized and evaluated for their anticancer activity over NCI 60 cell lines and A375 melanoma cell line; in order to investigate and increase the selectivity of compounds belong to imidazo[2,1-*b*]oxazol scaffold toward melanoma. **Kist 210, kist 211, kist 225, kist 230, kist 231, kist 232 and Kist 235** showed higher potency compared to sorafenib. Compounds containing m-OH phenyl at position 6 and 2-substituted pyrimidine at position 5 with propyl bridge between pyrimidine and sulfonamide moiety showed the highest activity. In addition, ten compounds exhibited 100% inhibition for BRAF, ^{V600E} BRAF and RAF1 at single dose 10 µM. The new series provides a good candidate for preclinical investigations in treatment melanoma.



General structures of the target compounds



Inhibitory effect of the new compounds represented as growth % of A375 melanoma cell line compared to sorafenib.

SERMACS 783

Aryl ring modifications of sphingosine kinase 2 selective inhibitors

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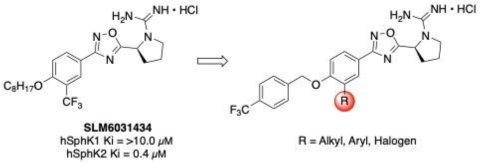
Sphingosine-1-phosphate (S1P) is a ubiquitous bioactive lipid synthesized from sphingosine (Sph) by sphingosine kinase 1 and 2 (SphK1 and SphK2). The S1P signaling pathway has been implicated in various disease states such as cancer, sickle cell disease and renal fibrosis. Inhibition of SphK1 and 2 to attenuate levels of S1P has exhibited therapeutic efficacy in animal models of these diseases. Recently, work done in our lab with **SLM6031434** demonstrated that introduction of a trifluoromethyl group on the internal phenyl ring increased potency toward inhibiting SphK2. Herein, we disclose the design, synthesis and evaluation of compounds with varying substitutions on the internal phenyl ring to gain insight on this region of the SphK binding pocket (Fig. 1). Our studies suggest that a small pocket in this region is present, and the current investigations probe this site.



SERMACS 784

Development and characterization of organic photoredox catalysts

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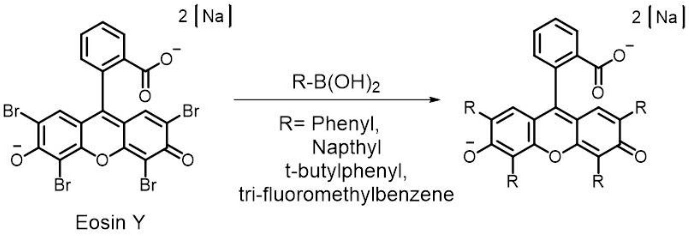
The photocatalyst Eosin Y, a known xanthene derivative, was chosen as a precursor to synthesize a new series of organic photocatalysts. Photoredox catalysis is a rapidly growing field that opens elegant and renewable pathways in pharmaceutical and polymer research. Transition metal complexes have been widely used as photocatalysts due to the wide range and tunability of their properties. However, the scarcity and toxicity of these transition metals are not ideal for sustainable practices. In order to create a sustainable system capable of broad ranges of reactivity the development, characterization, and evaluation of tunable organic light absorbing complexes capable of partaking in photoredox catalysis was undertaken. Working off these attributes, substitutions of the bromine atoms of Eosin Y led to four previously unreported photocatalysts with tunable properties. Reduction potentials of the new photocatalysts varied by 120 mV, which shows these catalysts can be tuned for specific reactions. The excited state lifetimes of the new photocatalysts are comparable to those of the parent complex, but the λ_{max} for absorbance was greatly red-shifted to take advantage of the most abundant part of the solar spectrum. The measured fluorescence quantum yields also out performed most transition metal photocatalysts. The high tunability of these dyes lead to rational design of organic photocatalysts for specific subsets of reactions.



SERMACS 785

Carolacton-inspired analogs for CH functionalization and biological exploration

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Carolacton is a natural product that selectively perturbs *S. mutans* biofilm, the leading cause of dental caries. Manipulations to the carolacton scaffold have led to the discovery of compounds with unique and improved activity against *S. mutans* biofilm. For this reason, we are interested in expanding the analog library. An analog bearing an alkyl sidechain was synthesized to probe the carolacton scaffold as a substrate for CH functionalization. We hope that CH functionalization will enable late-stage diversification of this auspicious natural product and aid in the discovery of biofilm specific therapeutics.

SERMACS 786

Using enyne metathesis to rerminate ROMP

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Ring opening metathesis polymerization (ROMP) is reaction of polymers with different functionalities involving Grubbs catalysts. Polymers produced via ROMP have been used as materials in material science and as probes bio-chemistry. To terminate a polymer produced via ROMP, an alkene metathesis reaction is utilized where a “terminating agent” bearing an alkene functional group is added to the polymerization reaction after all monomers have been consumed. Ethyl vinyl ether and its derivatives are commonly used as terminating agents. Terminating agents enable fictionalization of the polymers directly or through subsequent reactions. Enyne metathesis involving a terminal alkyne with a terminal alkene in the presence of Grubbs catalysts is used in multi-step syntheses but never to terminate ROMP. We report here the synthesis of an alkyne "terminating agent" and use it to terminate ROMP of N-butyl norbonene imide monomer. Polymer 1H NMR results are consistent with incorporation of the alkyne terminating agent at the end of the polymer.

SERMACS 787

Tetraarylphosphonium/tetrakis(pentafluorophenyl)borate (TAP^R/TFAB) salts as non-aqueous electrolytes for organic redox flow batteries

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Renewable energy offers the benefits of reduction in use of fossil fuels and global warming, as well as in sustaining society. One solution to this pressing issue is the development and implementation of grid-scale energy storage devices such as Organic Redox Flow Batteries (ORFBs). All recent advances in battery technology can be traced to improvement of the electrolytes thereof. A series of weakly coordinating cations/anions (TAP^R/TFAB) ion pairs are, herein, being proposed as non-aqueous electrolytes for high capacity ORFBs. These will be accessed via a Palladium-catalyzed approach followed by simple filtration/isolation of the product. These substituted tetraarylphosphonium/tetrakis(pentafluorophenyl)borate salts **1-3** (with R= *p*OMe **(1),** R= *p*Ph (**2**), R= *p*TMSA or para-trimethlysilylacetylene **(3)**) have potential use in several industries. They will be used to probe, and possibly fine tune ion association/dissociation in electrolytes owing to their unique solubility in low polarity solvents. These salts constitute a new class of molecular ion pairs which can promote charge dissociation even in low polarity solvents because of their large size and bulkiness. The result being an increased conductivity in those media that can be useful for electrochemistry, advances in catalysis, battery technology, petroleum handling etc. We investigate the proposed structures to test our hypothesis using DC conductivity, cyclic voltammetry (CV) and pulse radiolysis. Preliminary conductivity measurements show that salt **2** has a lower association constant than salts **1** and **3** while salt **1** is lower than **3**. These results confirm our assumption that the bulkier the salt the more dis-associated and more conductive it is in low polarity media. Our work supports BNL’s mission by fostering the development of affordable, clean and renewable energy source and storage. This summer I have acquired a broad training and developed a further understanding of several electroanalytical methods for characterization of materials.

SERMACS 788

Transmission µ-FTIR of unconventional source rocks using improved thin section preparation methods for monitoring changes in kerogen chemistry

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Kerogen, the insoluble component of organic matter, is responsible for the creation of hydrocarbons in source rocks. Micro Fourier Transform Infrared Microscopy (µ-FTIR) is a non-destructive technique that can be used to monitor the change in the kerogen’s chemical composition as it is thermogenically transformed into oil and gas. Transmission µ-FTIR provides reliable spectra for monitoring these changes, however sample preparation of the source rock, while straightforward, presents its own complications. To achieve a successful spectrum, a transparent sample of less than 50 µm thick is required. Due to the rock’s laminated structure, preparation of successful slides of intact samples with the required thickness is challenging. Moreover, traditional thin sections are mounted on a 1-mm glass slide and adhered using various epoxies, all of which are IR active. To address these challenges, the results of a transmission µ-FTIR study using a new thin section preparation technique are presented. A cyclododecane treatment is performed, which makes it possible to grind and polish the rock sample to under 50 µm. Replacement of the standard glass slide with a sapphire window removes the IR response from the glass, thereby acquiring a spectrum of only the source rock. The transmission µ-FTIR results show that these thin sections are more effective in determining the kerogen’s thermal maturity using peak ratios of VsCH2 to VasCH2 when compared to standard FTIR, Attenuated Total Reflection FTIR (ATR), and pyrolysis data. This new methodology for transmission µ-FTIR produces a more accurate spectrum, and thus a more reliable prediction for kerogen chemical composition. It also removes the need to isolate the kerogen, enabling rapid analysis of the kerogen, thereby encouraging the development of new approaches to investigating the individual organic macerals within the rock.

SERMACS 789

Purifying complex reaction mixtures via high-performance flash chromatography

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Synthetic chemistry is hard enough; purifying the reaction product can be even more challenging. If your reaction mixture shows you made your target but also many by-products, what do you do? You can resynthesize using different reaction conditions or you can purify using flash chromatography. For many chemists, purification is the logical option though it may be a challenge. In this poster, we show how using TLC and the right purification tools can overcome the purification challenge.

SERMACS 790

Elucidation of greener chemistry methods on the synthesis of O-methyl resveratrol derivatives

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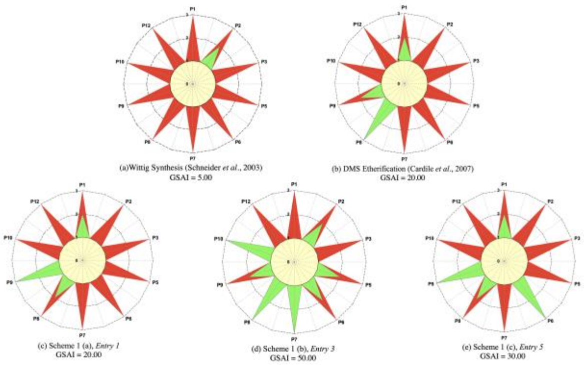
Trimethylated resveratrol analogs increase the bioavailability of resveratrol while maintaining therapeutic cancer activities. Previously reported synthesis of 3,4’,5-trimethoxyresveratrol (3,4’,5-MeORSV) has involved the use of harmful reagents and the production of hazardous byproducts. In the current study, three synthetic schemes are presented that successfully produce 3,4’,5-MeORSV under mild reaction conditions with increasingly benign reagents. Two procedures follow classic Williamson ether synthesis, where stoichiometric amount of strong base generates phenolate anions, which then react with a methylating agent. Of these two procedures, one is carried out at room temperature in DMF, and the other in DMSO under reflux. An additional reaction scheme implements green chemistry methods to methylate resveratrol with dimethyl carbonate as a benign methylating agent and solvent in a solid/liquid phase transfer system. The “Green Star” metric is used to evaluate the degree of greenness of previously reported and novel reactions. It is reported that as 3,4’,5-MeORSV synthesis becomes greener, greater byproduct formation of the dimethylated product, pterostilbene, is observed.



(a)Wittig Synthesis (Schneider *et al.*, 2003)
GSAI = 5.00

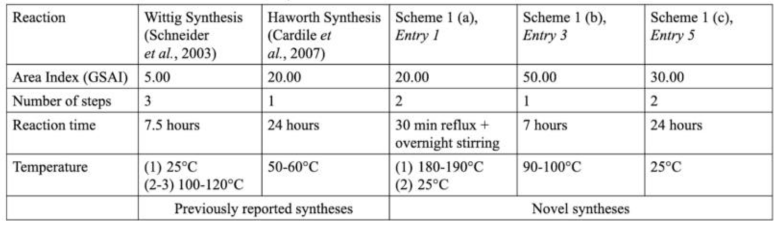
(b) DMS Etherification (Cardile *et al.*, 2007)
GSAI = 20.00

(c) Scheme 1 (a), *Entry 1*
GSAI = 20.00

(d) Scheme 1 (b), *Entry 3*
GSAI = 50.00

(e) Scheme 1 (c), *Entry 5*
GSAI = 30.00

Table 4. Reaction conditions of each synthesis.



Reaction	Wittig Synthesis (Schneider *et al.*, 2003)	Haworth Synthesis (Cardile *et al.*, 2007)	Scheme 1 (a), *Entry 1*	Scheme 1 (b), *Entry 3*	Scheme 1 (c), *Entry 5*
Area Index (GSAI)	5.00	20.00	20.00	50.00	30.00
Number of steps	3	1	2	1	2
Reaction time	7.5 hours	24 hours	30 min reflux + overnight stirring	7 hours	24 hours
Temperature	(1) 25°C (2-3) 100-120°C	50-60°C	(1) 180-190°C (2) 25°C	90-100°C	25°C
	Previously reported syntheses		Novel syntheses		

SERMACS 791

Design and synthesis of EF-24 analogs as anti-cancer agents

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Cancer is one of the leading causes of death in the world today, affecting people of all ages. In spite of how prevalent it is, a cure has not been discovered due to the difficulty of targeting only abnormal cells without harming normal cells. Any effective treatment would kill all cells indiscriminately, which would also risk killing the patient instead of the cancer cells. This has caused researchers in recent years to turn to natural remedies to potentially slow or inhibit cancer cell growth because they could be less likely to harm normal cells in the process of targeting abnormal cells. In Dr. Zingales’ research lab, we focus on chalcones, which are synthesized naturally by plants and have been used extensively in ancient Indian medicine, and determining how useful they may be as a form of cancer treatment. In order to accomplish this, a library of chalcones similar to EF-24, a molecule that has been explored as a potential chemotherapy alternative, were synthesized via the aldol condensation and tested against various types of cancer to determine the ability of each molecule to inhibit the growth of cancer cells.

SERMACS 792

Modeling reactive intermediate analogues of gold(I)-catalyzed reactions by Lewis acid mediated gamma-ionization

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Cationic gold carbene complexes have attracted significant attention, being postulated as intermediates in a range of gold-catalyzed transformations. Regardless of the remarkable progress in the gold (I) catalysis, there remains considerable debate regarding the electronic feature of those species as well as their reactivity. This is mainly due to the lack of proper model system with sufficient reactivity, as the majority of known gold carbene complexes are heteroatom stabilized or sterically hindered. Methoxy group abstraction from a neutral gold precursor with Lewis acids provides a convenient method for generating rare example of reactive gold carbene species in high yield and purity, therefore addressing the issue with isolation of such transient species as well as allowing in situ spectroscopic analysis. Recently, we have reported gold allenylidene species without pi-conjugated heteroatom stabilization. Guided by this, we have extended the gamma-ionization method to *in-situ* generation of gold vinyl carbenes as well as modeling of gold-catalyzed cyclopropanation for gaining mechanistic insight.

SERMACS 793

Corrosion Presentation: Building the First "Steamship" in History

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In 1807, a brilliant, creative, and controversial American by the name of Robert Fulton declared his intent to build an experimental “steamboat,” which would be used to initiate a continuous passenger service between New York City and Albany, New York. With the success of his *North River Steam Boat*, Fulton showed that it was possible to alter artificially both a person’s location and the amount of time it took to change it. In so doing, he also broke through the enormous psychological barrier that had existed in people’s minds; it was, in fact, possible to overcome Nature to practical effect. It took time for many people to accept Robert Fulton’s triumph as the truth. One man who did not need to be convinced was a sloop captain named Moses Rogers. He had witnessed the first successful runs of the *North River Steam Boat* to Albany, and the experience gave him the fever—steamboat fever. Moses soon became one of the first steamboat captains in history, taking command of one of Fulton’s first rivals, the *Phoenix*. In his new profession, Moses learned not only the technicalities of this revolutionary invention, but the peculiarities of a traveling public just getting used to this new mode of transport. In the years immediately following Fulton's success, running these steamboats on rivers, lakes and bays became a normal and accepted part of American life. But taking such a vessel on a voyage across the ocean was a different proposition altogether. Experienced mariners didn’t think it could be done. These early steamboats, they declared, were just too flimsy and unwieldy to withstand the dangers of the deep. Furthermore, corrosion had become an increasingly prominent problem, as steamers ventured into saltier and saltier waters. But Moses Rogers believed it could be done. Combining his knowledge of the old mode of transport (sail) with the new mode of transport (steam), he set out to design a vessel that was capable of overcoming the many dangers of the sea. This craft would be not a steamboat, but a "steamship," the first of its kind. This presentation will show how Captain Rogers specifically addressed the challenge of corrosion in the design and construction of this revolutionary vessel…two centuries ago!

SERMACS 794

Temperature dependent kinetic isotope effects reveal the origins of lipoxygenase C–H activation efficiency

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Enzyme catalyzed C-H activation is one of the most prevalent and fundamental reactions to occur in biological catalysis and their mechanistic understanding is sought to aid in bioinspired catalyst design. Native enzymes catalyzing such reactions are often observed with temperature independent kinetic isotope effects (ΔEa = Ea(D) – Ea(H) ~ 0). The magnitude of this kinetic parameter provides a critical descriptor for the precision of the active site along the reaction coordinate. Strategic site-directed mutations and surface modifications are often accompanied by increases in the magnitude of ΔEa (i.e. > 0) even in cases where the rate constants remain unaltered. Decades of accumulated experimental data could be rationalized from the emergence of a multi-dimensional, nonadiabatic quantum tunneling model, in which the ΔEa serves as a robust kinetic ‘ruler’ for an enzyme’s effectiveness to achieve hydrogenic wavefunction overlap at the tunneling ready state.1 In this talk, an overview of the theoretical model will be presented with references to semi-classic experimental data drawn from the studies on the model tunneling enzyme, soybean lipoxygenase. A more recent study using the ΔEa to provide kinetic characterization for the impact of N-linked glycosylation on tunneling efficiency for a lipoxygenase from a plant pathogen will be discussed.

SERMACS 795

Combined solution and crystal methods reveal the electrostatic tethers that provide a flexible platform for replication activities in the bacteriophage T7 replisome

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Recent structural studies on the bacteriophage T7 DNA replication system have shed light on how multiple proteins assemble to copy two antiparallel DNA strands. In T7, acidic C-terminal tails of both the primase-helicase and single-stranded DNA binding protein bind to two basic patches on the DNA polymerase to aid in replisome assembly, processivity, and coordinated DNA synthesis. Although these electrostatic interactions are essential for DNA replication, the molecular details for how these tails bind the polymerase are unknown. We have determined an X-ray crystal structure of the T7 DNA polymerase bound to both a primer/template DNA and a peptide that mimics the C-terminal tail of the primase-helicase. The structure reveals that the essential C-terminal phenylalanine of the tail binds to a hydrophobic pocket that is surrounded by positive charge on the surface of the polymerase. We show that alterations of polymerase residues that engage the tail lead to defects in viral replication. In the structure we also observe dTTP bound in the exonuclease active site and stacked against tryptophan 160. Using both primer/extension assays and high throughput sequencing, we show how mutations in the exonuclease active site lead to defects in mismatch repair and an increase in mutagenesis of the T7 genome. Finally, using small angle X-ray scattering we provide the first solution structures of a complex between the single-stranded DNA binding protein and the DNA polymerase and show how a single-stranded DNA binding protein dimer engages both one and two copies of DNA polymerase.

SERMACS 796

Conformational dynamics of G protein-coupled receptors: One receptor at a time

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G protein-coupled receptors (GPCRs) are expressed in all human tissues and have an important role in human physiology. The human genome encodes more than 800 GPCRs, and they represent the major target sites for more than 30% of current pharmaceutical drugs. GPCRs are allosteric machines that bind many types of ligands on their extracellular surface and undergo conformational changes of the seven-transmembrane domain (7TM) that activate signal transduction pathways inside the cell. Using single-molecule fluorescence (SMF), which allows direct visualization of individual receptors, we provide a conformational dynamic of the human β_2-adrenergic receptor (β_2AR), a representative class A GPCR. Here, we observed that individual receptor molecules in the native-like environment of phospholipid nanodiscs undergo spontaneous transitions between inactive and active-like two distinct conformational states. For the apo receptor, the inactive state populated more but frequently transitions to the active-like state even in the absence of extracellular ligand, which signifies the basal signaling activity of the receptor. Binding of the full agonist shifts the conformational distributions towards the active-like conformation by increasing the frequency of activation and decreasing the frequency of deactivation transitions. In contrast, binding of the inverse agonist stabilizes the inactive state of this receptor by increasing the frequency of deactivation transitions. Overall, these results help to rationalize the ligand-based transitions of the individual receptor, providing novel insights into a global signaling mechanism in class A GPCRs. This work presented here can provide a platform for understanding the underlying mechanism of GPCR-targeting drugs and expected to offer new opportunities to design and screen small molecules for improved drug efficacy.

SERMACS 797

Molecular mechanisms of enzyme catalyzed protein unfolding and translocation by class 1 AAA+ motors

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AAA+ molecular motors involved in protein quality control are at the heart of many biological functions. Here I will discuss our efforts on three model AAA+ driven motors, the prokaryotic ClpA and ClpB and eukaryotic Hsp104. ClpA is a hexameric ring motor that uses the energy from ATP binding/hydrolysis to processively translocate a polypeptide substrate through its axial channel for one of two purposes: protein remodeling or ATP dependent proteolysis. When catalyzing proteolysis, ClpA associates with the tetradecameric serine protease, ClpP, to form the ATP dependent protease ClpAP, which is architecturally identical to the 26 S proteasome in humans. ClpB and Hsp104, on the other hand, have the unique ability to disrupt protein aggregates in vivo and do not associate with any known proteases. Due to the structural similarity between ClpA and ClpB/Hsp104 it has long been proposed that ClpB and Hsp104 processively translocate a polypeptide through their axial channels of the hexameric ring structures they form; as do ClpA and ClpX. However, for ClpB/Hsp104 and related enzymes, this has been difficult to show because these enzymes do not covalently modify the substrate on which they translocate. We have developed a transient state polypeptide translocation strategy that is sensitive to processive translocation catalyzed by ClpA in the absence of proteolytic degradation catalyzed by ClpP. Using this approach, we have shown that ClpA employs a different molecular mechanism when translocating polypeptide in the absence of the protease vs. when it is associated with the protease. Applying this approach, we have shown, for both ClpB and Hsp104, that they take, at most, two translocation steps on the polypeptide substrate before rapid dissociation. These results reveal that ClpB and Hsp104 exhibit low processivity and are not likely to fully translocate a polypeptide through their axial channels during protein disaggregation. These findings and the application of these approaches have broad impact on the examination of many AAA+ molecular motors that do not covalently modify the substrate on which they operate.

SERMACS 798

Temeprature dependence of conformational heterogeneity of enzyme thermolysin

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Numerous studies have suggested a significant role that protein dynamics play in optimizing enzyme catalysis, and changes in conformational sampling offer a window to explore this role. Thermolysin from *Bacillus thermoproteolyticus rokko*, which is a heat-stable zinc metalloproteinase, serves here as a model system to study changes of protein function and conformational sampling across a temperature range of ambient temperature. The temperature dependence of kinetics of thermolysin showed a biphasic transition that points to potential conformational and dynamic differences across this temperature. The non-Arrhenius behavior observed resembled results from previous studies of a thermophilic alcohol dehydrogenase enzyme, which also indicated a biphasic transition at ambient temperatures. To explore the non-Arrhenius behavior of thermolysin, room temperature crystallography was applied to characterize structural changes in a temperature range across the biphasic transition temperature. The alternate conformation of side chain fitting to electron density of a group of residues showed a higher variability in the temperature range from 26 to 29 °C, which indicated a change in conformational sampling that correlated with the non-Arrhenius break point.

SERMACS 799

Hydrogen peroxide activated estrogen receptor beta ligands

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Chronic inflammation is linked to a variety of diseases including neurodegenerative diseases and activation of estrogen receptor beta apprears to provide neuroprotection. With chronic inflammation comes an overproduction of reactive oxygen species such as hydrogen peroxide. Therefore, we have synthesized boronate ester pro-estrogens that are activated selectively in the presense of hydrogen peroxide. The boronate ester decreases binding affinity for the receptor but the active ligand is released in cellular models with enhanced hydrogen peroxide.

SERMACS 800

Insights to a structure-based catalytic mechanism from neutron and X-ray crystallographic structures of the *Thermococcus thioreducens* inorganic pyrophosphatase

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The neutron crystallographic structure of the soluble Inorganic Pyrophosphatase (IPPase) from *Thermococcus thioreducens* has been determined to 2.2Å from microgravity-grown crystals. Coupling the neutron IPPase structure to those previously determined by X-ray: 1) substrate-free IPPase with Ca^{+2} analyzed at room temperature (22ºC) at 1.85Å (PDB ID 3I98); 2) Ca^{+2}-bound IPPase complexed with the $P_2O_7^{-4}$ substrate at 1.44Å (PDB ID 3Q4W); 3) Ca^{+2}-bound IPPase complexed with the $P_2O_7^{-4}$ substrate at 1.35Å (PDB ID 3Q9M); 4) Mg^{+2} activated IPPase bound to hydrolyzed substrate at 0.99Å (PDB ID 3Q46); and 5) Mg^{+2}-bound IPPase complexed with SO_4^{-2} at 1.08Å (PDB ID 3Q5V), a structure-based catalytic mechanism associated with the hydrolysis of pyrophosphate substrate is proposed. This investigation identifies the hydrogen atoms in IPPase that may be important for enzymatic activity. Since there are extensive active site homologies among the Inorganic Pyrophosphatases, the proposed catalytic mechanism may be a representative model for catalysis of all inorganic pyrophosphatases in the same family.

SERMACS 801

Radicals, switches, and a protein-based cofactor: Expanding the catalytic abilities of an old active site

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Catalase-peroxidase (KatG) is a bifunctional heme-dependent enzyme whose catalase activity rivals that of the most robust monofunctional catalases. KatG is widely distributed among prokaryotes and fungi and is particularly prominent among pathogens, owing to the copious quantities of H_2O_2 produced by higher eukaryotes in response to infection. In *Mycobacterium tuberculosis*, KatG activates the prodrug isoniazid, one of the most widely used agents in tuberculosis (Tb) chemotherapy, and mutations to the *katG* gene account for the large majority of isoniazid resistant Tb. KatG also represents a rich system for investigation of the relationship between enzyme structure and mechanism. It achieves its remarkable catalase activity with a structure that bears no resemblance to typical catalases. Instead, KatG belongs in the plant peroxidase superfamily, where it is the only member with appreciable catalase activity. A covalent adduct between a methionine, a tyrosine, and an active-site tryptophan (MYW adduct) generates a protein-based cofactor that is essential for KatG's catalase activity and gives rise to an entirely unique mechanism for H_2O_2 disproportionation. Our investigations center on the post-translational formation of the MYW adduct, the unique mechanism that KatG uses for H_2O_2 disproportionation, and the novel strategy the enzyme uses to protect itself from inactivation. We employ a range of steady-state and transient-state (e.g., optical stopped-flow and freeze quench EPR) techniques to investigate a panel of KatG variants. Our investigations suggest that all of these phenomena are anchored by essential intramolecular electron transfer events. These involve KatG's heme, its MYW adduct, and strategically arrayed oxidizable tryptophan/tyrosine residues. Further, a conformationally dynamic "arginine switch" appears to be a critical regulator of intramolecular electron transfer, and thus is a central player in almost every aspect of KatG catalysis. The mechanistic novelties of KatG catalysis may have important implications in the context of its use by several notorious pathogens and isoniazid activation and resistance in Tb.

SERMACS 802

Oxidative stress promotes altered YME1L conformational dynamics

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Oxidative stress is a common challenge to mitochondrial function where reactive oxygen species are capable of significant organelle damage. The generation of mitochondrial reactive oxygen species occurs in the inner membrane and matrix compartments as a consequence of subunit function in the electron transport chain and citric acid cycle, respectively. Maintenance of mitochondrial proteostasis and stress response is facilitated by compartmentalized proteases that couple the energy of ATP hydrolysis to unfolding and the regulated removal of damaged, misfolded, or aggregated proteins. The mitochondrial protease YME1L functions in the maintenance of proteostasis in the intermembrane space. YME1L is an inner membrane-anchored hexameric protease with distinct N-terminal, transmembrane, AAA+ (ATPases associated with various cellular activities), and C-terminal M41 zinc-dependent protease domains. The effect of oxidative stress on enzymes such as YME1L tasked with maintaining proteostasis is currently unclear. We show here that recombinant YME1L undergoes a reversible conformational change in response to oxidative stress that involves the interaction of hydrogen peroxide with YME1L with affinities equal to 31 ± 2 and 26 ± 1 mM for conditions lacking or including nucleotide, respectively. Our molecular dynamics data demonstrate that hydrogen peroxide alters the YME1L free energy landscape, thereby allowing for more frequent conformational transitions between states. Such conformational dynamics allow for increased ATP binding as observed by a 2-fold increase in the rate constant for high-affinity ATP binding from $(8.9 \pm 0.2) \times 10^{5}\ \mathrm{M^{-1}\ s^{-1}}$ to $(1.5 \pm 0.1) \times 10^{6}\ \mathrm{M^{-1}\ s^{-1}}$. Taken together, these data may suggest a mechanism for the regulated processing of YME1L by other inner membrane proteases.

SERMACS 803

AAA ATPase AFG1 helps maintain protein homeostasis in the mitochondrial matrix

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Failure to maintain proper mitochondrial function is associated with altered protein and ion homeostasis, increased oxidative damage, and a decline in ATP production. To avert such deleterious events, mitochondria are equipped with evolutionarily conserved, dedicated factors and mechanisms known as mitochondrial quality control (MQC) that assure the fidelity of the organelle. While the importance of MQC is commonly appreciated, the identities and roles of many of its individual components are only beginning to emerge. Here we identify a novel role for the conserved mitochondrial AAA ATPase Afg1 in mediating mitochondrial protein homeostasis during aging and in response to various cellular challenges. *Saccharomyces cerevisiae* cells lacking functional Afg1 are hypersensitive to oxidative insults, unable to tolerate protein misfolding in the matrix compartment, and exhibit progressive mitochondrial failure as they age. We also extended this investigation to a metazoan system to show that the roundworm Afg1 ortholog is also required for mitochondrial protein homeostasis: its loss impairs oxidative stress tolerance and shortens chronological lifespan. Our results indicate that Afg1 is a novel protein quality control factor, which plays an important evolutionarily conserved role in mitochondrial surveillance and cellular and organismal health.

SERMACS 804

Sequestered imine intermediate and interplay of nucleophilic catalysis with proton transfer during reduction of nitrile to amine by the nitrile reductase QueF from *Escherichia coli*

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Enzymatic reactions involving multiple catalytic step have drawn considerable interest across disciplines for their biological importance and for the mechanistic challenges they present. The enzyme QueF catalyzes the conversion of 7-cyano-7-deazaguanine (preQ$_0$) to 7-aminomethyl-7-deazaguanine (preQ$_1$), a biologically unique four-electron reduction of a nitrile to an amine. The catalytic reaction involves a covalent thioimide adduct between the enzyme and preQ$_0$ which undergoes reduction to preQ$_1$ in two NADPH-dependent steps, presumably *via* an imine intermediate. Imine intermediate is easily hydrolyzed to aldehyde by water attack. Protecting a labile imine is thus fundamental for the enzyme QueF to complete nitrile-to-amine reduction. In the QueF from *E.coli*, the conserved Glu89 and Phe228 residues together with a mobile structural element comprising the catalytic Cys190 form a substrate-binding pocket. The pocket precludes water from intercepting substrate or intermediate. We show here that residue substitutions (E89A, E89L, F228A) targeted at opening up the binding pocket weakened preQ$_0$ binding at the preadduct stage and profoundly affected on catalysis. Unlike wildtype enzyme, the QueF variants (including L191A and I192A) were no longer selective for preQ$_1$ formation. Obtained products were identified by LC-MS and ^{1}H-NMR analysis. The E89A, E89L and F228A variants performed primarily a two-electron reduction of preQ$_0$, releasing hydrolyzed imine (7-formyl-7-deazaguanine) as the product. The preQ$_0$ reduction by L191A and I192A gave preQ$_1$ and 7-formyl-7-deazaguanine. The proportion of 7-formyl-7-deazaugnaine and preQ$_1$ relied on substrate concentration, suggesting a competitor-induced release of the imine intermediate. Additionally, we show the functional interplay between Cys190, Asp197, and His229 residues in covalent catalysis. Substitution of Cys190 or Asp197 (C190A, C190S, D197A, D197H) eradicated preQ$_0$ covalent binding and largely disrupts the nitrile-to-amine reductase activity. The H229A variant forms the thioimidate adduct and shows less than 4% activity of wild-type *E.coli* QueF. Proton transfer upon non-covalent binding of preQ$_0$ was studied by using isothermal titration calorimetry. The enzymatic mechanism of preQ$_0$ reduction to preQ$_1$ with proton transfer is proposed based on the experimental data and protein structural analysis.

SERMACS 805

Synthesis of functionalized biodegradable poly(α-methylene-γ-butyrolactone)

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Due to their good mechanical properties, hydrolyzability and biocompatibility, aliphatic saturated polyesters have been extensively investigated with applications in packaging, drug delivery and medical implantation devices. The best and most reliable method of synthesizing high molecular weight polyesters is via ring-opening polymerization (ROP) of lactones with a relatively high strain energy using metal initiators for chain-growth polymerization. However, unsaturated polyesters, which show great scientific and technological promise for producing tailor-made functionalized biodegradable materials of commercial importance, have not been extensively studied. α-Methylene-γ-butyrolactone (α-MBL), also known as Tulipaline A, has received much interest in the synthesis of sustainable unsaturated polyesters since it is the simplest member of a class of naturally occurring sesquiterpene lactones found in tulips. The unfavorable thermodynamics involved in the ROP of MBL results in too small negative change of enthalpy (ΔH) to offset a large negative entropy change (ΔS). As a result, MBL prefers vinyl addition polymerization to ROP. Because vinyl-addition is favored over ring-opening at room temperature due to the stability and low strain energy of five membered γ-BL ring making it non-polymerizable, special conditions and reagents must be used to favor the ring-opening polymerization. We report the ring-opening homopolymerization of α-methylene-γ-butyrolactone using lanthanide catalyst at very low temperatures into unsaturated polyesters. The unsaturated polyesters can be functionalized by converting the exocyclic C=C double bonds in the polyester backbone into amino, hydroxyl, halogenated, or carboxylic acid functional groups for tailor-made applications in biomedical and shape memory research.

SERMACS 806

Bio-based composites with enhanced matrix-reinforcement interactions from the polymerization of *α*-eleostearic acid

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Vegetable oil-based composites have been proposed as interesting bio-based materials in the recent past. The carbon-carbon double bonds in unsaturated vegetable oils are ideal reactive sites for free radical polymerization. Without the presence of a reinforcement, typical vegetable oil-based polymers cannot achieve competitive thermo-mechanical properties. Compatibilizers have been utilized to enhance the adhesion between resin and reinforcement. This work discusses the antagonist implications of polarity and crosslink density of an unprecedented polar *α*-eleostearic acid-based resin reinforced with *α*-cellulose, eliminating the need of a compatibilizer. It is shown that the polar regions of*α*-eleostearic acid can interact directly with the polar reinforcement. The successful isolation of *α*-eleostearic acid from tung oil was verified via GC-MS, ^{1}H NMR, Raman, and FT-IR spectroscopies. The optimal cure schedule for the resin was determined by DSC and DEA. The composites' thermo-mechanical properties were assessed by TGA, DSC, and DMA.

SERMACS 807

Hydrogel stabilized, fully organic, X-ray radioluminescent crystalline colloidal arrays

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Fully organic, x-ray active colloidal crystalline arrays (CCAs) are encapsulated in hydrogel networks in order to generate thin film devices with controllable emission characteristics and color filtration capabilities. Encapsulating electrostatically stabilized CCAs of monodispersed polystyrene-co-poly(propargyl acrylate) nanoparticles in a poly(ethylene glycol) methacrylate based hydrogel network has advantages over the liquid system in regard to the stability of the crystal structure. The hydrogel can be post functionalized with organic scintillators (azide modified anthracene) and organic dyes (azide modified naphthalimide and rhodamine B) via a copper(I) catalyzed azide/alkyne cycloaddition (CuCAAC) "click" reaction. By coupling the organic scintillator with fluorophores that form x-ray induced sequential Förster Resonance Energy Transfer (FRET) pairs, the hydrogel's emission can be tuned to span the full visible spectrum. Blue-emitting, x-ray excited anthracene transfers energy to green-emitting naphthalimide which can then transfer energy to red-emitting rhodamine B. The rejection wavelength of the CCA encapsulated hydrogel can be coupled to the x-ray excited optical luminescence to fine tune color characteristics of the gel.

SERMACS 808

Synergistic effects of potassium dimethyl 5-sulphonatoisophthalate (LAK-301) and lignin coated cellulose nanocrystals (L-CNCS) on the nucleation and crystallization of poly(lactic acid) (PLA)

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Bio-based, biodegradable polymers have the potential to replace conventional, non-biodegradable, petroleum-based plastics. However, much like plastics derived from petroleum, bio-based polymers require additives to improve their thermomechanical properties. In this study, high torque melt mixing was utilized to fully disperse lignin coated cellulose nanocrystals (L-CNCs) and potassium dimethyl 5-sulphonatoisophthalate (LAK-301) in commercially available poly(lactic acid) (PLA) which is from a bio-based feedstock. The use of PLA has been limited by it slow crystallization rate. LAK-301 is used commercially as a nucleating agent to increase both the rate and degree of crystallization of PLA. We have found that the incorporation of both LAK-301 and L-CNCs in PLA led to a synergistic nucleation of PLA. We have utilized DSC, DMA, TMA, and XRD to characterize the rate and degree of crystallization as well as crystal morphology. The results of this work will be reported.

SERMACS 809

Preparation and characterization of poly(lactic acid) (PLA) and poly-3-hydroxybutyrate (PHB) polymer matrix nanocomposites prepared with bio-based, biodegradable cellulose/lignin nanofillers

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The use of biobased biodegradable fillers as reinforcement or nucleating agents in biobased biodegradable polymers is essential to provide the desired thermomechanical properties while maintaining 100 % biobased content and preserving biodegradability. Biobased polymers such as of poly(lactic acid) (PLA) and poly-3-hydroxybutyrate (PHB) are candidates to replace non-biodegradable, petroleum-based polymers; however, they both require fillers to impart desired thermomechanical properties. Based on the chemical, physical, and mechanical properties, and biodegradability cellulose nanomaterials (CNs) are excellent candidates to serve as fillers for biobased polymers. However, because of the hydrophilicity of CNs, achieving excellent dispersion and distribution in hydrophobic polymers is a challenge. We will report on our success in using lignin to support the dispersion and distribution of cellulose nanomaterials in PLA and PHB, and PLA/PHB blends via high torque melt mixing. With lignin serving as a compatibilizer, there is excellent interfacial interaction with the polymer matrix, which results in a significant improvement in rheological and thermo-mechanical properties. Excellent dispersion and compatibility of the CNs and lignin in the polymer matrix allowed the generation of a high density of nucleating sites and improved melt strength. This present study demonstrates that lignin/CNCs can serve as excellent fillers for PLA, PHB, and PLA/PHB blends for the development of fully biobased nanocomposites.

SERMACS 810

Bio-based antimicrobial coating

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Antimicrobial coatings have been extensively used to prevent growth and proliferation of pathogenic bacteria. General approaches include the incorporation of free biocides, and function via the release of biocides into the surroundings, so the antimicrobial activity would diminish in time. Even worse, leaching of biocides may cause environmental concern and trigger antibiotic resistance. We have designed and synthesized a series of reactive, hydrophobic quaternary ammonium compounds (QACs), and successfully developed non-leaching antimicrobial polymer coating. We have prepared antimicrobial coating on the basis of readily available soybean oil (SBO) derivatives, demonstrating strong antimicrobial property against both Gram-positive and Gram-negative bacteria. The strong antimicrobial activity is due to the significant surface enrichment of QACs at the coating surface. We further developed antimicrobial coating from SBO-based polyurethane dispersions (PUDs). The antimicrobial action of these coating is based entirely on contact killing, without leaching of bactericidal species.

SERMACS 811

Enzymatic synthesis of polylactide in ether-functionalized ionic liquids

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Polylactide (PLA), often referred as poly(lactic acid), can be prepared from renewable lactic acid or lactide, and thus is known as sustainable and biodegradable polymer. In addition to its uses in packaging and horticultural materials, PLA has important applications in biomedical fields including controlled drug delivery carriers, tissue engineering scaffolds, surgical suture and bone fixation materials. Enzymatic ring-opening polymerization (ROP) becomes a ‘greener’ approach to the synthesis of polylactides; however, this method is challenged by the lack of enzyme-compatible reaction system at high temperatures (>100 °C). Our group designed a series of lipase-compatible ether-functionalized ionic liquids that have high short-term and long-term thermal stability. These ionic liquids were used as viable solvents for the enzymatic ROP catalyzed by immobilized *Candida antarctica* lipase B at 130 °C, affording poly(L-lactide) with moderate yields (30–48%) and high molecular masses (M_w ~20 kDa).

SERMACS 812

Multifunctional polyacrylates with reducing properties in biomedical applications

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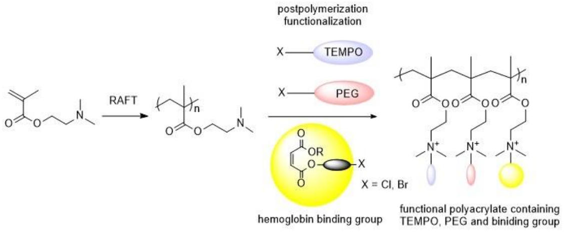
Polyacrylates containing ancillary NMe_2 groups were synthesized in controlled fashion via Reversible Addition/Fragmentation Chain Transfer (RAFT) polymerization. The resulting polyacrylates (DP = 20-50) were investigated via MALDI-ToF mass spectrometry and suggested good molecular weight control. In our efforts to generate new materials capable of detoxifying cell-free hemoglobin, the NMe_2 groups of the polyacrylates were functionalized with three different functionalities via quaternization with activated halido groups. In this combined fashion we accomplished the simultaneous attachment of three functionalities, 1) 2,2,6,6-tetramethylpiperin-1-oxy (TEMPO) as the reducing moiety, 2) polyethylene glycol (PEG) for water-solubility and improved protein stability and 3) various maleates as a binding group to the polyacrylate template, while also controlling the degree of functionalization and the ratio between those functionalities. This was demonstrated via ^{1}H NMR spectroscopy. While PEG and TEMPO derivatives were accessible in near-quantitative, one-step syntheses, a more elaborate route was needed to connect the maleate to the polyacrylate. We have started initial investigations into the synthesis of the hemoglobin complexes of these polymers.



Synthetic strategy to a trifunctional polyacylate for the detoxification of cell-free hemoglobin.

SERMACS 813

Physical insights on mechanism of photoinduced charge transfer & charge recombination transfer via internal acceptors in n,n'-dialkylaniline organic dyes: Computational approach

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Environment-friendly and renewable energy systems have drawn more attention nowadays due to increasing clean energy demands in “Generation Y”. Captivating advantages of high molar extinction coefficient, flexible assembling, low-cost fabrication, and metal-free organic dye-sensitized solar cells (DSSCs) have attained considerable interest as an alternative renewable energy source in present decade. A series of novel N,N-dialkyl-/diaryl-aniline (**NDI**)-based organic dyes with D-D-A-π-A motifs designed from the Quantitative Structure-Property Relationships (QSPR) and systematically studied photophysical properties and their relationship to photo-conversion efficiency (PCE) of DSSCs. To explore the potentiality of the dyes, we employed density functional theory (DFT) and time-dependent DFT (TD-DFT) for isolated dyes. The interfacial phenomenon of the dyes and semiconductor (TiO_2) revealed by cluster DFT and periodic DFT. Outstanding photophysical properties like electron injection driving force, electron injection time, dye regeneration were investigated of the isolated dyes as well the process and strength of charge transfer and separation visualized with charge difference density and index of spatial extent under DFT and TD-DFT framework in the present study in continuation of our earlier work to strengthen our claim. First principle approach including Van der Waals density functional calculation of **dye@TiO_2** interface indicates that all of the designed dyes have optimal interfacial behavior. Bader charge analysis, partial density of state, charge density and electrostatic potential difference of all the analysis confirms that designed dyes are the most efficient candidate for DSSCs and the properties to emerge as effective dye-sensitizers. **Key Words:** Dye-sensitized solar cell, Cluster DFT, Periodic DFT, Interface, Photosensitizers, PCE.

SERMACS 814

Preparation and characterization of poly(lactic acid) nanocomposites incorporating lignin-cellulose nanocrystals (SL-CNCS) prepared by sulfuric acid hydrolysis

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The development of environmentally friendly polymer matrix composites produced from renewable resources that can be biodegraded to benign carbon dioxide and water by microorganisms are of great interest. Biobased, biocompatible, compostable poly(lactic acid) (PLA) and nanocellulose/lignin (SL-CNCs), prepared by sulfuric acid hydrolysis, were processed into nanocomposites by high torque melting mixing with Haake Rheocord 90 melt mixer to give polymer matrix composites (PMCs) with excellent dispersion and distribution of the nanofiller. The new nanocomposites were compression molded using a Wabash G30H-15-CPX hot press. The use of lignin as a compatibilizer supported dispersion and distribution of CNCs in PLA by improving interfacial interaction with the matrix and led to increased thermal stability at low loadings in the PLA matrix. The sulfonated lignin acts as both a compatibilizer and a plasticizer in the PLA matrix. Neat PLA is brittle and has low stiffness, which leads to poor mechanical performance. The SL-CNCs act as nucleating agents, thus leading to faster crystallization, a higher degree of crystallinity, and a higher Young’s modulus in the nanocomposites. The objective of this research was to examine the behavior of SL-CNCS at various lignin/CNC ratios and loadings in NatureWorks PLA 4043D matrices by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), tensile testing, thermal gravimetric analysis (TGA), wide angle X-ray diffraction, and melt rheology.

SERMACS 815

The ARC network: Driving change through an empowered virtual community

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Reaching gender parity in science, technology, engineering, and mathematics (STEM) cannot be accomplished by approaches that solely focus on recruitment or “fixing” underrepresented groups; rather, efforts that connect and energize people, cross divides, and drive systemic change toward equity are needed. The ADVANCE Resource and Coordination (ARC) Network strives to advance STEM workplace equity nationally by facilitating the adoption and implementation of evidence-based systemic initiatives by institutions of higher education and other STEM organizations. Funded by the National Science Foundation, the ARC Network offers a virtual community platform for engagement in curated research, resources and tools: facilitates authentic, intentional dialogue between researchers and practitioners; and provides guidance on weaving inclusiveness into organizational principles and practices. The ARC Network inspires the community to move our knowledge on systemic change forward by using an intersectional lens to fluently adapt existing resources to organizational, departmental, and demographic contexts. This wide-reaching, action-oriented community bridges the gap between research and practice, empowers individuals across geographic, organizational, and social divides, and equips change agents with the tools they need for multiple levels of transformation. This session will share ARC's innovative virtual community engagement strategy with participants seeking to educate, mobilize, and empower others toward systemic change. Our strategy moves beyond traditional listservs and social media to a culture that incorporates regular programming, like live online chats, podcasts, and weekly shout-out threads as consistent ways for community members to interact, share their expertise, and create collective impact. As the go-to hub for the community collaboration, the ARC Network platform offers events hosted by the community and their institutions and provides online learning opportunities, such as webinars and virtual workshops, to continuously grow the capacities of those dedicated to STEM equity.

SERMACS 816

Starting a SACNAS chapter at the University of South Florida

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As a Hispanic female chemistry graduate student, I felt the need to connect with a community of fellow scientists who share a similar background. In searching for an organization which met these criteria, I found that my campus lacked a network specific for underrepresented minority students in STEM. Therefore, founding a local chapter of the Society for the Advancement of Chicanos/Latinos and Native Americans in Science (SACNAS) was imperative. Research shows that undergraduate and graduate students benefit from meaningful associations with peers, mentors, and teachers throughout the demanding process of earning a degree. Membership in clubs and organizations has been shown to profit students' overall educational experience, not only through greater involvement in the university's activities, but especially through supportive social networks that often transcend the college years. In an effort to increase minority participation in STEM areas, SACNAS at USF helps foster a network of students, faculty, and industry personnel in the Tampa Bay area. There have been difficulties and successes as part of this journey in the past year, as well a steady growth in membership, participation, and support. As a new local chapter, SACNAS at USF looks forward to providing all of its members and the local community a safe space to share experiences, bring their own strengths and ideas to construct a strong web of scientists from all backgrounds that will impact society in a meaningful way.

SERMACS 817

Transgender and gender non-binary STEM students: Academic climate and persistence

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Past studies suggest that institutions of higher education remain organized—systemically, structurally, and programmatically—around discourses and practices that uphold traditional notions of sexuality and gender identity. For many LGBTQPIA+ (queer-spectrum) college students, their undergraduate experience is heavily influenced by these heteronormative academic environments. Over the last decade, campus climate literature has examined the experiences of queer-spectrum college students. Other studies have begun to illuminate queer-spectrum student experience within STEM disciplines. Our presentation focuses on a sample of queer-spectrum students in a variety of STEM disciplines. This presentation will help faculty within Chemistry to develop a better understanding of these students' experiences in their courses. Our presentation will illuminate the specific academic contexts that influence trans-spectrum STEM students' perceptions about persisting in their STEM majors. Understanding how these students navigate their academic climate while immersed in these contexts encourages thoughtful dialogue and fosters resistance to the hetero cis-normative barriers queer-spectrum students face in their pursuit of a STEM degree, thereby facilitating trans-spectrum students' persistence and success. Our study adds to the emerging literature on queer-spectrum STEM students by focusing exclusively on the academic climate and perceptions of persistence. As part of a larger and on-going study, we conducted in-depth interviews with seven STEM majors at six universities who identified their gender identity as transgender or non-binary. Our sample included three Asian/Chinese students, three White students, and one American Iranian student. Six of our participants were in their senior year of study and one had just recently graduated. A variety of STEM majors are represented in our sample, as shown in the table below. This study helps fill the gap in the literature by focusing specifically on trans-spectrum STEM majors. A narrative analysis of in-depth interviews allows us to capture the academic climate and its effects on trans-spectrum student experiences in STEM majors. of seven trans-spectrum identified STEM majors. The interviews covered a range of experiences in the students' lives, including their experiences of the academic climate and their perceptions of their interest in maintaining a STEM Major.

SERMACS 818

Out of the closet and into the chemistry classroom: Importance of visibility

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How and when to share LGBTQ+ identity in the chemistry classroom can be challenging. "Does it matter if my students know I'm gay?" However subtle or grand, communicating such identity builds opportunities for connection that can have lasting impact on our students and colleagues. Through personal anecdotes, we will explore why being visible in our LGBTQ+ identity is important to creating inclusive classrooms and an inclusive chemistry discipline.

SERMACS 819

Increasing diversity in chemistry and physics graduate programs by focusing on best practices in inclusion and recruitment

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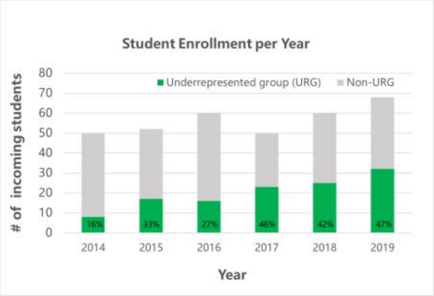
In 2017, the Inclusion & Diversity Initiative within UO's Master's Industrial Internship Program was launched to create a more inclusive and diverse student population. Currently in the second year of a 5 year timeline, the program has instituted a multi-tiered recruitment, retention and mentorship approach. Additionally, a weekly workshop series and symposium has been created to empower all students with the foundational knowledge necessary to be inclusive team members and future inclusive leaders while concurrently promoting a sense of belonging for all students in the program. To date, the program has observed a promising improvement in the culture and rapport among students and a notable increase in enrollment of traditionally underrepresented groups in chemistry and physics.



SERMACS 820

Student projects in the quantitative analysis laboratory

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Chemistry majors in our undergraduate program are required to take a Quantitative Analysis course where students acquire theoretical and practical knowledge on quantifying analytes in a variety of samples. Aside from in-class instruction and lecture, students also participate in weekly laboratory experiments in which they take a hands-on approach to learning techniques commonly used in analytical chemistry following a given procedure with little opportunity to think independently. Students in the Honors College have the option of being involved in independent research projects for Honors credit hours, and along with the course instructor, work on developing and optimizing new laboratories for this course. This approach challenges students to become more independent in their laboratory work and gives them the satisfaction of creating a useful product. Student participation in these projects has resulted in new high-performance liquid chromatography and cyclic voltammetry experiments which are currently carried out by students enrolled in the course.

SERMACS 821

Project-based integrated lecture and laboratory upper division analytical chemistry curriculum

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Over the last few years, we have worked to develop our Analytical curriculum that incorporate a scaffolded project-based learning approach and prepares students to carryout independent projects. In these courses, students work in teams to complete a series of projects. Within the Quantitative Analysis course the projects are designed to review relevant General Chemistry concepts, introduce and review new course content and develop both laboratory and interpersonal skills. The complexity of the projects increase over the course of the semester culminating in an end of the semester project where students are asked to plan and carryout an analysis involving the determination and quantification of caffeine. This design then follows into the Instrumental Analysis course where students work in teams on projects of their own design within a set of selected research areas. In these projects, the theory of the chosen instrument is learned and the necessary Quantitative Analysis principles are reviewed during hands-on experimentation. The general approach and setup of these courses and student impressions will be addresses.

SERMACS 822

Bioanalytical chemistry: Classroom undergraduate research experience

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The Department of Chemistry and Biochemistry at College of Charleston serves undergraduates exclusively and strives to provide both rigorous coursework and practical laboratory training. Our department offers separate B.S. degrees in Chemistry and Biochemistry, both of which are ACS-certified. Chemistry majors are required to take Instrumental Analysis lecture and lab, but Biochemistry majors are not due to their higher credit load. In order to provide further training to these students, as well as Biology majors who minor in Chemistry, we sought to develop a research-based course focused on the analysis of biological molecules. Here, we describe Bioanalytical Chemistry, which has been taught twice in the past two years. It features one hour of lecture and three hours of lab per week and is co-taught by a mass spectrometrist and a bioorganic chemist with expertise in peptide synthesis and structural analysis. Students work in teams of two to three persons, and each team is provided an unknown peptide to characterize throughout the semester. Students gain hands-on experience with high-performance liquid chromatography (HPLC), matrix-assisted laser desorption/ionization – time-of-flight mass spectrometry (MALDI-TOF MS), electrospray ionization – linear quadrupole ion trap tandem mass spectrometry (ESI-LQIT MS/MS), and nuclear magnetic resonance (NMR). The peptides and experiments chosen to date have been based on the interests of our respective research programs, which focus on prebiotic peptide evolution and neuropeptide structure and function. Student contributions from this course have advanced research projects in both groups.

SERMACS 823

Incorporating current events in the undergraduate analytical chemistry laboratory

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From new and emerging drugs of abuse to a medical mystery resulting in the accidental poisoning of a child by an arts and craft toy to the Curiosity rover's ChemCam zapping lasers at rocks on Mars, scientific writing is more and more prevalent on social media and popular news outlets. Figures of merit, units of concentration, etc. are used mainstream, sometimes inappropriately. Through oral and written assignments, students are asked to find and critique a popular source that links current events to their curriculum. Then, when possible, develop a quantitative or instrumental analysis laboratory. This presentation will provide examples and an overview of the efforts we have taken to incorporate current events into the coursework for general chemistry 2, quantitative analysis, forensic chemistry and instrumental analysis.

SERMACS 824

How clean is the water: Student designed analytical lab project

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An integral part of teaching a laboratory chemistry course is helping students to see the real world connections. For the past three years, we have made use of the WaterHub, a first of its kind water recycling plant on the Emory campus, to bring these connections into the undergraduate analytical chemistry lab course that is required for BS and BA chemistry majors. As part of the laboratory curriculum, students learn about the mission and operation of the WaterHub, and how the water is cleaned. They then collect samples of the recycled water and design protocols to test various chemical properties of their samples. This talk will present a quantitative analysis of student results for this laboratory exercise. Student attitudes toward the project and the advantages and limitations of this student-driven experiment will also be discussed.

SERMACS 825

Measuring mass percent calcium in *E. carinifera* and *E. modesta* gastropod shells: Pilot course-embedded undergraduate research experience for analytical chemistry laboratory

***Kathryn Zimmermann**, kzimmermann@ggc.edu, Xiaoping Li, Wenlin Huang, Rashad Simmons, Michael Kirberger, Hongxia Guan, Simon Mwongela, Christopher Brown, Riccardo Fiorillo. Georgia Gwinnett College, Lawrenceville, Georgia, United States*

A pilot course-embedded undergraduate research experience (CURE) was implemented into the Georgia Gwinnett College analytical chemistry laboratory curriculum during the 18-19 academic year. The research question and subsequent study focused on the analysis of calcium concentrations in *E. carinifera* and *E. modesta* gastropod shells, comparing populations infected by parasitic trematodes. This undergraduate research project utilized EDTA titration and focused on building and assessing STEM competencies such as technical skills (method development and titration skills) and quantitative reasoning skills. Preliminary self-reported student gain and instructor-assessed data from an experimental and control section of CHEM 3000K from the first year of pilot implementation will be presented.

SERMACS 826

Using nanoparticles in undergraduate research to teach analytical techniques

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Analytical techniques are one of the most widely required skills by the chemical work force. As such, it is crucial for undergraduate students in pre-health and chemistry programs to master them. However, it is quite a challenge to teach these skills effectively in the traditional classroom, as the examples used have no significance to the students and the lab experiments are often done incorrectly. These issues hamper the connection (i.e. the “ah ha” moment) for students known to improve comprehension and retention. In addition to the traditional classroom, analytical skills can be taught to undergraduates through research. Specifically, nanoparticle research has been shown as an effective medium to impart analytical skills on undergraduates. In this research, students synthesized the material they used analytical techniques on. Students used multiple methods including UV-Vis, fluorescence and SEM imaging to quantify various properties of the nanoparticles they made. From these studies, analytics such as calibration curves for concentration determinations, line fitting to match isotherms for adsorption studies, and sizing analyses were conducted. Analytical techniques as such being taught in undergraduate research enhances what is taught in the traditional classroom as it gives the students ownership in the analytical process. Incorporating such techniques into the undergraduate program greatly improves comprehension and retention of much desired analytical skills required for the workplace.

SERMACS 827

Flux crystal growth and characterization of new oxides containing early transition metals

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The use of the flux growth method for exploratory crystal growth has proven successful in the discovery of a vast number of new materials. Specifically, adapting the molten flux growth method to be carried out within sealed systems has provided a route toward reduced transition metal species, reduced lanthanide cations, and oxyhalide type materials. Using the high temperature flux growth method, crystals of a new series of lanthanide tungsten oxychlorides of the compositions $La_{8.64}W_6O_{30.45}Cl$, $Ce_{8.64}W_{5.74}O_{30}Cl$, and $Ln_{8.33}W_6O_{30}Cl$ (Ln = Pr, Nd) was grown out of a eutectic NaCl/CsCl flux in a sealed silica tube. All four compounds crystallize in a new structure type consisting of a complex network of lanthanide cations with large amounts of site disorder. The cerium compound was obtained via the in situ reduction of Ce(IV) to Ce(III) using Zn metal. The complex structure and magnetic properties of these materials will be examined. This same method has also led to the successful crystal growth of other tungsten and reduced vanadium oxides, which will be discussed.

SERMACS 828

$CsFeGeO_4$: Non-centrosymmetric ABW-zeotype iron germanate grown from molten alkali halide flux

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$CsFeGeO_4$ was crystallized by soaking FeF_3 and GeO_2 in a CsCl/CsF eutectic flux at 900 °C over a dwell time of 12 h. The compound crystallizes in the non-centrosymmetric space group $P2_1$ and is second harmonic generation active. It consists of corner-sharing FeO_4 and SiO_4 tetrahedra with eight-sided cavities running down the *c*-axis occupied by monovalent Cs cations. Interestingly, a centrosymmetric polymorph of $CsFeGeO_4$ is obtained if the soak time is increased from 12 h to 24 h which crystallizes in the centrosymmetric space group *Pbcm* and is comprised of mixed or disordered $(Fe/Si)O_4$ tetrahedra creating an overall ABW-zeotype structure. Both polymorphs are paramagnetic down to 2 K and exhibit large negative Weiss temperatures indicative of strong antiferromagnetic interactions.

SERMACS 829

Design and electronic exploration of crystalline corannulene-integrated materials

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Crystalline covalent-organic frameworks (COFs), made entirely out of organic building blocks, offer the unique opportunity for material engineering due to virtually no limitations in the choice of organic linker. Taking advantage of COF modularity and tunability, we utilized a self-assembly approach typically used for COF synthesis to prepare the first example of a crystalline (purely organic) donor-acceptor corannulene-based material, which merges the intrinsic properties of COFs and π-bowls. To engineer a corannulene-containing crystalline material, two methods for post-synthetic integration of π-bowls were utilized: azide-alkyne 1,3-cycloaddition and non-coordinative inclusion. These efforts produced the first example of a crystalline corannulene-COF with the highest surface area among corannulene-based extended structures reported to date, which will be examined further. Integration of corannulene inside insulating porous scaffolds provided an opportunity to tune electronic properties resulting in a four-orders-of-magnitude conductivity enhancement. Moreover, the porosity of the prepared crystalline hybrids was maintained providing a pathway to re-enforce semi-conducting behavior in typically insulating porous materials (for example, covalent-organic or metal–organic frameworks(COFs/MOFs)). In combination with spectroscopic and structural analysis, we employed theoretical calculations, which allowed us to probe charge transfer rates within the Marcus theory as a function of π-bowl mutual orientation for the first time, as well as to shed light on the density of state distribution near the Fermi edge. These studies could foreshadow new avenues for π-bowl utilization for the development of optoelectronic devices or a route for highly efficient porous electrodes.

SERMACS 830

Photophysics control by confinement environment: Cage, MOF, and COF

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Tailoring the photophysical properties of chromophores without their derivatization but as a function of their confined environment is a viable solution for developing novel materials with a tunable photoluminescence profile. This concept can be realized through the integration of chromophores inside metal-organic frameworks (MOFs), molecular cages, or covalent-organic frameworks (COFs). In this talk, we will discuss the relationship between chromophore structure and their photophysical response inside rigid frameworks. In addition, new pathways for photophysics modulation of chromophores incorporated in MOFs as unbound and covalently-bound guest molecules will be presented. We will focus on modulation of the photophysical response as a function of time addressed by *in situ* chromophore formation inside porous COFs. To summarize, systematic investigation of confined environment effects on the photophysical and structural properties of incorporated guest molecules could provide a pathway for the development of novel materials with tunable photophysics properties.

SERMACS 831

Crystal growth, structures and properties of inorganic fluorides and oxyfluorides

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The most popular synthetic method used for the growth of inorganic fluorides during the early 1960’s involved the combustion of simple reagents in a fluorine (F_2) gas atmosphere. The fluorides prepared in this way tended to be highly unstable, and often exploded when handled. This was the primary reason fluorine chemistry was all but abandoned by the early 1970’s, which creates a gap in the understanding of fluorides. Hence, solid state fluorides is one of the areas where scientists interested in chemical and physical properties are confronted with the greatest difficulties in synthesis and characterization, as well as in safety requirements and where chemists mastering new preparation techniques feel the strongest call for new opportunities and synthetic breakthroughs. In recent years, an increasing number of solid inorganic fluorides and oxy-fluorides have been studied. The more ionic nature of the fluoride and its single negative charge are its prominent difference from the oxides, which allows for obtaining materials with completely new architectures and properties. Furthermore, although the application of solid fluorides have remained relatively restricted, many developments can be achieved in different fields (e.g. related to optical, electrical, magnetic and energetic properties) like energy production and storage, microelectronics and photonics, catalysis, automotive etc. Hence, many research fields and applications are indeed concerned by a better knowledge of the relationships occurring between the structure of such compounds and some pertinent physical properties.

SERMACS 832

Single source precursor route to isolate controlled metal carbide and metal nanocrystals

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Prussian Blue Analogues (PBA) have been extensively studied for applications such as gas adsorption, catalysis, Na-ion batteries, etc. Additionally, these PBAs have been employed as single-source precursors in the thermal conversion from PBAs to heterometallic nanoalloys. Recent advances in the field demonstrated that under specific thermal conditions, PBAs exhibit a size-dependent conversion behavior. It has been speculated that the conversion follows a templated mechanism, in which the framework and size are motivating factors on the eventual composition and size. However, little is known about the templated conversion from analogue to alloy. In this study we present a thorough analysis of the conversion from FeCo-PBA to nanocarbide to nanoalloy through the systematic altering of reaction conditions (such as size, chain length, temperature, solvent, etc.) and their effect on the eventual outcome. These nanomaterials were characterized using pXRD, SEM, TEM, FT-IR.

SERMACS 833

Chemical substitutions and structure-property relationships of bismuth mixed-metal oxides

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Chemical substitutions are used to alter the properties solid-state materials utilized in a variety of applications. Substitution of specific ions may result in incorporation into the host structure, induce structural changes, or result the formation of secondary phases. Each of these may noticeably impact the properties and aid in the development of structure-property relationships. For many mixed-metal oxide systems, the limits of chemical substitution and impact on the crystal structure are not known. A series of experiments were conducted to prepare and examine well-characterized bismuth containing mixed-metal oxides. Phase compositions and crystal structures were determined using diffraction techniques. Property measurements, including variable temperature electrical and dielectric property measurements, were conducted to study structure-property relationships.

SERMACS 834

Oxygen, carbon dioxide and carbon monoxide sensing properties of oxygen-deficient perovskites, aa'bb'$o_{6-\delta}$ (a = Ca, Sr; b = Fe; b' = Fe, Mn)

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Oxygen-deficient perovskites $Ca_2Fe_2O_5$, $Sr_2Fe_2O_5$, $Ca_2FeMnO_{5,}$ and Sr_2FeMnO_5, have been investigated as oxygen, carbon dioxide and carbon monoxide gas sensors at 700 °C. The response and recovery transients of these materials for sensing analyte gases were studied using DC conductivity measurement, AC impedance spectroscopy, powder X-ray diffraction, and scanning electron microscopy. Among the studied materials, $Ca_2Fe_2O_5$ displays an outstanding sensing property for various percentages of O_2 gas and ppm level detection of CO_2 and CO gases. We attribute the remarkable sensor property of this material to the stability of its brownmillerite-type structure, and the ability of Fe to change oxidation state upon exposure to various concentrations of gases at high temperature. Furthermore, this material displayed an increase of electrical conductivity for various concentrations of O_2 gas and a downturn response of conductivity toward ppm level concentration of the other two gases. Given the versatility of $Ca_2Fe_2O_5$ as gas sensor at high temperature, this material could find important applications in various processes such as in combustion engines to monitor air/fuel ratio, enhanced oil recovery, pollution control to monitor regulated species, such as CO, hydrocarbons, and CO_2 at ppm level.

SERMACS 835

Experimental and theoretical studies on lithium-ion conductivity of novel layered perovskites $Li_2LaMTiO_7$ (m = Ta and Nb)

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The development of fast lithium ionic conductive materials has attracted attention due to their applications as electrolytes in all solid-state lithium-ion battery technology. The use of solid electrolytes has been identified as an ideal solution to potential leakage and combustibility of secondary lithium-ion batteries. This work presents the experimental and theoretical investigation into the ionic conductivity of novel solid materials, $Li_2LaMTiO_7$ (M = Ta or Nb) with Ruddlesden-Popper type structure. These two materials contain bilayer stacks of corner-sharing $(M/Ti)O_6$ octahedra separated by lithium ions, and were designed with the aim of shortening the lithium hopping distances to enhance the mobility of lithium ions in this family of oxides. Further enhancement in the ionic conductivities in these materials was observed through the introduction of defects in the structure. Characterization of these oxides by neutron diffraction, impedance spectroscopy, and DFT analysis offered an understanding of the conduction mechanism, diffusion pathways and lithium-ion mobility. Theoretical calculations disclose the orientation of lithium diffusion pathways and the energy barriers which are directly linked to the arrangement of constituent atoms in these materials. Finally, the experimental and theoretical results indicate that designing materials with shorter Li-Li hopping distance and defect creation in the Li-layer can successfully enhance the lithium-ion conductivity in Ruddlesden-Popper type oxides.

SERMACS 836

X-ray excited luminescence studies of rare earth oxide nanospheres as a potential light source for optogenetics

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Optogenetics is a new technique used to analyze and regulate targeted neurons in vivo using visible light. Currently, the visible light sources are surgically implanted into the brain tissue, but this harmful and invasive technique may be avoided if suitable scintillating nanoparticles can be inserted via injection. The proposed nanoscintillator particles must adhere to rigorous parameters including being under 100nm, nontoxic, and dispersible to be successful in this biological system. Herein we report the synthesis, optimization, and radioluminescence of lanthanide doped- yttrium oxide, gadolinium oxide, and lutetium oxide nanospheres to determine their potential for optogenetic application. The rare earth oxide particles (RE2O3) were produced via an urea assisted homogenous precipitation followed by annealing. The effects of different annealing conditions on the particle morphology and radioluminescent intensity was investigated. MTS assays were ran on human embryonic kidney (HEK) cells incubated with the nanoparticles as an early cytotoxicity assessment. The ability to produce these particles in a straightforwardly, uniform, and dispersible manner as well as their relative chemical and biological inertness make them exciting candidates for optogenetics. Furthermore, we've explored the potential for the RE2O3 particles to be advantageous building blocks to other more complex nanomaterials. We have reported the production of various gadolinium silicates by using the rare earth urea precipitation method onto silica nanoparticles to form a shell that can be annealed to produce the silicate phases as nanospheres. Initial exploration on using the rare earth oxides as cores to produce other nanoscintillators such as rare earth oxysulfides (RE2O2S) will also be discussed.

SERMACS 837

Synthesis and characterization of rare earth uranium sulfides

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Actinide and rare earth containing compounds are of great interest due to their varying structures and unique properties arising from the introduction of *f*-orbital electrons into their electron configurations. Uranium sulfides with incorporated rare earth elements are of special consideration because of the potential magnetic properties that may arise from the interplay between 4f and 5f electrons. Due to uranium's affinity to exist in its 6+ oxidation state in oxygen-rich environments, synthesis using uranium in its lower oxidation states is relatively less studied. In atmospheres with high sulfur concentrations, uranium has been found to exist in its 4+ oxidation state forming air stable compounds that can be analyzed. To explore uranium in its lower oxidation states as well as the effect rare earth elements have on these crystal systems, the synthesis and characterization of a series of rare earth uranium sulfides is examined.

SERMACS 838

Nanoparticle fullerene is a stellar candidate for treatment of back pain

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Low back and leg pain are the leading sources of disability in working adults with a prevalence of over 80%, an estimated annual cost of $100 billion per year in the U.S. Despite the clinical significance of this public health issue, unfortunately, low back/leg pain is treated with symptomatic relief interventions, which does not adequately improve long-term outcomes, as no effective and disease-modifying medications are yet available. Given the critical role of inflammation and oxidative stress on the pathology of back/leg pain, fullerene nanoparticle may serve as a great therapeutic candidate. Fullerene is a powerful antioxidant due to delocalization of the π-electrons over the carbon cage, which can readily react with free radicals and subsequently deliver a cascade of downstream possessions in numerous biomedical applications. Numerous studies have demonstrated their free radical scavenging capabilities, to such a degree that fullerenes have been described as "free radical sponges". Due to the long lasting activity and its excellent cell membrane-penetrating abilities, fullerene and its derivatives are superior to growth factors, antibodies, and other biological treatments. We have demonstrated the therapeutic potential of nanoparticle fullerenes in the diagnosis and treatment of degenerative musculoskeletal disorders and associated back/leg pain, and holding great promise in becoming a novel generation of nanomedicine.

SERMACS 839

Functionalization and polymerization of fullerenes

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Functionalization of fullerenes, such as C_{60} and endohedral metallofullerenes, e. g., $Gd_3N@C_{80}$, is essential for their application in a variety of technologies, such as medical imaging and photovoltaic cells. In this presentation work aimed at functionalization of both C_{60} and elndohedral metallofullerenes will be described. In particular, use of Bingel reactions will be exploited for this purpose. First we will discuss Meldrum's acid as a special case of a malonate; its reaction products are labile and upon heating yield ketenes, which serve as reactive intermediates for polymerization processes. Secondly we will discuss attachment of a difunctional dibenzo-24-crown-8 to C_{60}, forming a cryptand via the macrocyclization process and its ability to complex secondary ammonium ions.

SERMACS 840

Fullerene-based nanomaterials for cancer diagnosis and therapy

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Carbonaceous nanomaterials, including fullerene, carbon nanotube, graphene, and carbon dots, have attracted increasing attention during past decades for their potential applications in fields of biological imaging and therapy.We developed a fullerene-based tumor integrin $\alpha_v b_3$-targeted positron emission tomography (PET) imaging probe. *In vivo* serial PET studies showed preferential accumulation of cRGD-conjugated C_{60}-based nanoprobes in U87MG tumors. The renal clearance of C_{60}-based nanoprobes is remarkably fast, which makes this zero-dimensional material promising for safer cancer diagnostic applications.Magnetic resonance imaging (MRI) is also considered to be another non-invasive modal but with high spatial resolution. Different from our previous reported gadolinium metallofullerene, we focus our attention on activatable exohedral metallofullerene nanoprobes. The novel fullerene derivatives have tunable fluorescence emission and super hydrophilic surface which make them high-performance longitudinal T_1 relaxivity contrast agents. By capper the fullerene derivatives with amorphous MnO_2 nanosheet, both fluorescence and magnetic resonance are at Off state. Upon introduced with reducing biological environment, significant fluorescence recovery and dramatic r_1 relaxivity enhancement were obtained both in live cells and in vivo. The therapeutic effects of fullerene-based nanomaterials have also been explored. We constructed ICG@C_{60} nanostructures for photothermal/photodynamic therapy upon single NIR laser irradiation both in vitro and in vivo. Our results demonstrate that the interaction between C_{60} and ICG can be used to modulate the phototherapy to transfer excess thermal energy to high cytotoxic OH to obtain high synergistic therapeutic performance. Our strategy significantly optimizes the anticancer effects, reduces the heat-induced surround tissue damage, inflammations and greatly simplifies the treatment process of tumors. In summary, we believe that versatile carbonaceous nanomaterials are highly translational from proof-of-concept to clinical practice.

SERMACS 841

Regioselective multi-addition reactions for endohedral metallofullerenes

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Endohedral metallofullerenes (EMFs) are a class of molecules that have unique host-guest structures, with a positively charged metal ion or cluster encapsulated within a closed, negatively charged fullerene cage. The fullerene cage can undergo numerous organic reactions, making EMFs very attractive nanoscale building blocks that can carry isolated metal ions and meanwhile can be manipulated by organic chemistry. However, unlike empty cage fullerenes that can make isomerically pure mono- and multi-adducts, most regioselective reactions and isomerically derivatives of EMFs are related to mono-addition, with a few exceptions in bisadducts. This would significantly limit the versatility of using EMFs to build hierarchical nanostructures, as mono-adducts can only be used as the termini (as opposed to “cores” and “connectors”) in molecular designs. In this talk, we would present our effort towards regioselective reactions of EMF $Lu_3N@C_{80}$. A tris-adduct is identified and as the major product in a 1,3-dipolar addition and an unambiguous structural characterization is underway. We expect this reaction to open up future avenues towards diversified EMF utility in nanomaterials.

SERMACS 842

Density functional theory investigation of fulvene derivatized fullerenes as candidates for organic solar cells

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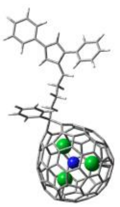
Interest in organic solar cells has been on a rapid increase over the last two decades. Derivatives of fullerenes and endohedral metallofullerenes have shown great promise for use in this field, as have fulvenes, but molecules containing both fullerene and fulvene groups have not yet been studied. Computational study of molecules this size is difficult due to the band gap accuracy limitations present in most density functional theory (DFT) methods. Herein we present a computational study of the band gaps and dipole moments of four test fullerene/fulvene molecules using a density functional that we have newly designed for the purpose of computing accurate band gaps in fullerenes and endohedral metallofullerenes. The new DFT approach shows great promise in modeling systems of this type and our findings support idea that fullerene/fulvene complexes are valid candidates for future experimental research in organic solar cell applications.



SERMACS 843

Synthesis and characterization of terbium containing endohedral metallofullernes

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Endohedral metallofullernes have been intensely studied as promising molecular systems with for materials science and biomedical applications. Also, terbium containing endohedral metallofullernes have recently demostrated suitability as single molecule magnets. Our work reports on the synthesis, isolation and characterization of $Tb_2O@C_{74}$, $Tb_3N@C_{78}$, and $Tb_3N@C_{82}$. We will also report on a previously unreported isomer of $Tb_3N@C_{86}$. The two smaller fullerene cages do not obey the isolated pentagon rule.

SERMACS 844

Study of dual modality anti-oxidant and fluorescent properties for terbium endohedral metallofullerenes derivatives

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In the current study, we employ HPLC techniques to purify $Tb_3N@C_{80}$ and related endohedral metallofullerene samples that contains a trivalent terbium(III) cation in a fullerene cage. Terbium(III) has been shown in several studies to exhibit fluorescence in aqueous solution and this property makes it useful as a fluorescence probe in biological applications. However, quenching of the fluorescence by the fullerene cage has limited these application. In previous studies, we have developed a targeted conjugate, $cFIFIFK(Cy5)PEG_{24}K(NH_2)CONH_2\text{-}C_{60}$, which utilizes fullerene anti-oxidant property to alleviate discogenic lumbar radiculopathy. In the current study we will describe the fluorescence and anti-oxidant properties of newly synthesized $Tb_3N@C_{80}$ derivatives.

SERMACS 845

Preparation of red emissive carbon dots for biomedical applications

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Carbon quantum dots (CDs) are a class of carbon nanomaterials discovered in the beginning of the 21st century. They have been widely studied due to their excellent photoluminescence properties, ease of surface modification, and low toxicity. Because of CDs' favorable properties they have been applied in fields such as bioimaging, drug delivery, photocatalysis, and 3D-printing. Despite the large interest in CDs' biomedical applications, they remain limited due to commonly possessing short wavelength emission of blue and green light which can be reabsorbed by biological tissue or concealed by autofluorescence. CDs' photoluminescence wavelengths have been increased in recent years, but there are few reports containing CDs with emission of red light and there appears to be none which have the desired emission in aqueous solutions. In this talk the preparation of CDs utilizing a solvent of sulfuric acid will be presented. The crude reaction mixture as well as different fractions which were separated using precipitation and thin layer chromatography were characterized by their optical, morphological, and surface properties. Fraction of the crude mixture of CDs possess emission across the visible spectrum of light, culminating with emission approximately at 700 nm. The red emission of these CDs occurs mainly in alcohol-based solutions; therefore, strategies must be sought after which can transfer this long wavelength photoluminescence from organic solvents to water. This will be a necessity in order to utilize these CDs in biomedical applications.

SERMACS 846

RPA renormalized perturbation theory applied to the asymmetric Hubbard dimer

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<p>The adiabatic connection fluctuation-dissipation theorem (ACFDT) formulation of density functional theory (DFT) seamlessly connects time-dependent DFT to the computation of the ground state correlation energy in many-electron systems. The random phase approximation (RPA), the most popular variant of the ACFDT in use today, has proven to be superior to semi-local density functionals for prediction of thermochemistry, weak interactions, and structural properties for molecules and materials alike.[1,2] RPA has even been shown to mimic static-correlation through its self-correlation error[3], which leads to more accurate barrier heights and kinetic predicitions compared to semi-local methods and hints at RPA's ability to perform even for "more strongly correlated" systems. Our previous results have shown that RPA is superior to exchange-only kernel approximations as the strength of correlation increases, but that other adiabatic approximations can still work well. In this work, we explore the structure and behavior of RPA renormalized perturbation theory for capturingt he beyond-RPA correlation with the exact adiabatic approximation, and attempt to correlate this with the behavior of the same perturbation expansion for real molecules and materials.[4] **References** 1. G. P. Chen et al. *Ann. Rev.*

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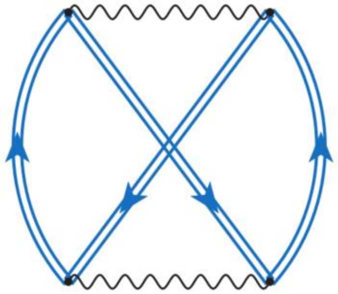

SERMACS 847

Classical-wave based simulation of chemical reaction dynamics: Avoiding the curse of multi-scale time problems in MD simulation

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The limitations in conventional molecular dynamics (MD) simulations, for studying reacting events, are primarily attributed to the small time step, dt, which must be small enough to resolve the shortest duration events (e.g., vibrational motions with time periods of the order of a femtosecond, 10^{-15} s). Such high frequency events may occur billions or trillions of times before one observes the reactive events of interests. This is sometimes called the large “incubation time problem” in MD simulation. An MD simulation long enough to include a single reactive event would take on the order of 10,00 years of CPU time on the fastest computer! Given the impracticality of direct simulation, a different approach bears consideration, for example, one may completely bypass the time domain and embrace, instead, the spatial domain. This is the primary interest of this talk. Bypassing the time-step in favor of a spatial step requires redefining chemical dynamics as a simulation problem where one wants to find paths between two given configurations on the potential surface. Thus, the problem is cast as a boundary value problem instead of the initial value problem as in MD simulation. To this end, we have recently investigated a new approach based on the most general formulation of classical mechanics, the Hamilton-Jacobi (HJ) formulation. We proposed a slightly modified Hamilton-Jacobi (MHJ) equation which we have solved by a newly proposed fast marching algorithm. The multi-scale time problems on standard MD simulation is thus, entirely removed in our proposed method. We will discuss our method with reference to a 4-well model potential surface that mimics the conformational dynamics of alanine dipeptide in gas phase. If time permits, we will show a few other results from several different chemical reactions. Our method provides a robust way to calculate an ensemble of paths. This talk is based up our two recent publications.

SERMACS 848

Thermodynamic and modeling study of cyclopropane adsorbed on graphite

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There has been fundamental interest in cycloalkanes for decades from organic and physical chemists alike. Cyclopropane, the only planar cycloalkane, has been principally studied due to the ring molecule’s reactivity which stems from the strain in bond angle. However, it is not well known how symmetry, or lack thereof, influences the rotational and vibrational dynamics or film growth processes from the monolayer to bulk behavior. This study investigates the effect of surface symmetry on the molecular conformation and configuration as well as on the layering of adsorbed cyclopropane molecules. High resolution volumetric adsorption isotherms of cyclopropane on graphite, as well as on the (100) surface of MgO (if time permits), have been recorded over a range of temperatures above and below the triple point (145.5K). The isotherms have been analyzed to obtain thermodynamic properties (heats of adsorption, isosteric heats, differential enthalpy and entropy) and possible phase transitions. Molecular dynamics simulations of mono- and multilayers of cyclopropane on these surfaces have been used to obtain binding energies, molecular trajectories, pair-correlation functions and Z-distribution of molecules from the surface. Future neutron diffraction and inelastic neutron scattering studies will be used to investigate the microscopic structure and molecular vibrations in the adsorbed layers.

SERMACS 849

QM level investigation into binding of aromatic and non-aromatic ionic liquid cations to active site of cytochrome P450 employing DFT calculations

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Ionic liquids (ILs), owing to their characteristics like inherent low vapor pressure and flammability have been deemed to be environmentally benign. They have negligible role in air emissions as compared to conventional industrial solvents due to their extremely low vapor pressures. Their physical properties can be tuned by flexibly designing them. Though efficacious, investigations by various experimentalists have raised questions on their environmental degradability. Thus, including rational design into their synthesis becomes imperative. Despite a lot of experimental efforts in this direction, molecular level details have not been explored in detail computationally. The present work aims to provide physical insight into the phenomena of ionic liquid biodegradability to aid in their rational design. The Cytochrome P-450 enzymatic superfamily has been identified and widely studied for its role in oxidation of

a wide variety of aromatic molecules in different environments. Oxygen insertion through hydroxylation at the terminal position of alkyl chains in the cation have been shown to aid in their ability to biodegrade. Thus, to develop a computational framework for IL biodegradability, it was included as the receptor. In the present work, different IL cations have been included in the model as substrates responsible for the reorganization of the binding pocket of cytochrome P-450 receptor. DFT calculations were performed on these systems to explore their binding and electronic properties. Among the cations considered, three were of aromatic nature, namely, 1-n-alkyl-3-methylimidazolium, 1-n-alkyl-pyridinium, and 1-n-alkyl-thiazolium while one was of non-aromatic nature, namely, 1-n-alkyl-1methylpyrrolidinium. These were chosen based on availability of biodegradation data and effect of side chain length on degradation. The alkyl chain on the cations were progressively increased at each step (n = 2,4,6,8,10). Binding energy and other relevant analyses were performed on the resulting structures to provide mechanistic insights into the system. Also, the electronic level donor-acceptor interactions were probed by using NBO analysis on the systems and correlating them with the structure of the interacting cation.

SERMACS 850

Computational investigations of the structure and bonding of group IV allenylidenes $CP_2M=C=C=CH_2$

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A recent report described the preparation of a dititanium-bridged hexapentaeene $[(Cp'_2Ti)_2C_6H_4]$ and proposed an unobserved titanabutatriene intermediate ($Cp'_2Ti=C=C=CH_2$). We confirm the stability of all of the group 4 allenylidenes ($Cp_2M=C=C=CH_2$, M=Ti, Zr, Hf) as well as the nature of the M=C bond. Using recently developed density-functionals with triple-zeta quality basis sets, we find that the metallabutatriene fragments are slightly twisted and bent only very slightly from the ideal geometry. The NBO and QTAIM analyses show the M=C bonds are covalent double bonds, with almost equal contributions of the metal and carbon atom orbitals to both the σ and π bonds. Although there are few examples of early transition metal allenylidenes known, we believe that the molecules considered here are candidates for experimental observation, and we provide predictions of observable infrared absorptions of the molecules.

SERMACS 851

Molecular structures and energetics of small copper, silver, and gold nanoclusters

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There is a substantial interest in the study of small atomic clusters due to the role that they can play in understanding the physical and chemical properties of the bulk as well as their inherent properties as catalysts. Density functional theory (DFT) level and correlated molecular orbital theory at the coupled cluster (CCSD(T)) level are used to predict the structures and energetic properties of group 11 metal clusters ($n \leq 20$). Geometries are optimized with the B3LYP, PW91, M06, and ωB97xD exchange correlation functionals with the aug-cc-pVDZ-PP basis set. Single point energies are calculated at the CCSD(T) level with the optimized geometries and in a number of cases extrapolated to the complete basis set limit. The normalized clustering energies (NCE) and the atomization energies were calculated. Heats of formation of the clusters were also calculated. Spin-orbit corrections are added in to the CCSD(T) results to predict the cohesive energy of the bulk as a function of NCE vs cluster size, $n^{-1/3}$. Spin orbit corrections are small for the Cu and Ag extrapolations and are critical for the Au extrapolation. There is good agreement between our calculated cohesive energy from our extrapolation and the experimental bulk. The values in kcal/mol are: Cu (80.9, calc.; 80.6, expt.), Ag (66.8 calc.; 67.9 expt.), and Au (85.3, calc.; 87.5 expt.). Extensive studies of the trimers were made as they undergo a Jahn-Teller distortion arising from the e^1 electron configuration ($^2E'$ state) resulting in $^2A_1$ and $^2B_2$ states. Au_3 exhibits bond angle isomerism with a second vibrationally bound bent $^2B_2$ state with $\theta \sim 125°$.

SERMACS 852

Understanding the complex adsorption equilibria of small alkanols on $SrTiO_3$(001) using density functional theory

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With interests in understanding the catalytic and surface properties of industrial perovskites, we present a density-functional-theory approach to understanding the adsorption of several simple alkanols on the (001) surface of strontium titanate, $SrTiO_3$. Beginning with 2-propanol, or isopropanol, which is commonly used as a surface-probe molecule for its divergent acid-base reaction pathways of dehydrogenation (acetone formation) and dehydration (propylene formation), we used a Hubbard-corrected version of the PBE density functional to investigate the adsorbed states of alkanols in several different orientations. We report that, upon room-temperature adsorption, alkanol adsorbates readily transfer their hydroxyl hydrogen atom to an oxygen atom on the perovskite surface. This adsorbed species resulting from hydrogen transfer exists in a two-state equilibrium, wherein the now surface-bound hydrogen atom is hydrogen-bonded to the alkoxy oxygen in one state and not hydrogen bonded in the other state. Theoretical vibrational frequency calculations of these states corroborate and help to elucidate experimental sum-frequency generation spectra, which show multiple features in the -OH stretching region. Interestingly, with our consideration of multiple adsorption orientations for a given alkanol, we report qualitative agreement not only in the frequency of spectral features but also in feature width. A comparison of reaction and barrier energies across multiple adsorbed alkanols reveals the role of dispersion forces (through the size of the alkyl group) on adsorption kinetics and the two-state equilibrium between hydrogen-bonded and non-hydrogen-bonded structures. Finally, by comparing adsorption geometries of the states within a given equilibrium, we speculate the role of each state on subsequent reaction steps along the divergent acid-base reaction pathway. With a more complete understanding of adsorption, we hope to provide insight into the development and enhancement of catalysts by studying the effects of this two-state adsorption equilibrium on pathway selectivity of different small alkanols.

SERMACS 853

Structures and properties of mixed metal / metalloid clusters

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Atomic clusters are frequently used as models for the reactive sites of different materials. We present results on the structures and properties of mixed metal semiconductor clusters containing between 2 and 25 atoms, and the global optimization techniques that are utilized to search for these low energy isomers. This presentation will discuss the transition between exohedral and endoheral mixed clusters for different compositions, the unique cluster structures of mixed elemental clusters, and the relative stability of each cluster composition.

SERMACS 854

^{13}C fractionation during aqueous alanine transamination

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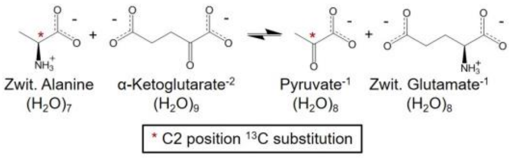
The alanine aminotransferase (ALT) enzyme catalyzes the transfer of an amino group from alanine to a-ketoglutarate to produce pyruvate and glutamate. Isotope fractionation factors (IFFs) for this reaction were calculated from the partition functions of explicitly and implicitly solvated alanine, pyruvic acid, glutamic acid, a-ketoglutaric acid, and their various derivatives using gas phase- and aqueous-optimized clusters with explicit H_2O molecules at the MP2/aug-cc-pVDZ and MP2/aug-cc-pVDZ/COSMO levels. The results are compared to simpler approaches that estimate the IFFs based solely on changes in the zero point energies (ZPEs). Calculations on the substitution of ^{13}C at the C2 position of alanine and pyruvic acid and their derivatives shows that pyruvic acid/pyruvate will be enriched in ^{13}C by 9 ‰. This is consistent with the expectation that the ^{13}C isotope exchange reaction between alanine ($H_2NCH(CH_3)COOH$) and pyruvate ($CH_3C(O)COOH$) preferentially enriches pyruvate in ^{13}C because of the strength of the C=O bond relative to that of C-NH_2. The ZPE-only values for gas phase- and aqueous-optimized clusters without explicit H_2O molecules are consistent with the values including all terms, showing that thermal corrections have virtually no effect on isotope fractionation for this reaction and that explicit H_2O molecules do not significantly contribute to the magnitude of the calculated IFFs. In addition to the ^{13}C equilibrium between pyruvic acid and alanine or their derivatives, ZPE-based IFFs were also calculated with simpler analogues of the molecules of interest, formaldehyde and methylamine, which predicts an enrichment in formaldehyde of 7 to 8 ‰ at the MP2/aug-cc-pVDZ and aug-cc-pVTZ levels.



Overall ALT reaction equilibrium between zwitterionic alanine with 7 explicit H_2O molecules and doubly deprotonated α-ketoglutarate with 9 explicit H_2O molecules forming pyruvate with 8 explicit H_2O molecules and zwitterionic glutamate with 8 explicit H_2O molecules. Zwitterionic alanine and pyruvate are each ^{13}C-substituted at the C2 position.

SERMACS 855

Thermochemistry of phase-changing borane containing hydrogen storage materials

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Useful chemical hydrogen storage materials are required for powering fuel cells in portable electronics and for the transportation industry. Ammonia borane, a solid, is a chemical hydrogen storage material. Amine boranes readily produce hydrogen with improved safety and less environmental impact as compared to other chemical hydrogen storage materials including sodium aluminum hydride. Mixtures of ammonia borane and methylammonia borane demonstrate greater solubility than either component individually, allowing for production of hydrogen dense mixtures. Gaseous heats of formation were calculated for various amine boranes, and in combination with boiling point and enthalpy of vaporization calculations, the solid heats of formation were estimated. Calculated solid heats of formation were compared to experimentally determined heats of formation. Solvation of amine boranes and their respective first dehydrogenation products were studied computationally. Computational solvation data was compared to experimental solvation data to provide guidance in searching for optimal solvents and amine borane mixture components. Gaseous, non-hydrogen, dehydrogenation products of ammonia borane and methylammonia borane were studied computationally and using mass spectrometry to quantify loss of dehydrogenated amine borane materials. The calculations were done at the density functional theory and composite correlated molecular orbital theory G3MP2 levels with solvation predicted using a self-consistent reaction field approach with the COSMO approach.

SERMACS 856

Heterogeneous oxidation of aqueous organic aerosols by OH radical

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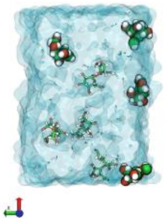
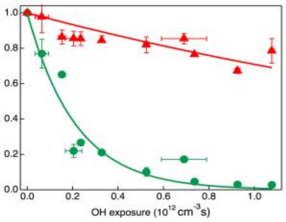
The OH-initiated heterogeneous oxidation of aqueous and organic aerosols is investigated using an atmospheric-pressure flow tube reactor aided by computational chemistry. The investigation looks at the reaction kinetics of the various heterogenous oxidations, with emphasis placed on the reactive uptake of OH radicals. Great interest is placed in identifying the various products (in both the gases phases and condensed phase) and in understanding the state of the different aerosol interface surfaces before and after oxidation. The research also investigates the reaction mechanisms occurring during this oxidation and how transport processes in the multiphase system affect the chemistry observed. Preliminary results from the MD simulation of an aqueous mixture of two saccharides (lactose and β-D-glucopyranoside) showed the formation of a disaccharide exclusion layer below the water surface of 10Å. The simulations predict monosaccharide concentration to be low at the surface and to increase rapidly within the first 10 Å of the air-water interface. The simulations were inspired by an experiment that showed that for an equimolar monosaccharide/disaccharide aqueous aerosol mixture, the decay of the disaccharide is found to be significantly slower than that of the monosaccharide. The observed decay is consistent with a poor OH and disaccharide interaction at the interface suggested by the simulations due to the exclusion layer.



Snapshot of the molecular dynamics simulations showing three of the four MGP molecules at the air/water interface.



SERMACS 857

Nanoscale spectroscopy and chemical imaging with conventional and with nanophotonic AFM probes

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Photothermal induced resonance (PTIR) combines AFM with IR (or visible) absorption spectroscopy, enabling identification and imaging, of chemical composition, molecular conformation and electronic bandgap at the nanoscale. In PTIR, the absorption of a laser pulse induces a rapid thermal expansion of the sample. Conventional cantilevers are too slow to track the sample thermal expansion dynamics; however, the fast sample expansion kicks the cantilever in oscillation (like a struck tuning fork), with amplitude proportional to the absorbed energy. In this talk, I will introduce PTIR working principles and several measurements schemes using conventional AFM probes either in contact-mode or in tapping-mode. As examples of PTIR applications I will discuss i) the identification of nano-contaminants 2D materials heterostructures ii) phonon polaritons imaging in 2D materials nanostructures and slabs, and iii) the determination the molecular conformations in peptide fibrils related to Alzheimer’s disease in water. If time allows, and additional example among plasmonic nanomaterials, organic-inorganic perovskites solar cells, drug nanocarriers, polymers, metal-organic frameworks or oil paints will be presented. Later, I will introduce novel nanoscale AFM probes that leverage cavity optomechanics to break the trade-off between AFM measurement precision and time resolution. These probes improve the PTIR sensitivity, signal to noise and throughput by a few orders of magnitude each. Additionally, they enable capturing the sample thermal expansion dynamic with 10 ns time-resolution, thus providing both chemical composition and thermal conductivity of the sample at the nanoscale. This new capability is leveraged to measure the intrinsic thermal conductivity (η) of metal-organic framework (MOF) individual microcrystals, a property not measurable by conventional techniques. MOFs are a class of nanoporous materials promising for catalysis, gas storage, sensing and thermoelectric applications where accurate knowledge of η is critically important.

SERMACS 858

Monitoring charge transfer in thin films and single crystals with femtosecond stimulated raman microscopy

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Determining the mechanism behind the workings of photovoltaics and photocatalysts is of critical importance in improving their efficiency. However, uncovering the step-by-step processes that occur upon photoexcitation is challenging, as the timescales for charge transfer and molecular bond making and breaking processes are incredibly fast, in the femtosecond to picosecond range. Additionally, the intrinsic environmental heterogeneity of most photovoltaic materials, including nanoscale variations in size, chemical composition and/or degree of crystallinity, can greatly impact performance. Here we describe how femtosecond stimulated Raman microscopy can provide a mechanistic understanding of a wide range of photoactivated processes, from charge transfer to singlet fission to exciton transport. Specifically, we focus on the process on singlet fission in photovoltaics, determining how molecular motion in materials such as pentacene and rubrene crystals can efficiently create two charges from a single photon. Additionally, we have developed a spatially-resolved ultrafast vibrational technique to quantify how vibrations contribute to exciton transport and how environments affect losses. Together, these examples highlight how obtaining molecular movies – vibrational spectra on the timescale of nuclear motion – can identify key components of photo-driven mechanisms which can be used to optimize efficiency of sunlight-powered devices.

SERMACS 859

Near-field optical spectroscopy for the study of electronic properties in semiconducting nanostructures

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Semiconducting nanostructures have been proposed as material platforms for a wide variety of photonic, electronic, and photovoltaic elements. In order to realize these applications, careful design and characterization of electronic properties such as dopant concentration, activation, and distribution is needed. I will discuss the use of near-field optical microscopy as a non-destructive method to extract information about conductivity and optical parameters for devices *in operando*. In particular, I will focus on the study of free-carriers in axially-doped silicon nanowires (SiNWs) using infrared nanospectroscopy. Using this technique, we can detect local changes in the electrically-active doping concentration from the free-carrier absorption in both n-type and p-type doped SiNWs. The high spatial resolution (< 20 nm) allows us to directly measure P and B dopant transition abruptness in single and multi-junction SiNWs. This is especially valuable in boron-doped p-type SiNWs, for which nanometer-scale information on the junction properties is difficult to obtain without intensive processing. This approach can be extended to other semiconductors, including 2-dimensional materials, and different doping strategies for advanced optoelectronic control.

SERMACS 860

Applications of nanoscale functional imaging to reveal the role of heterogeneities in complex systems for sustainable energy applications

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Engineering materials to meet the rapidly increasing demands in energy finds applications in a vast array of devices in energy, electronics and chemical conversions. Composites and their interfaces, doping or defect engineering are commonly used to tweak the performance of active materials for energy harvesting, energy storage, nanoelectronics, or catalysis. The confinement of interactions, such as between a nanoparticle and a 2D layer, are challenging to resolve with conventional characterization tools. As a result of long standing limitations in conventional analytical tools, alterations in the electronic or vibrational states of the lattice that hinder or boost the performance of an active material are not well understood. This is further limited by the paucity of experimental tools capable of probing materials properties beyond morphology with nanometer scale resolution. Exploiting the functional modes of atomic force microscopy, including nanomechanical spectroscopy and nanoscale infrared spectroscopy, has the potential to circumvent these restrictions. In this presentation, we will discuss how such approach can reveal local heterogeneities to explain behaviors at the micro- and macro-scales. The study constitutes a new approach toward understanding changes in local structural, compositional, electronic properties and reactivity at the nanoscale. The results provide some insight on the mechanisms of reactivity of various materials at the nanoscale, with implications for large scale production for nanoelectronics and for chemical reactions. In closing, we will provide a perspective on the required steps for nanoscale characterization to further impact applications of emerging materials.

SERMACS 861

Hyperbolicity and polaritonic strong coupling: Towards enhancing IR sensing and imaging platforms

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The current state-of-the-art in materials used for IR optical components exhibit significant limitations. This is exacerbated by the long free-space wavelengths in this spectral region. However, through the use of polaritons one can surpass the diffraction limit and thus many of these limitations can be circumvented. Hyperbolic polaritons are a distinct class of polaritons occurring within materials whereby the real part of the permittivity is opposite in sign along orthogonal axes. Such materials offer significant advantages, such as the ability to support a suite of hyperbolic polaritons with ever increasing wavevector, enabling confinement of light to arbitrarily small dimensions and the frequency dependent propagation of these modes. Within the context of imaging, these two properties enable label-free imaging of deeply sub-wavelength objects with low energy, long wavelength infrared light via the hyperlensing concept. Furthermore, this approach is compatible with spectrally dispersing the collected light, offering the potential for spectroscopic imaging. This talk will focus on recent advances towards hyperlensing and chemical sensing platforms using the naturally hyperbolic medium hexagonal boron nitride.

SERMACS 862

Infrared spectroscopic imaging of microplastic contamination <20u

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Plastic contamination is a widely spread and global problem in our environment. Our interest are those particles which are smaller than 20 microns and have the possibility of cell membrane penetration and interaction. The study of these microplastics and the chemical interaction is essential to understand the long term and potential catastrophic effects that these smaller microplastics have on the environment. Previous studies have been limited in their effectiveness by the limitations of spectroscopic instrumentation that meet the specific length scales to study these problems. We will introduce a new technique called O-PTIR which overcomes these spatial limitations even to submicron spatial length. This technique can be coupled with another spectroscopic technique, Raman, to provide a simultaneous collection of submicron spatial resolution infrared (IR) and Raman spectra to help characterize the particles of contamination and the effects on the environment. These two complimentary vibrational spectroscopy techniques provide key insights into the identification, distribution, and effect of samples being tested.

SERMACS 863

Investigating chemical heterogeneities in organohalide perovskites with multiscale infrared imaging

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Hybrid organic inorganic perovskites have seen a surge in popularity for photovoltaic applications, leading to rapid rise in perovskite solar cell efficiencies. However, there are fundamental challenges that remain to be addressed before large scale development of perovskite solar cells is viable. One critical aspect is understanding the structural defects in perovskite films and how defect densities affect photovoltaic efficiency. It is well known that the choice of solvent and additives affects the final device efficiency and grain morphology. Solvent molecules form Lewis acid adducts with the metal ions (typically Pb2+), and upon post-synthetic annealing, these intermediate complexes start losing the solvent molecules, leading to formation of perovskite films. The presence of such species in the final perovskite film determines defect densities and hence efficiency, but it is not apparent to what degree these intermediate states persist after post-synthetic annealing. Traditionally the morphology of the perovskite films is evaluated with electron microscopy techniques, which provide very high morphological resolution, but little insights into the chemistry of the films. The chemical composition is measured using spectroscopic techniques such as X-Ray diffraction, infrared and NMR spectroscopies, which fail to provide any information on the chemical inhomogeneities across the sample. In the absence of spatial resolution, the spectral signatures from defect states are either averaged out or have to be interpreted as homogeneously distributed within the sample. Knowledge of structural inhomogeneities is imperative for correlating morphology and chemistry, which in turn allows for improved design. AFM-IR is a novel technique that integrates infrared spectroscopy with an atomic force microscope and bypasses resolution limits in conventional IR microscopy to provide unprecedented nanoscale detail on the structural and chemical heterogeneity in perovskite films. The distribution of intermediate states containing adducts with commonly used solvents and additives such as dimethylformamide and dimethylsulfoxide in perovskites, as revealed by AFM-IR, will be presented, and their potential implications towards device efficiencies will be discussed. The extension nanoscale spectral data to rapping mapping of defects in perovskite films for device characterization using all-optical implementations of infrared imaging will also be presented.

SERMACS 864

Nonlinear phonon polariton spectroscopy and microscopy

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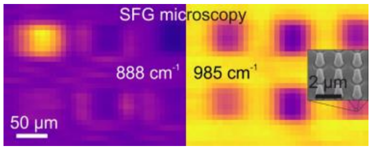
Infrared nanophotonics based on phonon polaritons have received considerable attention recently due to the immense potential for novel infrared-to-THz device concepts ranging from hyperpolic flat lenses to phonon polariton lasers. However, as of now, the optical field enhancement associated with subdiffractional light localization is hardly exploited for phonon polariton resonances, in stark contrast to the large field of nonlinear plasmonics. We have developed several new experimental approaches based on nonlinear optics to address this issue. Specifically, we have demonstrated second harmonic generation (SHG) spectroscopy in the mid-infrared as a unique tool to directly access the optical field enhancement at polariton resonances: For these experiments, we use an infrared free-electron laser (FEL) as a narrowband, tunable, and intense light source. More recently, we addtionally implemented FEL-based infrared-visible sum-frequency generation (SFG) spectroscopy as a complementary technique, and demonstrated its sensitivity to surface phonon polariton resonances in sub-diffractional nanostructures. In comparison to SHG, SFG additonally provides the opportunity to spatially resolve the signals with a lateral resolution that is limited only by the wavelength of the visible SFG photons. As a proof-of-concept, we recently acquired the first long-wave infrared SFG images of SiC nanoresonator arrays, see Fig. 1. In general, SFG microscopy presents itself as a powerful new plattform for mid- to far-infrared resonant super-resolution imaging, with a vaste of potential for applications across disciplines, ranging from resonant imaging of low-dimensional nanophotonic structures to in-situ imaging of spatial heterogeneity in electrochemical systems.



Polariton-resonant (left) and off-resonant (right) infrared-visible sum-frequency generation micrographs of SiC nanopillar (inset) arrays.

SERMACS 865

Doped semiconductors as components in infrared plasmonic systems

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The mid- and long-wave infrared houses the vibrational and rotational resonances of many molecules of interest. Unfortunately, gas sensing in this frequency range is difficult due to a lack of optical devices as well as the relatively low interaction cross section between molecules and infrared light. One way to strengthen the interaction between infrared light and molecules is by concentrating light into small volumes using plasmonic devices. Doped III-V semiconductors like InAs and InSb have been shown to be tunable infrared plasmonic materials. These materials can be grown using molecular beam epitaxy, which enables precise control over the doping density and film thickness. In this talk, I will review our previous efforts to use single layers of semiconductor material for infrared sensors. I will then focus on our recent efforts to grow semiconductor-based hyperbolic metamaterials. I will show that alternating layers of doped and undoped semiconductor can be used to create a tunable infrared hyperbolic metamaterial that exhibits a discontinuity in the Brewster angle and negative refraction. I will then discuss our efforts to determine how the material building blocks influence the optical response of the metamaterial. By choosing the optimal materials, I will show that we can excite volume plasmon polariton modes with mode indices ~15 while maintaining lifetimes. Finally, I will demonstrate our ability to selectively outcouple these volume plasmon polariton modes in a thermal emission geometry. Together, these efforts show that semiconductor-based hyperbolic metamaterials can significantly confine infrared light while maintaining relatively low losses. This sets the stage for the epitaxial integration of other semiconductor-based optical components for future infrared devices.

SERMACS 866

Exploring and exploiting the properties of highly anisotropic media with infrared spectroscopy

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Anisotropy is a property of many materials, arising either from natural crystal structure, or engineered through the use of artificial structuring. Anisotropic materials have optical properties which are inherently highly polarization and/or orientation sensitive. This can play an important role in creating new types of infrared optical components or enhancing the local electromagnetic field for surface enhanced sensing schemes. For surface-based sensing, anisotropic materials which support surface and hyperbolic polaritons are of particular interest as they exhibit strong local field enhancements. Surface polaritons occur when the dielectric permittivity of a material is negative along all of its optical axes, whereas hyperbolic polaritons occur when only one or two of the crystal axes have negative permittivity. Both have been demonstrated as excellent candidates for surface enhanced infrared spectroscopy, and can even support strong coupling to local vibrational modes. However, it is critical to accurately characterize the bulk properties of the associated materials in order to design the properties of a sensor, which can be particularly challenging in anisotropic media. In this talk I will show how we can use infrared spectroscopy techniques, including attenuated total reflectance, to study the properties naturally anisotropic crystals which support hyperbolic phonon polaritons. I will then go on to discuss how highly anisotropic grating structures which support surface polaritons can be designed and leveraged for surface enhanced sensing in liquid environments.

SERMACS 867

Active tuning of phonons and surface-phonon polariton resonances

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The infrared spectra of many polar semiconductors are dominated by highly reflective reststhralen bands that occur between the transverse and longitudinal optical phonons. Through the LOPC effect, free carriers shift the reststrahlen band to higher frequencies. We have previously shown that photoinjected carriers transiently and reversibly modify the infrared reflectivity of bulk SiC. Within the reststrahlen band, SiC and InP nanostructures can exhibit surface-phonon polariton resonances. Here we report, for the first time, active tuning of SiC and InP surface-phonon polariton resonances *via* carrier photoinjection, achieving better modulation depths than active tuning in plasmonic systems. In SiC, ultraviolet excitation with femtosecond laser pulses induces >10 cm^{-1} shifts in the transverse dipole resonance (width = 7 cm^{-1}). Time-resolved infrared reflection spectroscopy reveals that the photoinduced shifts decay in tens of ps, depending on the initial carrier density. Our results suggest that spatial redistribution of photoexcited carriers dominates the time dependence of the active tuning. We also report, for the first time, direct time-resolved infrared spectroscopy of the LO mode of GaN, made experimentally accessible through the Berreman effect.

SERMACS 868

Far-infrared synchrotron spectroscopy of some important interstellar molecules

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A number of small organic molecules that contain hydroxyl group(s) are thought to play important roles in the prebiotic chemistry occurring in interstellar space. Lately, we have been focusing on investigating the far-infrared spectra of some of these molecules in an effort to refine or determine their spectroscopic parameters. These parameters are useful for (1) predicting rotational line positions such that radio astronomers can perform efficient searches for them in molecular clouds, and (2) improving the accuracy of reported column densities by refining their vibrational partition functions. The specific molecules we have targeted by far-infrared spectroscopy are vinyl alcohol and formic acid, which have been observed towards Sagittarius B2(N). Both have a low and high energy rotamer (trans and cis) that we observe thanks to the high brightness of the far-infrared beamlines at the Australian Synchrotron and the Canadian Light Source. Analyses of the high resolution spectra collected at these facilities will be presented, along with a discussion of how the resulting parameters are useful for improving our understanding of their astrochemical behaviour.

SERMACS 869

Tools to rapidly assign the rotational spectra of molecules in vibrationally excited states

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In spectral survey data from radio telescopes, a substantial fraction of the observed peaks of molecular origin are unassigned (U-lines). While some of these features are due to new molecules whose existence in the ISM has not yet been confirmed, it is likely that many of the observed U-lines are due to rotational transitions of already known molecules in excited vibrational states. In this talk, I will discuss the instrumentation, theory, and experimental techniques that our lab uses to collect and assign the rotational spectra of vibrationally-excited molecules. Our work is done at a principally undergraduate institution, and so the tools and techniques we employ need to be effective in our context, in which undergraduate researchers only have a limited amount of time to spend in the lab.

SERMACS 870

Rovibrational Spectroscopy of magnesium acetylide (MGCCH) and its detection in the interstellar medium

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For gas phase organic molecules, *ab initio* composite methods exist that are able to predict accurate rovibrational spectra. Typically, fundamental vibrational frequencies can be obtained to within 1 cm^{-1} of known experimental values. However, the question remains as to whether a similar methodology can be developed for metal-bearing molecules. Rovibrational spectroscopic properties have been computed for the putative interstellar molecules magnesium acetylide (MgCCH) and its cation ($MgCCH^+$). Using a “black box” coupled cluster theory-based quartic force field (QFF) with second-order vibrational perturbation theory, pure rotational spectra have been simulated at 15 K. Our QFF composite approach provides agreement to within 18 MHz (6.0×10^{-4} cm^{-1}) for three rotational lines observed in the carbon-star envelope of IRC +10216 and tentatively assigned to neutral MgCCH. Neutral and cationic MgCCH spectroscopic results will also be compared to newly obtained data using Fourier transform microwave spectroscopy.

SERMACS 871

Interstellar inheritance of primitive bodies in the solar system

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The isotopic enrichments measured in volatile primitive materials probably had their origin in low-temperature (10K) chemistry similar to that found in molecular clouds. This has led to the proposal, supported by theory, that these anomalies derived their heritage from the prestellar period. Previous ground- and space-based observations of small bodies, recent Rosetta results, as well as laboratory measurements of cometary material obtained from Stardust and other primitive materials, suggest that small bodies, contain a mixture of the products from both interstellar and nebular chemistries. A major observational challenge in cometary science is to quantify the extent to which chemical compounds, including complex organics, can be linked to either reservoir and what the native molecular complexity is within a comet. As technology and new facilities come on-board, we are carefully considering ways to remotely detect the complex species identified in situ and in returned samples. This presentation will include new observations with ALMA and other facilities and plans for future facilities, such as JWST.

SERMACS 872

Infrared spectroscopy of hydrogen molecular ions and their clusters

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Hydrogen is the most abundant element in space, and small molecules formed from hydrogen are also likely to be present throughout the universe. To explore the possible molecules that can be produced, cations of the form $H^+(H_2)_n$ are produced in pulsed supersonic molecular beams by pulsed discharge sources. These ions are mass-selected and studied with infrared photodissociation spectroscopy in a specially designed reflectron time-of-flight mass spectrometer. Infrared spectra are compared to the predictions of theory (DFT, MP2, CCSD(T)) to elucidate the structures of these ions and their different isomers, if any. The ionized species studied include $H_3^+Ar_n$, H_5^+, H_6^+, H_7^+ H_9^+ and the proton-bound dimer $Ar\text{-}H^+\text{-}Ar$. These hydrogen ions represent challenging problems for spectroscopy and theory.

SERMACS 873

Challenges and opportunities in the investigation of astrochemical surface chemistry

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Gas-solid reactions are believed to contribute significantly to the observed abundance of molecules in astrochemical environments such as the interstellar medium and cometary coma. These reactions may also play an important role on the surface of planetary objects, including icy moons and some asteroids. However, relatively few laboratory measurements investigating astrochemical gas-mineral interactions have been performed. Extraterrestrial samples are rare and often composed of a complex mixture of minerals. Thus, the samples are expensive, and data interpretation can be challenging. In addition, mineral samples can be difficult to analyze by traditional surface science methodology. One way to address these issues is to produce synthetic minerals conducive to surface-sensitive analysis. We have developed a protocol for preparing synthetic samples of the meteoritic mineral schreibersite, Fe_2NiP, that are optimal for analysis under ultrahigh vacuum conditions. The preparation and surface characterization of synthetic schreibersite will be discussed. While schreibersite appears to interact weakly with prebiotic ices at cryogenic temperatures, there is evidence of surface phosphorus activation at elevated temperatures. Additionally, on-going efforts to develop thin films of phosphate minerals amenable to surface-science techniques such as reflection-absorption infrared spectroscopy will be described.

SERMACS 874

Ab initio predictions for the formation of SO_X and NO_X based Brønsted acids with atmospheric and astrochemical implications

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The formation of the SO_x and NO_x based Brønsted acids of H_2SO_4, H_2SO_3, HONO, and $HONO_2$, have long been of interest for their presence and role in Earth’s atmosphere. One means of atmospheric Brønsted acid formation that receives little attention is that by way of reacting with H_2S through a process similar to that of SO_x hydrolysis. Such processes have planetary atmosphere implications due to significant amounts of H_2O (~ 20 ppm), H_2S (~ 70 ppm) SO_2 (~ 150 ppm), and H_2SO_4 (< 2.5 ppm at latitudes lower than 45°) in the atmosphere of Venus. An extensive computational investigation into the potential energy surfaces (PESs) for the reactions of SO_x (x = 2 or 3) with H_2S and H_2O in both gas phase and aqueous solution at the CCSD(T)/CBS level of theory have been performed. Sulfuric and thiosulfuric acids can form from H_2O catalyzed reactions of H_2O and H_2S with SO_3 at 298 K ($\Delta G < -6$ kcal/mol). Additional water molecules have a profound catalytic effect on the SO_3 reactions in the gas phase, with barriers dropping to < 5 kcal/mol after only two additional waters and disappearing altogether under aqueous conditions. The addition of water molecules for the SO_2 reactions results in a small increase in the overall endothermicity and a much smaller catalytic effect than that for SO_3, so that H_2SO_3 and $H_2S_2O_2$ formation is unlikely at 298 K. Similarly, the PES for the hydrolysis of NO_2 to form HONO and $HONO_2$ in both gas phase and aqueous has been studied extensively. We find the formation of atmospheric HONO and $HONO_2$ to be possible through the hydrolysis of the often overlooked NO_2 dimer of *trans*-$ONONO_2$. At 298 K, A distinct $T\Delta S$ effect of ~ 10 kcal/mol per H_2O and H_2S is calculated for all Brønsted acid formation reactions, emphasizing the need to consider ΔG for Brønsted acid formation at higher temperatures. This work also has implications for acid gas capture by MOFs.

SERMACS 875

Effects of nutrient overload and environmental conditions on algal bloom formation: Case study of private ponds in Madison County, Kentucky

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Madison County in Eastern Kentucky is home to many private ponds used for agricultural and recreational purposes (livestock watering, fishing, swimming, etc.). Each year, the owners of these ponds observe harmful algal blooms (HABs) that release toxins into the water, potentially damaging the local ecosystem. Building off a small pilot study in summer 2018 which observed a harmful algal bloom (HAB) occurring in one pond in this area that roughly correlated with a rise in water sulfate levels rather than in nitrate and phosphate levels as expected, a multifactorial study of ponds in this area was undertaken in summer 2019. The purpose of this project was two-fold: 1) to identify trends in water nutrient levels and environmental conditions that would indicate the imminent formation of HABs and 2) to determine if commercially-available test kits would provide adequate information for a non-scientist to monitor their private water sources and predict HAB formation. The nutrient levels and environmental conditions of at least five private ponds within a six-mile radius were monitored thrice weekly from June through August 2019. Taxonomical characteristics identified the strain(s) of algae present in potential HABs and nutrient level quantification achieved using a combination of EPA-validated laboratory techniques including those for major anions (ion chromatography, EPA method 300), phosphates (spectrophotometry, EPA method 365.3), and turbidimetry (EPA method 180), as well as using test kits available from Hach Company (phosphates, nitrates, nitrites, and sulfates). Environmental conditions such as rainfall, water pH, dissolved oxygen, conductivity and temperature were also monitored. This presentation will outline the results of monitoring at each location as well as any identified correlations between the formation of algal blooms and the monitored variables as a means of identifying underlying trends that could be easily monitored by lay persons to predict HAB formation in rural areas.

SERMACS 876

Strategies toward industrial paints with improved safety- and eco-profiles: Design of high-performance polymers for imetal coating applications

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Easy to apply waterborne coatings, with an improved eco-profile over their solvent-borne counterparts, are used in many applications such as paper and leather coatings, as well as construction, automotive, architectural and traffic paints. In contrast to solvent-borne coatings, waterborne coatings display several advantages, for example, lower VOC emissions. Additionally, replacing solvent-borne with waterborne technology facilitates the syntheses of a wide range of polymers with non-linear morphology (hard and soft composites, hollow spheres, etc.) thereby providing distinct coatings performance platforms. High performance waterborne, industrial coatings are designed to resist harsh conditions and must display good chemical resistance, hardness and scratch resistance, toughness and flexibility, and block resistance. In addition, excellent moisture and UV resistance, as well as durability are important properties for high performance coatings. Resins and by extension coatings that possess these attributes provide the longest possible lifespan for substrates, for example, wood and metal (Figure 1). The literature describes several approaches for the preparation of coatings with improved an eco-profile and good barrier properties. Now described are the recent efforts aimed at preparing high performance coatings with enhanced water resistance and improved anti-corrosion properties.

SERMACS 877

Rapid removal of emerging pharmaceutical contaminants from aqueous solution by adsorption on magnetized Douglas fir biochar

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The occurrence of emerging contaminants in wastewater and their behavior during wastewater treatment are key issues in the production of potable water and re-use of water sources. In order to assist answering these matters, in this study batch sorption experiments were performed to study the adsorption of three emerging pollutants from aqueous solution as a treatment method, using magnetized Douglas fir biochar as the adsorbent. Magnetic biochar (MBC) was produced by iron oxide precipitation onto Douglas fir biochar (BC) surface using an aqueous Iron(III)/Iron(II) solution followed by NaOH treatment. Caffeine, ibuprofen and acetylsalicylic acid were selected as representative contaminants and both BC and MBC were used to remove the contaminants from water. The surface morphology of the modified biochar was confirmed by scanning electron microscopy, scanning electron microscopy/energy dispersive X-ray spectroscopy, transmission electron microscopy, point of zero charge, and surface area measurements. The effects of several operational parameters, such as pH, initial concentration of the contaminant, mass of adsorbent, temperature, and contact time on the sorption behavior were evaluated. MBC suspensions in the contaminated solutions were shaken and then magnetically removed. Remediated solutions were then analyzed using UV–Visible spectroscopy. The contact time to attain equilibrium for maximum adsorption was found to be less than 5 min. The kinetic data were correlated to several adsorption models, and the adsorption mechanism found to follow pseudo-second-order adsorption model. The equilibrium adsorption data were analyzed using the Freundlich and Langmuir isotherm equation models. The fast adsorption kinetics and high adsorption capacities demonstrate that MBC is an excellent, low cost and environmentally friendly adsorbent for the removal of contaminants from aqueous solutions.

SERMACS 878

Multi-pronged strategy for treatment of emerging and conventional persistent organic contaminants in real wastewater by electroperoxone

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Population explosion has resulted in rapid increase of inappropriate disposal of generated wastewater and hence, environmental pollution. Emerging and conventional persistent organic contaminants are being generated by industries across the globe, thereby challenging the capability of conventional wastewater treatment plants in removing them. In this study, we consider (i) landfill leachate wastewater and (ii) pharmaceutical wastewater as conventional and emerging persistent organic wastewaters respectively. Electroperoxone, being a promising advanced oxidation process, is herein investigated in the treatment of raw landfill leachate and pharmaceutical wastewaters for (i) disinfection, (ii) decolorization, removal of (iii) organic contaminants, (iv) suspended solids and (v) turbidity. A comparative study is done to understand the relative performance of electroperoxone with electrolysis and ozonation, for the removal of (i) humic acid, a major component of leachate, and (ii) ibuprofen, a model pharmaceutical contaminant. Secondly, a comprehensive treatment of the leachate and pharmaceutical wastewater was carried out using Reticulated Vitreous Carbon (RVC) cathode and Platinum-coated Titanium anode. Effect of aeration rates, applied current, electrode surface area and solution pH on H_2O_2 generation was studied. $\cdot$OH radical quantification showed maximum radical generation in the case of electroperoxone as compared to electrolysis and ozonation. TOC mineralization upto 72%, 82% and 84% turbidity and suspended solids removal within 480 min, 99.72% decolorization within 240 min, and 99.93% disinfection within 180 min in leachate wastewater. In the case of pharmaceutical wastewater, we observed a TOC degradation of 86% within 480 min, 99.96% disinfection in 20 min, 89.7% decolorization and 86.7% removal of suspended solids within 120 min. Mechanisms of removal were also investigated. Electroperoxone thus paves way for a sustainable and efficient approach for the efficient removal of such persistent organic contaminants from wastewater systems.

SERMACS 879

Pattern-based recognition of environmental pollutants using simple optical spectroscopic measurements

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We develop sensing systems for a range of water-soluble or dispersible environmental pollutants, detected using optical spectroscopic signals and pattern-based recognition techniques. Among others, we target simple carbohydrates, heavy metal ions, and polycyclic aromatic hydrocarbons. We developed a series of cross-reactive chemical sensors that respond to these analytes differentially. The information provided by each set of sensors is then analyzed, reduced, and presented by applying algorithms such as Linear Discriminant Analysis (LDA) and Principal Component Analysis (PCA). Poly(amidoamine) (PAMAM) dendrimers covalently modified to carry boronic acid moieties on their surface were used for the detection of simple carbohydrates in water. Conjugated fluorene polymers appropriately appended with recognition units selective for metal ions and PAHs were used for the detection of these two categories of pollutants. In all cases, appropriate polymeric scaffolds allowed us to improve water solubility of the receptor chemistry as well as to take advantage of multivalency to increase the apparent affinity of these receptors, which ultimately translated to higher sensitivity for the analytical methods being developed. In these systems, analytical selectivity is recovered through chemometric analysis of the data set obtained upon interaction of a series of poorly selective receptors with the analytes of interest. In the case of PAHs, a further source of selectivity was also put in place based on their intrinsic UV-Vis absorption characteristics, and the interaction of that absorption with the emission properties of the fluorene polymers.

SERMACS 880

Preparing vulnerable populations for the impacts of climate change: Family/community emergency preparedness and resiliency

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The Fisk University Community Environmental Awareness and Sustainability Program, in partnership with the Metro Nashville-Davidson County Public Health Department's Office of Emergency Preparedness, has been actively working to educate vulnerable populations on how to effectively prepare for emergencies. These populations include communities whose residents are elderly, communities with young or low-income residents, and residents with poor or declining health. Resiliency is a key factor since these identified groups may have fewer resources to prepare for a disaster, a limited ability to evacuate, or the limited capability to bounce back. The key learning objectives of our workshops include: Residents gain an understanding of the forces that drive climate change and the necessary steps for mitigation; Residents become aware of the impacts of climate change on our environment, ecosystems, and human health; Residents are able to identify the hazards that will most likely impact their community (Middle TN) during and after a natural or man-made disaster and the risk from those hazards; Residents are able to describe what to do prior to a disaster (family emergency disaster plan, family communication plan, build an emergency supply kit); Residents are able to describe what to do during an emergency (safe spaces, stay informed, evacuation vs shelter-in-place); Residents are able to describe what to do following an emergency (care for family and neighbors, avoid hazards, safe clean-up, outside agencies that can provide resources); and Residents are able to explain the steps and importance of producing a neighborhood/community resiliency plan (neighbor helping neighbor). Active learning is encouraged throughout the workshop. Overall the training has been very effective based upon evaluations conducted at the end of each workshop.Word of mouth networking by participants has been key to community outreach.

SERMACS 881

Removal of molybdenum from water using Douglas fir biochar/iron oxide nanocomposites

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Molybdenum (Mo) is a naturally occurring trace element that is present in drinking water. It is most commonly found in the molybdate form in well water and breast milk and used in medical image testing. Recently, the EPA deemed Mo as a potential contaminant as it leads to bodily complications like gout, hyperuricemia and even lung cancer. In this work we have assessed the sorptive removal of Mo using Douglas fir biochar (BC) and its iron oxide analogues (MBC). Adsorption was studied as a function of pH, equilibrium time (5 min-24 hours), different initial Mo concentrations (2.5-1000 mg/L), different temperatures (5, 25 and 40 C°) and equilibrium method (batch sorption and fixed-bed column). Preliminary data suggest that MBC is a potential candidate (at pH 3 and 2 hours equilibrum) for Mo sorption. Langmuir capacities for MBC were in the range of 196-234 mg/g. Adsorbents and Mo-laden adsorbents were characterized by BET, PZC, SEM, TEM, EDS, XRD and XPS. The adsorption was sought to be governed primarily via chemisorption mechanisms driven by the surface hydroxyl groups of magnetite particles. Stoichiometric precipitation triggered by iron dissolution was also considered.

SERMACS 882

Periodic table-based descriptors for chemometric modeling of toxicity of metal oxide nanoparticles: Exploration of toxicity mechanisms to multiple species

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A pool of second-generation periodic table descriptors were developed for better understanding the mechanism of toxicity of metal oxide nanoparticles (MNPs) towards three species namely E. coli, human keratinocyte cell line (HaCaT) and Zebrafish embryos.

These descriptors are easily derived from the molecular formula and periodic table in no time and can be used in models with prediction ability similar to or even better than those involving quantum chemical descriptors and physicochemical indices. Previously we have developed 1st generation periodic table descriptors. Now, employing the developed 1st and 2nd generation periodic table-based descriptors, we have developed single species quantitative structure-toxicity relationship (QSTR) models and interspecies quantitative structure-toxicity-toxicity relationship (i-QSTTR) models to understand the relationship among the toxicities of metal oxide nanoparticles to different species along with the identification of the major mechanism(s)for such toxicities. These models further helped in extrapolating toxicity when the data for one species is available and the data for other species are unavailable. Further, we have predicted for a set of 42 true external MNPs employing all three QSTR models individually the toxicity data for all three species. This is one of the first reported modeling studies where a considerably a large number of MNPs are employed to predict for three different species with two stage prediction confidence checking through applicability domain and prediction reliability indicator. Thus, this study will allow a better and comprehensive risk assessment of MNPs for which toxicity data is missing for a particular endpoint.

SERMACS 883

Assessing Latin American *Guadua chacoensis* bamboo biochar and activated magnetite analogues for aqueous arsenic(V) remediation

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In this work, discarded bamboo culms of *Guadua chacoensis* were used for biochar production and remediation of aqueous As (V). Raw biochar (BC), activated biochar (BCA), raw magnetized biochar (BC-Fe), and activated magnetized biochar (BCA-Fe) were prepared, characterized and tested their performance in order to develop an economic, viable, and sustainable adsorbent to provide safe arsenic-free water. Adsorbents were characterized using SEM, SEM-EDX, TEM, TEM-EDS, S_{BET}, PZC, XRD, XPS, FT-IR, and elemental analysis. Activation with KOH increased the surface area of BC from 6.7 m^2/g to 1239.7 m^2/g (BCA), but decreased O/C ratio. The As(V) sorption achieved its equilibrium within < 2 hours and kinetics were described using the pseudo-second-order model. BC-Fe showed a 100 % As (V) removal at a 10 mg/L initial concentration in a wide pH window. Sorption followed endothermic nature for all four adsorbents and the capacities rose with the increasing temperature. Langmuir capacities at 40 ºC for BC, BCA, BC-Fe and BCA-Fe were 256, 217, 457 and 868 mg/g respectively and they were comparable with other sorbents. Breakthrough fixed-bed column sorption, regeneration, and performance in real water samples were assessed. Chemisorption and stoichiometric precipitation mechanisms were proposed.

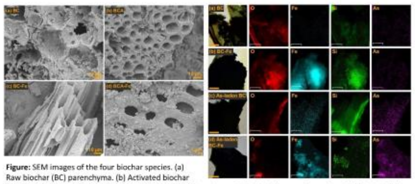

Figure: SEM images of the four biochar species. (a) Raw biochar (BC) parenchyma. (b) Activated biochar (BCA) sclerenchyma fiber cap in transverse section. (c) Magnetized raw biochar (BC-Fe) sclerenchyma fiber cap draped with iron in lateral view. (d) Magnetized activated raw biochar (BCA-Fe) detail of a xylem pitted vessel draped with iron.

Figure: TEM-EDS elemental maps for BC (a), BC-Fe (b), As-laden BC (b), and As-laden BC-Fe
*Scale bar size - 2.5 µm.

SEM images and TEM-EDS

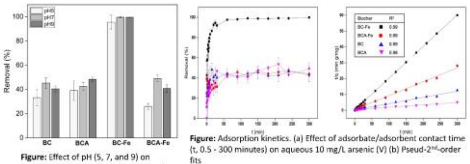

Figure: Effect of pH (5, 7, and 9) on sorption, for a 10 mg/L aqueous arsenic (V) solution (2 hrs at 200 rpm)

Figure: Adsorption kinetics. (a) Effect of adsorbate/adsorbent contact time (t, 0.5 - 300 minutes) on aqueous 10 mg/L arsenic (V) (b) Pseud-2nd-order fits

pH dependency on sorption and sorption kinetics

SERMACS 884

Liquid crystal electrode-assisted hybrid bio-electrochemical treatment technology: Sustainable approach towards biofilm enhancement and wastewater treatment

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Lack of access to ample quantity of safe water has become a major crisis; this emphasizes that wastewater from different sources should be subjected to appropriate treatment followed by efficient reuse. Most conventional wastewater treatment plants have economically viable biological treatment units in place. However, some common problems exist in conventional attached growth wastewater systems which include (i) long start-up times and (ii) frequent biofilm sloughing thus leading to an inconsistent performance. Here, we report a novel electrically bound biofilm reactor (a hybrid bio-electrochemical system), to accomplish augmented bacterial adhesion for the removal of organic contaminants. The reactor comprises a conductive nematic liquid crystal display electrode (NLCE) as the anode, obtained from electronic waste. Pt, Cu, Al were assessed as potential metal cathodes. At

optimized conditions, up to 79.3% of the total suspended biomass formed a stable biofilm on the NLCE, with a 71.2% bio-degradation of organic contaminants within 28 h. The effects of operating conditions such as varying electric potentials, dissolved oxygen concentrations and shear rates on bacterial adhesion and stability were investigated. Raman, Fluorescence and Fourier transform infrared spectroscopy, and cyclic voltammetry confirmed the presence of C=O, C≡N and NH_2 functional groups on NLCE. Commendable stability of biofilm and accelerated start-up phases were achieved, which can be ascribed to (a) the positive functional groups on NLCE, (b) electrostatic attractive forces between NLCE and negatively charged bacteria, and (c) advection-driven mass transport (oxygen and substrate) across the biofilm. Mechanisms of enhanced bacterial adhesion and advection-driven mass transport were investigated. Such a hybrid bio-electrochemical technology with accelerated start-up phase and augmented bacterial adhesion offers a sustainable and promising approach towards the treatment of toxic and complex wastewaters.

SERMACS 885

Base pair sequence and minor groove shape in the design of mixed sequence DNA-binding agents

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AT base pair (bp)-specific, dicationic heterocycles from our laboratories that bind in the DNA minor groove have shown excellent clinical activity and general low human toxicity against several parasitic diseases. This result has encouraged us to try to design and characterize related heterocyclic cations with broader DNA minor groove sequence recognition capability. Such compounds would have important new properties such as more specific DNA sequence targeting capability and the potential to inhibit transcription factors that have been classified as "undruggable". Since the original compounds are all AT base pair binders with H-bond donor groups, for GC base pair (bp) binding we need to add appropriate H-bond acceptors to interact with the exocyclic G-NH_2 group that projects into the minor groove. While this idea is conceptually simple, it has never been accomplished in a systematic set of heterocycles of this type. When considering recognition of even a single GC bp in an AT sequence context, the difficulties become apparent. The H-bond accepting groups for GC and donating groups for AT must be placed appropriately to match the bp groups and curvature at the floor of the minor groove. The design must be done in the context of available synthetic procedures and materials. It is also essential to have adequate compound solubility and to limit the aggregation properties of the complex systems. Starting with our understanding of AT specific compound binding in the minor groove, we designed new model compounds for potential recognition of a single GC bp in an AT sequence. The compounds were prepared, purified and evaluated against selected DNA sequences by biosensor-SPR and spectroscopic methods. We were able to obtain three quite different compounds with strong and specific binding to the target, mixed-base-pair DNA sequences and these initial compounds are being expanded.

SERMACS 886

Targeting the mammalian high mobility group protein AT-hook 2 for drug discovery

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The mammalian high mobility group protein AT-hook 2 (HMGA2) is an embryonic protein associated with epithelial-mesenchymal transition (EMT) during embryogenesis. Its over and/or abnormal expression is directly linked to obesity and oncogenesis. After over a decade of studies, we now understand the biochemical and biophysical properties of HMGA2 binding to its target DNA sequences. Recently, utilizing the knowledge that we learned from the biochemical and biophysical studies, we invented a high throughput-screening (HTS) assay to screen compound inhibitors targeting HMGA2-DNA interactions and identified several unique inhibitors of HMGA2-DNA interactions including suramin, a century-old antitrypanosomal drug. Interestingly, suramin has been tested as an anti-cancer and anti-metastasis agent for over two decades. Recently it was also used to treat autism spectrum disorder. However, the mechanism of suramin's anti-cancer and anti-metastasis activities is unknown. Our recent results show that HMGA2 may be the biological target of suramin.

SERMACS 887

Sequence-dependent DNA minor groove recognition by an extended heterocyclic dication

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Blockade of the DNA minor groove is increasingly recognized as an attractive strategy to inhibit transcription factors, by denying them access to the promoters and enhancers of genes. DNA selectivity is a critical attribute of prospective ligands. We therefore investigated the binding and volumetric properties of DB1976 (Figure 1), a model bis(benzimidazole)-selenophene diamidine with therapeutic potential in acute myeloid leukemia and several debilitating fibroses. To cover the range of sequence preferences for AT-rich DNA by extended dications such as DB1976, we evaluated three duplexes that spanned $>10^3$-fold in binding affinity. The attendant volume changes also varied substantially, ~100 mL/mol, but not in step with binding affinity, suggesting distinct modes of interactions in these complexes. Given their compositional similarity, the volumetric variations are expected to arise from differences in conformational dynamics (thermal volume) or disposition of hydration water (interaction volume). Independent measurements by osmotic stress limit an exclusive contribution from hydration changes and, in the alternative, suggest significant dynamic perturbations due to ligand binding. Explicit-atom molecular dynamics simulations showed that DB1976 modifies the helical dynamics of the bound DNA in a strongly sequence-dependent manner. These results reveal conformational contributions to the thermal volume that are not fully captured by linear scaling of the solvent-accessible surface area. Such an interpretation is consistent with classical scaled-particle theory and its variants that emphasize solute geometry in cavity formation in solution.

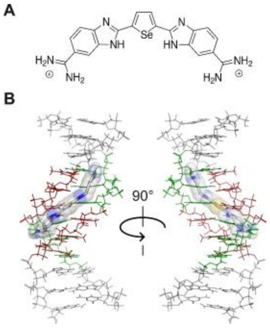

Figure 1. **DB1976, a model extended heterocyclic diamidine with therapeutic potential.** *A*, Structure of DB1976/ *B*, Docked model of DB1976 to 5'-CGCAAATTTGCG-3'.

SERMACS 888

Mechanisms and specificity of Cas10 mediated interference

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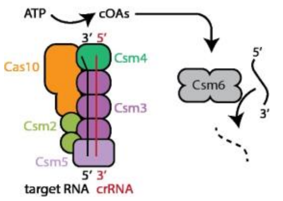
Recently it was discovered that CRISPR-Cas10 synthesizes a previously unknown class of second messenger molecules upon detecting foreign RNA transcripts. The second messengers, cyclic oligoadenylates (cOA), activate the Csm6 nuclease to promote RNA degradation and may also coordinate additional cellular responses to foreign nucleic acids. Using the *S. epidermidis* Cas10-Csm complex, a longstanding model for CRISPR-Cas function, we have reconstituted cOA synthesis and have found that it performs Mg^{2+}dependent synthesis of 3-6 nt cOAs. We show that activation of cOA synthesis is perturbed by single nucleotide mismatches between the crRNA and target RNA at discrete positions, and that synthesis is antagonized by Csm3-mediated target RNA cleavage. Altogether, our results establish the requirements for cOA production in a model Type III CRISPR-Cas system and suggest Csm3 mediated target RNA cutting acts as a molecular switch to shut off cOA synthesis.



SERMACS 889

Design and use of oligonucleotide substrates to probe the mechanism and inhibition of type IA topoisomerases

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Every organism requires the function of a type IA topoisomerase. This subfamily of topoisomerases bind to single-stranded DNA for preventing hypernegative supercoiling of DNA, and facilitate resolution of replication and recombination intermediates that require the cutting and rejoining of single-stranded DNA. The topoisomerase IA present in bacterial pathogens is a validated new target for the discovery of novel antibiotics that can be used to treat multi-drug resistant infections. We have employed oligonucleotides of various lengths and sequences as substrates in biophysical and structural studies of bacterial topoisomerase IA for elucidation of the enzyme structure, conformations and catalytic mechanism. Modified oligonucleotides are designed for cross-linking to the enzyme, and utilized in high through-put screening of small molecule inhibitors that can act as type IA topoisomerase poisons to result in bacterial cell killing.

SERMACS 890

Targeting breast and prostate cancer cells with DNA-methylating molecules bearing nuclear receptor targeting ligands

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The focus of our research is to design molecules that can target specific cancer cells and generate cytotoxic DNA adducts in those cells thus triggering their destruction. We have developed DNA-methylating molecules that can selectively target prostate and breast cancer cells due to their ability to bind to the nuclear receptors (androgen and estrogen receptors) which are overexpressed in these cancer cells. These receptors facilitate the delivery of the the DNA-methylating molecules to the nucleus, where they can then generate N3-methyladenine adducts due to their site-specific binding at adenine thymine rich regions of DNA. The design of these molecules, their interaction with nuclear receptors, their reaction with genomic DNA, and their toxicity towards the targeted cancer cells will be presented.

SERMACS 891

Mixed DNA sequence binding compounds: Promising approach to convert “undruggable” DNA targets to “druggable” receptors

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Although only about 5% of the human genome codes for the protein, it is now well known that most of the DNA has some function, such as synthesis of specific, functional RNAs and/or control of gene expression. The goal to modulate transcription factor (TF) activity has been of significant interest but due to the lack of proper binding sites, targeting the TFs has been quite difficult and TFs have been described as “undruggable”. This is in spite of significant efforts in chemical biology for over a decade to find methods to control cellular TF activity. A goal of this work is to prepare DNA sequence-specific binding ligands that can bind to the DNA minor groove. Another goal for the designed ligands, is that they allosterically inhibit the binding of TFs at the major groove and control cellular gene expression. In *in vitro* applications, such specific recognition compounds will allow new diagnostic applications. In this project we are focusing on (i) designing a new series of highly selective heterocyclic diamidines for both, pure AT and mixed DNA sequences with cell-permeable pharmacophores, (ii) biophysical analysis for detailed understanding of the interactions of designed heterocyclic diamidines with both cognate and non-cognate DNAs and to use this to improve recognition modules, and (iii) the development of biophysical allosteric inhibition assay techniques to monitor the inhibition of TF binding to cognate binding sites. The most important considerations of this work are how the affinity and kinetics change with the DNA sequence and compound structure, chemistry and also their ability to inhibit protein-DNA complexes. Our initial biophysical development with PU.1 TF shows quite clearly that our minor groove binding compounds can allosterically inhibit major groove binding TF, including in cells, such as leukemia cells from patients.

SERMACS 892

Structure-antioxidant correlations of heterocyclic thioether derivatives of carvacrol and thymol

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Carvacrol and thymol are the primary monoterpene components of the essential oils of oregano and thyme. The compounds show a broad range of biological activities, which include anticancer, antibacterial, antimicrobial, insecticidal and antioxidant effects. Owing to their biological properties, carvacrol and thymol are used as food preservatives, and also as ingredients in cosmetics and toiletries. Previous studies have shown that semi-synthetic modification of carvacrol and thymol often result in derivatives with enhanced biological activities relative to the parent compounds. In the current study, a series of heterocyclic thioether derivatives of carvacrol and thymol were synthesized in three steps, in moderate to excellent yields. The derivatives were evaluated for their antioxidant properties by measuring their ability to reduce Cu (II) ions to Cu (I) ions in the CUPRAC (CUPric Reducing Antioxidant Capacity) assay, using trolox and ascorbic acid as positive controls. Most of the derivatives exhibited greater reducing capacity than the positive controls, as well as carvacrol and thymol. Compounds containing oxadiazole, thiadiazole or triazole moieties were the most effective antioxidants, with carvacrol derivatives showing slighter better activity than the thymol derivatives.

SERMACS 893

Protein–protein networking: Discovering mitochondrial metabolic disease pathways

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During the hormonal stimulation substrate cholesterol is transported into mitochondria and is catalyzes by enzyme CYP11A1 to form first steroid- Pregnenolone in the mitochondria. Mitochondria can be subdivided into four mitochondrial compartments: the outer mitochondrial membrane (OMM), the inner mitochondrial membrane (IMM), the intermembrane space (IMS), and the mitochondrial matrix. The presence of mitochondrial protein import channels on the OMM and an electrochemical gradient across the IMM is required for efficient metabolic regulation.In our studies, we have found that during translocation these mitochondrial proteins interact with mitochondria-associated ER membranes, outer mitochondrial proteins such as VDACs, and translocase of the outer membrane of mitochondria (TOM) complex to regulate steroid hormone biosynthesis. Researchers have explored the connections between cardiovascular diseases and changes in specific endocrine functions. The physiological regulation of aldosterone production is very important in controlling blood pressure and for the prevention of cardiovascular diseases like hypertension. Steroid hormone biosynthesis takes place inside the mitochondria and is a complex mechanism. Mitochondrial proteins, most of which are transported from cytosol, catalyze steroid hormone synthesis inside the mitochondria. Similar to most of the mitochondrial proteins, aldosterone synthase (AS), which is an IMM-targeting protein and is transported to mitochondria from the cytosol, interacts with various mitochondrial proteins, specifically CYP11A1, which are the most abundantly expressed inner mitochondrial proteins. At the IMM, AS remains associated with several mitochondrial proteins but directly interacts with CYP11A1. In the absence of CYP11A1, AS processing into the mitochondria is significantly ablated. It is evident that in the absence of CYP11A1, AS cannot be transported into the mitochondria therefore, aldosterone production is inhibited. This study provides a mechanism of hypertension regulation through the networking of mitochondrial protein. The outcome of the research will provide a new approach for the treatment of cardiovascular diseases.

SERMACS 894

Sigma-1 receptors in mitochondrial steroid synthesis: Potential new therapeutic target

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The sigma-1 receptor exists in the central nervous system as well as in peripheral organs, including the lung, liver, adrenal gland, spleen and pancreas. Sigma-1 receptors are over expressed in all types of cancer cells and it appears that this protein contributes to cancer activity as well as neurodegenerative diseases. Sigma-1 receptor helps in the folding of proteins appropriately at the Endoplasmic Reticulum (ER to regulate metabolic activity of receptor-mediated calcium influx. This protein is widely expressed in a variety of tissues however, we performed majority of our experiments in NCI H295 cells. Other cell lines including breast cancer MCF-1, and mouse Leydig MA-10 cells were also used for comparison studies. However similar results were observed. The Mitochondria-Associated-ER-Membrane (MAM) is a small section between outer mitochondrial membrane (OMM) and ER; and is made of lipid and protein filaments. This Mitochondria-Associated ER Membrane region is the physical interaction between the ER and mitochondria which plays a significant role in cholesterol transport, energy metabolism and apoptosis. Sigma-1 receptor is present at the junction of the ER and mitochondria and is a potential target for many proteins, peptide and drug molecules. To understand the role of sigma-1 receptor, we study the effect of synthetic benzofuran compounds with NCI H295. We observed that incubation of these chemical compounds with the cells for 24 hrs increased expression of the sigma-1 receptor and mitochondrial porin proteins. On the other hand, treatment of cells with these compounds led to decrease cell viability indicating the toxic effect of compounds specifically at higher concentrations. This experiment suggests specific effect of the ligands on the sigma-1 receptor, at the junction of the ER and mitochondria. We observed that these compounds by their potential binding to sigma-1 receptor, enhanced the expression of MAM proteins and plays a key role in substrate transport into the mitochondria. This suggests that the sigma-1 receptor contributes to the transport of mitochondrial proteins from the ER to mitochondria for steroid synthesis. These sigma receptor binding ligands can help in proper folding of proteins at MAM region hence regulating the function of proteins related to neurodegenerativediseases.

SERMACS 895

Chemistry research: Making bonds in your community

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Actively engaging the community at large in open dialogue and linking our scientific research to relatable real-world issues is often not an investigator’s highest priority. However, this can be meaningful and transformative for both researchers and the public. From Alzheimer’s research in a synthetic chemistry laboratory at Savannah State University to collaborative biomedical investigations on the International Space Station (ISS), there are opportunities to engage fellow citizens and educate them as to the significance of our work. Good and generous communication with the public allows citizens to value and trust the scientific research experience. We are reminded that it is the citizenry that funds our work and must therefore be served by it. Our strongest advocates are found in the community, and they provide the much-needed motivation and enthusiasm to sustain us as scientists to discover and to create.

SERMACS 896

Communicating chemistry through the local cuisine and beyond

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Food as the object of scholarly attention is not new. In Fall 2008, Food Chemistry was introduced to the Spelman College curriculum as an interdisciplinary science course that allows non-science majors to explore chemical principles through cooking. The course unpacks the function and structure of biomolecules (water, fats/lipids, carbohydrates/sugar, and proteins) in the body. Each week students create an edible experiment and look at the science behind how it all works. Experimental and hands-on approaches illustrate the chemical, biochemical, and physical principles of chemistry, including extraction, denaturation, and phase changes. The overall goal is for students to learn about the interconnectivity of science, culture, and the environment through the exploration of basic food processes. Since its debut, the course’s enrollment is always at maximum capacity. This talk will outline how food and chemistry intersect to solve everyday real-world problems; and, how food as the centerpiece of communicating chemistry, whether it is through research or science demonstrations, can be used to teach chemical concepts to the community at large.

SERMACS 897

Challenges, methodologies, and benefits associated with community-based participatory research

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There is a consensus about the benefits of community-based participatory research (CBPR) and the important role it can play in reducing health differences for populations by combining culturally-relevant knowledge and action for social change. CBPR has proven to be especially valuable with respect to the recruitment and retention of individuals from minority and medically underserved communities where mistrust concerning medical research is relatively high. Indeed, because of that, CBPR has grown exponentially since it was first used as an approach for dealing with health issues in Black communities in the early 1990s. CBPR has been used, for instance, as a cancer prevention and control strategy for African American communities with a number of different disease sites (e.g., breast, colorectal, prostate) across the continuum of care in both urban and rural settings. It is now the primary approach of the 23 Community Network Program Centers (CNPC) that were funded by NCI’s Center to Reduce Cancer Health Disparities (CRCHD) to work with minority and underserved communities around the country on cancer research. The principles of CBPR as well as methodologies associated with its use are laid out in this presentation; in short, CBPR relies on a fairly extensive collaboration between researchers and community members (individuals, organizations, agencies, etc.) where the research is being conducted. It involves collaboration from the onset, continuing throughout the project, and extending through the dissemination of the findings. Implementing the spirit and ideals of CBPR in prevention and control research can be challenging because practical considerations often must take precedence over ideological notions. This presentation revolves around three themes: community representation, possible tensions within CBPR projects, and staffing CBPR projects. It concludes with advice that may be useful to researchers interested in improving lives and reducing health differences using a CBPR approach.

SERMACS 898

Decarboxylative amination of redox-active esters using diazirines

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Amines, hydrazines, and nitrogen-containing heterocycles are found not only in a wide range of natural products, pharmaceuticals, and chemical probes, but also catalyst systems, porous materials, and active surfaces. Despite many recent advances in the field, the development of new, practical methods for C-N bond formation remains a critical challenge for organic chemists. This challenge can be tackled by the invention of new electrophilic and radical amination methods that overcome several of the existing limitations including stability of the amination reagents, regioselectivity, and functional group tolerance. To address some of these drawbacks we have developed diazirines as a reagent-based platform capable of engaging in either radical or electrophilic aminations, depending on the conditions. Redox-active esters (N-(acyloxy)phthalimides) are a convenient way to generate alkyl radicals and have been successfully used in borylations, alkenylations, alkynylations, Michael additions, and other transformations. Herein we report the decarboxylative amination of redox-active esters with diazirines, a method that converts ubiquitous alkyl carboxylic acids into high value nitrogen-containing compounds. This protocol is versatile, user-friendly and scalable, which should allow it to be of general use. Details including reaction optimization, substrate scope, functional group tolerance and diversification into variety of nitrogen-containing compounds will be discussed.

SERMACS 899

Access to and derivitization of heterocycle-rich sulfamate esters and sulfamides

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Transition metal-catalyzed C(sp^2)–N bond-forming reactions have transformed access to arylamines. Most protocols developed to convert (hetero)aryl halide substrates to these valuable aniline analogues rely on palladium catalysis. Fewer technologies rely on copper and/or nickel catalysis. This talk will highlight the development of the first general *N*-arylation reactions that engage sulfamate esters as nitrogen nucleophiles. This technology relies on a mild photochemically-driven nickel-catalyzed strategy. To put this arylation process in context, several other mild heteroatom-tolerant sulfamate ester and sulfamide-engaging and generating processes will be discussed.

SERMACS 900

Functionalized benzo-fused heteroaromatics via metal-catalyzed cascade benzannulations

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Benzo-fused heteroaromatics are important frameworks with broad applications in natural products synthesis, medicinal chemistry, chemical biology, and materials science. The classical synthetic approach to access these systems involves functional group manipulation of preformed benzo-fused derivatives. However, the aromatic products formed display limited substitution patterns. A more efficient strategy to construct these molecules is benzannulation, which involves appending the benzene ring directly onto a pre-existing ring. Benzannulation is preferable due to the likely reduction of reaction steps and better control of regiochemical outcomes. Herein, a series of efficient metal-catalyzed, cascade benzannulation reactions to form benzo-fused heteroaromatics is reported. The scope of reaction, reaction intermediates, reaction mechanism, and control of regioselectivity will be discussed. The formation of functionalized indoles and their subsequent biological evaluation will be used as a means to showcase the broader potential and impact of the methodology.

SERMACS 901

Native chemical ligation: Potential synthetic strategy for drug development

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Proteins are macromolecules that carry out most of the biochemical functions of a cell and also feature widely as structural units. In addition, both linear and cyclic peptides have found use as pharmaceuticals and components of various conjugate molecular systems. Many methods were developed for the synthesis of polypeptide over several decades and solid phase peptide synthesis (SPPS) is one of the most adopted methodologies. However, most of the methods are suitable for peptide chains of less than 50 amino acids. The most successful method of in-solution fragment condensation for chemical synthesis of large proteins is native chemical ligation (NCL). NCL is also an important tool for cyclic peptide synthesis. We have explored intramolecular chemical ligation and utilizing cysteine, serine, tyrosine, and tryptophan. We have used this synthetic strategy to develop cyclic peptidomimetics as potential antifungal agents. The details of our findings will be discussed in the symposia.

SERMACS 902

Cabotegravir: Playing the long game to combat HIV

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The discovery and development of antiretroviral agents for the treatment of HIV/AIDS has changed the prognosis of infection from a death sentence to a manageable chronic disease. Three decades of work has delivered a plethora of drugs and drug combinations to battle the virus and patients can now live healthy and otherwise normal lives. However, therapy is life-long and the consequences of non-compliance can be severe over time. Additionally, stigma remains in many settings with daily therapy creating and unwelcome reminder of their disease. Our group sought to provide a new option for patients wherein infrequent dosing in the realm of once a month or less would take daily therapy out of their lives. This work resulted in the discovery of cabotegravir, a novel long acting HIV integrase inhibitor delivered along with the NNRTI rilpivirine both as monthly parenteral injections. This presentation will cover the synthetic and medicinal chemistries that led to the discovery of this novel medicine along with a brief end to end overview of the program which is currently under FDA review for the treatment of HIV.

SERMACS 903

Cycloadditions using photocatalysis based on earth-abundant metals with heterocyclic ligands

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The invention of novel metal-catalyzed cycloadditions can provide new entry into a diverse array of decorated ring structures. Toward the development of photocatalysts based on earth-abundant metals, our research group has been investigating a series of chromium-based complexes with bipyridyl and phenanthrolinyl ligand systems. These species, when activated by light, are capable of inducing electron transfer events, generating highly reactive intermediates that will engage with pi systems. In this presentation, we will discuss our investigations into these photocatalytic manifolds, demonstrating the capacity of these systems for initiating unique (4+2), (3+2), and (2+1) cycloadditions. Unique mechanistic implications in all of these transformations will also be described.

SERMACS 904

Photoassisted synthesis of structurally complex natural products

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Photochemical reactions provide an efficient means of builidng molecular complexity, often via mechanisms that are inaccessable by any other means. Our group is broadly interested in the strategic application of photochemistry to prepare biologiaclly active natural products in a practical fashion. Photochemical reactions provide an efficient means of building molecular complexity, often via mechanisms that are inaccessible by any other means. Our group is broadly interested in the strategic application of photochemistry to prepare biologically active natural products in a practical fashion. This lecture will focus on our efforts to harness photochemical ring-opening reactions of pyridazine *N*-oxides to develop a unified entry point to certain strychnos, aspidosperma and amaryllidaceae alkaloids.

SERMACS 905

Copper-catalyzed amino difunctionalization of alkenes using nitrogen-heteroatom bonds

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Olefin amino difunctionalization represents a direct and powerful strategy to transform simple and readily available olefins into diverse nitrogen-containing acyclic and cyclic skeletons that are valuable in the synthesis of functional material and biologically important compounds. This talk will present our recent development of copper-catalyzed alkene amino difunctionalization transformations using nitrogen-heteroatom bonds for the synthesis of 1,2-diamine, 1,2- amino alcohols, and 1,2-amino halo containing skeletons.

SERMACS 906

Functional dynamics of human cyclophilin

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Cyclophilins, also known as peptidyl-prolyl isomerases (PPIases), catalyze the cis-trans isomerization of proline. Of the 17 unique human cyclophilins, five closely related homologues (CypA-E) were the focus of this project. These five isoforms all have highly conserved genomic sequences and are very similar in structure, yet function in a variety of environments and participate in diverse cellular processes. As dynamics are known to couple protein function, looking into the conserved dynamics among different isoforms can provide insight into the catalysis of peptidyl-prolyl isomerization by cyclophilin. Functional dynamics were compared using multiple statistical analyses on multiple microsecond-long MD simulations, after which a set of key dynamical residues were identified in the gatekeeper 2 region. This region contains a highly conserved glycine, hypothesized to be responsible for the high flexibility in the region. This glycine (GLY79) was mutated to alanine in CypE, and additional simulations were run to analyze the effects of this mutation. Mutation of GLY79 to ALA79 leads to increased rigidity of CypE during substrate binding (free → cis) but increased flexibility during catalysis (cis → ts). Dynamic changes occur in the mutated region, as well as in another loop downstream of the mutation site. Effects on catalysis were also studied; mutated CypE shows a shift of the cis state to a more positive delta G bind, while the trans state shifts to be more negative, as compared to the wildtype. This suggests a reversal in the direction of catalysis for the mutant.

SERMACS 907

Synthesis of hydroxyl polyester for medical and pharmaceutical applications

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Petroleum based polymers have had a huge industrial impact with two large setbacks that have yet to be solved. First, being that these conventional plastics are made of non-renewable petroleum resources. As a result, there is a high demand for fossil fuels, which is expected to cause petroleum depletion. Secondly, is that the same conventional plastics are also bio-resistant causing an environmental impact. The use of these valuable plastic materials requires a specific type of waste management as it imposes severe environmental problems. As a result, a more environmentally friendly packaging material that does not depend on fossil fuel is of high importance. The interest in the production of environmentally friendly polyesters as an alternative polymeric alternative has been increasing in the last couple of decades since they are produced from renewable resources. As a result of their biodegradable and bioassimilable nature, polyesters have been studied for applications in packaging, drug delivery, surgical sutures and medical implantation devices. Hydroxylpoly(α-methylene-γ-butyrolactone) was done in two steps: The first step involves the synthesis of unsaturated polyester via Ring-Opening Polymerization (ROP) of α-methylene-γ-butyrolactone using 1mol % lanthanide catalysts at low temperatures. The second step is hydrolysis of unsaturated polyester in DMSO using dilute HCl and polymer was isolated using dichloromethane. Both unsaturated and hydroxylpolyester was analyzed with 60 MHz NMR and GPC. Proton NMR indicated that the exocyclic C=C protons found in the unsaturated polyester disappeared in the hydroxylpolyester. The hydrophilicity of the polymers also increase with addition of polar OH groups. GPC analysis showed molecular weights of the polymer to be about the same, Mn about 50 kDa.

SERMACS 908

Expression and purification of the R367H mutant of bovine nitric oxide synthase III oxygenase domain.

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Endothelial nitric oxide synthase is an important enzyme known for its catalytic production of nitric oxide needed for cardiovascular homeostasis. The conversion of the substrate L-arginine to L-citrulline and nitric oxide depends upon key interactions between the substrate, heme, molecular oxygen, and tetrahydrobiopterin. Our lab has used site-directed mutagenesis of the eNOS oxygenase domain from bovine to generate the R367H mutant to perturb the active site for structure/function studies. Here, we describe the expression of the R367H mutant in *E.coli* B21-RIPL competent cells and its subsequent purification for use in single turnover activity assays and X-ray crystallography studies.

SERMACS 909

Using M062X/aug-cc-pVTZ model chemistry to study the lowest energy isomers of sulfuric acid-water clusters

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We have employed the use of a density functional and an augmented basis set in order to study the lowest energy conformations of very small clusters, which form the basis of a lot of atmospheric ultrafine particulate matter. We are currently using the M062X-D3/aug-cc-pVTZ model chemistry along with the CLUSTER program, which uses a genetic algorithm in conjunction with the Gaussian suite of programs to locate all isomers of the clusters that are present under ambient conditions. The clusters are composed of one sulfuric acid molecule and one to four water molecules. So far, our results have been found to be consistent with existing literature in terms of the structures, which indicates that our method is accurate. We have also discovered new structures not yet present in literature.

SERMACS 910

Synthesis of diphenyl oxalates used for testing the chemiluminescence characteristics of multiple fluorophore dyes

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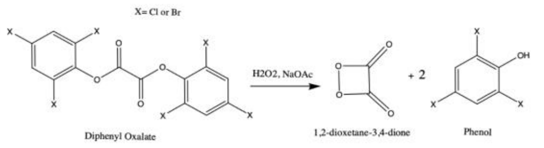
Rasha Al-Daghir, Don McTaggart, Andrew Zeng, Derek Chen

SERMACS Abstract 07/20/2019 Chemiluminescence observed in glow sticks occurs through combining a diphenyl oxalate compound such as bis(2,4,6-trichlorophenyl)oxalate (TCPO) and a fluorophore dye mixed with hydrogen peroxide resulting in the emission of light. The reaction between the oxalate and hydrogen peroxide produces 1,2-dioxetane-3,4-dione an unstable excited intermediate that releases energy as it decomposes. This energy is absorbed by a dye and emitted as visible light, which is observed as a glow. The chemiluminescent properties of TCPO and a brominated alternative (TBPO) made by exchanging chlorine for bromine on the aromatic rings were tested along with a mono-brominated derivative (MBPO) to study the effects that TCPO and its derivatives had on the chemiluminescence characteristics of different fluorophore dyes. The chemiluminescent oxalates TCPO, TBPO, and MBPO were tested in a solution of the fluorophore dyes 9,10-diphenylanthracene and rhodamine B with a weak base such as sodium acetate dissolved in diethyl phthalate. Chemiluminescence was observed for all three compounds with the addition of hydrogen peroxide. Qualitative visual analysis and spectroscopy assisted in the comparison of relative intensity and duration of chemiluminescence among the three compounds. Each compound and dye combination was analyzed via visible spectroscopy.



SERMACS 911

Progress towards a micro-structured Stark quadrupole guide

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Polar gas molecules in electrostatic fields experience rotational energy level splitting due to the Stark effect. While some M_J states go up in energy in the presence of the field, others go down in energy. The ones that go up in energy in the field, feel a force in the direction of lower field and hence are referred to as Low Field Seeking (LFS) states, while those that go down in energy are High Fields Seeking (HFS). Researchers have successfully manipulated the trajectories of both LFS and HFS states using quadrupole fields that are similar to those found in quadrupole mass spectrometers. In 2004, Rempe and coworkers demonstrated such a macroscopic device to transversely trap and guide polar molecules from a helium buffer gas cryogenic molecular beam source. In in this poster we outline our efforts to design, model and construct a micro-structured quadrupole guide device for conventional molecular beams. Our trajectory simulations give the appropriate voltages and frequencies to apply. Despite miniaturization, the design still requires voltages larger than normal solid-state electronics typically handle. The poster will focus on custom electronics we have designed, built and tested which makes use of standard electronics (MOSFETs). The poster will also outline any preliminary results from the full micro-structured quadrupole guide device which we hope to begin testing in Fall 2019.

SERMACS 912

Synthesis, characterization, and biological analysis of opioid peptides and cyclic derivatives containing a Sonogashira linkage

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Opioid drugs have been used for centuries for their pain-relieving properties. Both endogenous and synthetic peptides which bind to the opioid receptors have been identified. Some of these peptides contain cyclic structures, mainly with disulfide or lactam linkages. These cyclizations can help to “lock” a peptide into its bioactive conformation, increasing the affinity of the peptide for its receptor. A linkage which has not been used extensively in peptide chemistry is the Sonogashira bond. This bond is formed between an alkyne and an aryl halide moiety to create a rigid linkage between sp and sp^2 hybridized carbons via a palladium and copper mediated transmetallation reaction. A rigid linkage through cyclization of peptides could help prevent enzymatic degradation, increasing both the potency and stability of the drug. The opioid peptides TAPP, DPDPE, CTP, CTOP, and CTAP were synthesized and purified. Derivatives of each of these peptides with a Sonogashira cyclization were also synthesized by microwave-assisted solid phase peptide synthesis, cyclized on resin, then cleaved and purified. All peptides were tested for binding at the human mu, delta, and kappa opioid receptors. Three novel cyclic peptides containing the Sonogashira cyclization with moderate nanomolar affinity for the opioid receptors were identified using this methodology.

SERMACS 913

Serum stability of opioid peptides incorporating a Sonogashira cyclization

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Cyclization is commonly used in peptide drug design to increase the potency of drugs and help prevent enzymatic degradation of the peptide. Linear peptides are especially vulnerable to the action of acid in the stomach and enzymes present in the small intestine whose job it is to break down proteins or peptides in the diet. However, modifications can be made to cyclize the peptides and help them survive these enzymes to increase the metabolic stability of the peptide. Classically, peptide cyclization usually occurs through disulfide or lactam bond formation. Both of these motifs, found naturally in peptides and proteins, may be broken down by enzymes thereby limiting the amount of active peptide to reach the site of action. Thus, in the field of drug discovery, it is desirable to synthesize drug compounds that are able to withstand the harsh conditions of the body. The Sonogashira bond is a unique approach to peptide cyclization. The bond is formed between an alkyne (sp hybridized) and an aryl halide (sp^2 hybridized), resulting in a highly constrained, flat bond. The linkage was tested for binding to the opioid receptors and led to novel cyclic peptides based with nanomolar affinity for the opioid receptors. This study investigates the serum stability of the opioid peptide DPDPE, which has pain-relieving properties, and a Sonogashira derivative of DPDPE in an effort to develop peptides with a greater half-life *in vitro* and eventually *in vivo*.

SERMACS 914

Molecular modeling of the opioid peptide DPDPE and a derivative of this peptide containing a unique sonogashira cyclization

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DPDPE is a cyclic opioid peptide which is selective for the delta opioid receptor (DOR). The selectivity for the DOR over the mu (MOR) receptor may result in a reduction in the deleterious side effects often seen with MOR agonists. DPDPE is a synthetic cyclic opioid peptide. The cyclization is a disulfide bond formed between the sulfur atoms of two D-penicillamine residues. We have shown that the disulfide bond can be exchanged for a more rigid Sonogashira bond formed between an alkyne and an aryl halide, with moderate nanomolar retention of DOR binding affinity. Computer modeling can be used to visualize the 3-dimensional conformations of these peptides and show how they may be docked into the human delta opioid receptor.

SERMACS 915
Squalene hopene cyclase from *Alicyclobacillus acidocaldarius* as a biocatalyst

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Biocatalysts provide an alternative to traditional catalyst approaches as an enzyme is used to convert a reactant to a desired product. The enzyme squalene hopene cyclase (SHC) is known for its complex single step reaction of squalene to hopene, in which thirteen covalent bonds are broken, nine chiral centers are formed, and five rings are closed. To examine the catalyzing ability of SHC, the SHC gene from *Alicyclobacillus acidocaldarius* was cloned in the pET-22(b+) expression vector, expressed in E. coli BL21(DE3) cells, and purified using a Ni-NTA column. Expression of the SHC has been confirmed by gel electrophoresis. Western blot experiments with a histidine expression tag have been performed and additional enzyme activity experiments are planned to confirm wild-type function prior to site directed mutagenesis experiments. It is hoped this enzymatic conversion may be manipulated through recognition of other substrates similar to squalene or by modification of amino acids within the active site to exploit the SHC as a biocatalyst for other reactions.

SERMACS 916
Multimer networks for recyclable materials

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Crosslinked thermoset polymers are an important class of both chemically and thermally resilient materials. However, the covanent crosslinks that give these important properites also prevent the recycling of these materials. Recently, significant attention has been paid to covalently adaptable networks containing crosslinks that undergo dynamic chemistries that allow these materials to be reprocessed through either an associative or dissociative pathway. We have become interested in exploring networks with both associaitve and dissociative dynamic chemistries that we have coined ‘multimers’. We have focused on systems that undergo transcarbonation or transesterification reactions along with the retro-Diels-Alder reaction in hopes of synthesizing a material that may be reprocessed differently under different thermal regimens. Much of our work has focused on the optimization of the synthesis of these networks along with interrogating the mechanism of this chemistry.

SERMACS 917
Solubility of select azolium compounds

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The solubility of novel -azolium salts were determined by measuring the log P value between water and n-butanol. Select compounds were also tested for anti-proliferative effects.

SERMACS 918
Synthesis of transition metal-based catalyst using functionalized nanoclay for oxidation reactions

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Transition metals are known for oxidation reactions in homogeneous catalysts, but there are some deficiencies to using them. They require stoichiometric amounts to perform the reaction and consequentially produce large sums of toxic inorganic waste. Transition metal based heterogenous catalyst have increased benefits in sustainability and cost effectiveness, so exploring the use of these catalysts is valuable to oxidation studies. This project targets synthesis of naturally available nanoclay functionalized with organosilane group, which acts as a handle to attach the transition metal enclosed ligands. The production of this catalyst will help push more sustainable, economical and effective methods for oxidation reactions.

SERMACS 919
Investigation of amine substituted 4-oxazolidinones and their biological activity

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The synoxazolidinone and lipoxazolidinone families of marine natural products contain an unusual 4-oxazolidinone heterocyclic core and possess antimicrobial and anti-biofilm activity. In this work, we expand the original chemical synthesis of these two natural products to access analogs that contain a variety of heteroatoms. These analogs were tested against ESKAPE pathogens—multi-drug resistant bacteria such as *Staphylococcus aureus* and *Pseudomonas aeruginosa*. We hypothesize that the 4-oxazolidinone scaffold paired with the substituted heteroatoms will exhibit unique antimicrobial and anti-biofilm activity including an increased scope of activity against various pathogens.

SERMACS 920
Quantitative analysis of the components of gun shot residue (GSR) deposited at various distances using different caliber firearms

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Gunshot residue (GSR) is a common component found at crime scenes. Ample research exists on the appearance of gunshot wounds and GSR when a gun is fired at certain distances or from various calibers of weapon. However there is minimal research on the amount of each elemental component found when guns are fired at various distances, or when different caliber weapons are utilized. This study examined the levels of each metal elements common to GSR (lead, barium, copper, and antimony) found on clothing targets when various ranges and calibers of weapon were used. Different caliber firearms were each fired at white and dark cotton T-shirt targets at close range and from a series of increasing distances. The clothing samples were then dissolved in acid to extract the different metal components from them. The samples were then analyzed using flame atomic absorption spectroscopy (AAS) to determine the amount of each component found at the various distances and calibers. The resulting data was used to determine the existence of GSR patterns found between specific firearm calibers and certain firing distances.

SERMACS 921

Immobilized metal affinity chromatography polymeric high internal-phase emulsion foams for protein purification

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Ni-NTA immobilized metal affinity chromatography (IMAC) resins require long protein-resin contact times that significantly diminish their efficiency. Ni-NTA functionalized styrene will be synthesized, then polymerized via a water-in-oil emulsion with the radical initiator AIBN. Trials with varying concentrations of 6xHis-tagged protein will provide information on separation rate, binding capacity, optimal flow rate and retainment of biological activity. Consequently, we expect to improve binding capacity, and separation rate resulting in faster throughput. By conserving the Ni-NTA complex, we expect to retain the advantages of the traditional resin system, namely a more secure protein-nickel interaction, a reduction in the instances of metal leaching, preservation of biological activity and high selectivity for polyhistidine tags (which are easily incorporated into a protein of interest).

SERMACS 922

Achieving chemiluminescence with dyes isolated from natural products

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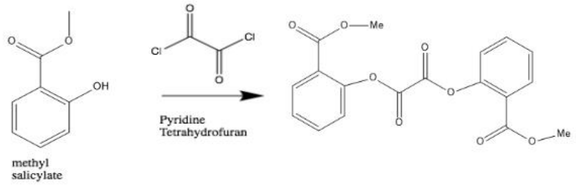
The focus of our research efforts was investigating chemiluminescence through more environmentally-friendly materials. Chemiluminescence of bis-aryl oxalate esters with the addition of fluorescent dye perylene has been reported. Our studies replaced perylene with dyes isolated from spinach (riboflavin) and turmeric (curcumin) in order to explore how these naturally occurring dyes affect the color, longevity, and intensity of chemiluminescence of a bis-aryl oxalate ester, specifically bis[2-(methoxycarbonyl)phenyl]oxalate (Figure 1). The compound riboflavin derived from spinach is responsible for a red chemiluminescence and curcumin in turmeric is responsible for a yellow chemiluminescence. The diester bis[2-(methoxycarbonyl)phenyl]oxalate was synthesized by addition of oxalyl chloride to stirred solution of methyl salicylate in THF. The fluorescent dyes were extracted from frozen spinach and tumeric with a 1:1 mixture of EtOAc and CH_2Cl_2. The oxalate ester, ethyl acetate, and the extracts from the spinach or tumeric was combined and concentrated H_2O_2 was added to generate chemiluminescence. Chemiluminescence from spinach displayed a vibrant red glow from the spinach and the tumeric a faint yellow glow.



Synthesis of bis[2-(methoxycarbonyl)phenyl]oxalate

SERMACS 923

Utilizing chemiluminescence for metal detection in tap water

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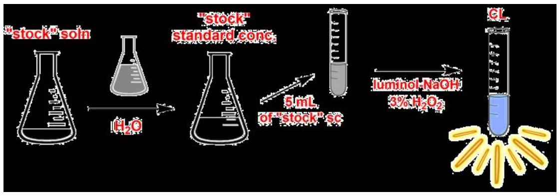
There has been an increase in awareness of the safety of consumer products, such as organic and all-natural food, soap, clothing, etc. National scares such as the Flint, MI water crisis are the motivation behind this research. The goal of this research is to develop a technique to use chemiluminescence to quickly establish whether the metal ion concentration in tap water is too high. Aqueous solutions with varying concentrations of Al^{3+}, Cu^{2+}, Fe^{2+}, Ni^{2+} Pb^{2+} and Zn^{2+} were treated with an aqueous luminol, NaOH and H_2O_2 solution. A visible chemiluminescence was observed at some concentrations of metal ions, specifically Cu^{2+}, Fe^{2+} and Pb^{2+}. Further analysis using fluorimetry allowed quantitative data to be obtained. While further development of the method is needed, preliminary results indicate that chemiluminescence can be used to detect harmful levels of metal ions in tap water.



SERMACS 924

Second-generation kappa opioid agonist as a peripherally-restricted analgesic in the ProNeura platform

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Today, mu opioids are prescribed for peripheral pain, but they come with the risk of many toxicities including gastrointestinal issues, sedation, and addiction. The compound of study, referred to as JT09, has shown peripheral pain alleviation with high selectivity of kappa opioid receptors compared to mu and delta opioid receptors; this prevents the drug from having any affect on the central nervous system as it cannot cross the blood brain barrier. JT09 has been incorporated into ProNeura rods, subdural implants that continually administers the drug for up to 12 months. This technology may render the need for oral and intravenous administration unnecessary, as well as decrease the number of addictive drugs available to the public. Rats were implanted with the ProNeura rods and blood samples were taken at various time intervals. Results are expected to show effectiveness of JT09 as a peripheral pain reliever in the ProNeura platform and not cause symptoms similar to other medications that cross the blood-brain barrier. Future directions include immmunohistochemistry studies on the effect of JT09 on myocardial infarctions and pharmacokinetics studies.

SERMACS 925

Microwave-assisted synthesis of zinc oxide nanoparticles using diethylene glycol as the surface capping ligand

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Zinc oxide nanoparticles show promising applications in biomedical fields. Their antimicrobial properties make them attractive materials for the use in clinical settings. Our current research is focused on developing synthetic methods to prepare highly monodispersed zinc oxide nanoparticles. In this work, a microwave method was used to prepare highly monodispersed zinc oxide nanoparticles using zinc acetate as the reactant and diethylene glycol as the surface capping ligand. Our microwave synthetic method enabled a significant reduction of reaction time when comparing to traditional heating methods. The nanoparticles were characterized using dynamic light scattering, powder X-ray diffraction, and transmission electron microscopy techniques. The reaction conditions including reaction time and reactant to surface capping ligand ratio were optimized. Preliminary antimicrobial studies will also be presented.

SERMACS 926

Microwave-assisted synthesis of europium-doped calcium fluoride nanoparticles for potential biomedical applications

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Europium-based nanoparticles have potential applications in optical materials, biological sensors, and biomedical assay technologies. They have promising applications in biomedical field due to their long luminescence lifetime, nearly monochromatic emission at 614 nm, large Stokes' shift, and limited photobleaching. In this work, a microwave-assisted reaction method was optimized for synthesizing europium-doped calcium fluoride nanoparticles. Microwave reaction time and europium doping levels were optimized to improve the monodispersity and the luminescent properties of the nanoparticles. Particle characterization using dynamic light scattering, transmission and scanning electron microscopy, and luminescent spectroscopy will be presented. The microwave method produced highly monodispersed calcium fluoride nanoparticles with europium metal doping. Preliminary in vitro imaging and cell uptake studies will be presented.

SERMACS 927

Synthesis and characterizatio of Si(bzimpy)$_2$ analogs for application within organic light emitting diodes

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The growing electronics industry shows current demand for more efficient and renewable materials for organic light emitting diodes (OLEDs) and solar cells. Recently, hexacoordinate silicon complexes were shown to represent a promising new class of material for organic electronic devices with excellent electron transport properties and electroluminescence properties. The goals of this research project were (1) to develop synthetic variants of a class of hexacoordinate silicon complex and test the optical and electronic properties of the new materials, (2) to determine the effect of synthetic modifications on these properties, and (3) to see how well the experimentally determined properties compare to properties predicted by computer modeling. A series of complexes were synthesized containing two modified 2,6-bis(benzimidazol-2′-yl)pyridine ligands (bzimpy), each attached to a neutral silicon molecule in the center. The complexes synthesized for this study were Si(bzimpy)$_2$, Si(MeO-bzimpy)$_2$, Si(Me$_4$bzimpy)$_2$, and Si(MeOMe$_4$bzimpy)$_2$. The electron mobility and optical properties of the complexes were measured to determine how the synthetic variations might impact organic devices. X-ray crystallography was used to observe the crystal structure, and ultraviolet-visible and fluorescence spectroscopy were used to determine the optical properties of each of the four modified complexes. Additionally, thermally deposited films were also studied to determine solid-state properties of each of the materials. Prototype devices containing the hexacoordinate silicon complexes are being developed.

SERMACS 928

Toward the stereoselective synthesis of olefins

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To practice synthetic organic chemistry, is to practice the law of diminishing returns. To date, a synthetic organic chemist seeking to synthesize a product through the combination of reactants must accomplish this task, in its most simplistic form, by combining the reactants and a solvent in a flask followed by mixing. Through this process, the chemist hopes the reactants will collide with sufficient velocity and in the correct, three-dimensional, orientation such that a reaction will take place and the new product will be synthesized. Painstaking effort is spent keeping optimal conditions for product synthesis; it is common for these conditions to be held for days. Even when the conditions are optimal, most reactions fail to yield 100% pure product. When the reactions inevitably stall, the resulting mixture of compounds requires tedious purification. This additional step increases the amount of time required to obtain a pure product and diminishes synthetic yield. It is not uncommon for a reaction to take a week from start through purification only to end up with 60% yield – which is generally accepted in synthetic circles as ‘good yield’. Issues with yield compound when reactions produce the desired product as a pair of isomers. A reaction that converts 60% of the starting material becomes far more problematic if only 50% of the product is the desired isomer! Synthetic methodologies that afford stereoselective control of product distribution remain paramount. The use of swellable organically modified silica (SOMS) nano-reactors seeks to overcome the reactivity challenges of conducting synthesis using traditional methods by ensuring reactivity through the restriction of reactants to nano-sized reactors. It is believed that the rate of SOMS nano-reactor collapse upon solvent removal to be not only the driving force in reaction completion, but also the isomeric distribution driving force and as such, when the SOMS nano-reactors collapse, reactant molecules become trapped in the pi-pi scaffold of collapsing BTEB molecules. When locked in this orientation, the reactant molecules trapped in the pi-pi scaffold present significant steric challenges to approaching free-floating reactants, and as such, the free-floating reactants are far more likely to react when oriented in the more favorable E orientation. The authors report Initial investigations into the use of SOMS nano-reactors to facilitate olefin synthesis, efforts were focused on the Wittig reaction.

SERMACS 929

Detailed investigation of the nitroxide-mediated oxidation of primary alcohols

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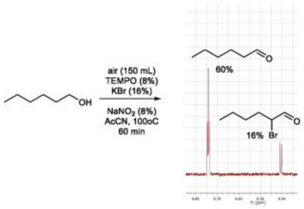
The oxidation of primary alcohols to their respective aldehyde is an important transformation in organic synthesis. Most routes employ strong and hazardous oxidants under sensitive reaction conditions. Recently, it was found that such reaction can be selectively and quantitatively facilitated by organic nitroxides, specifically 2,2,6,6-tetramethylpiperidine, or TEMPO, using oxygen gas under pressure. The catalytic cycle was perpetuated by the presence of bromine and sodium nitrite. We modified the procedure using potassium bromide instead of bromine, and air instead of pure oxygen in a standard pressure flask. Factors such as temperature, nature and quantity of acid, and the nature of the solvent on the oxidation of benzyl alcohol and 1-hexanol were investigated in detail. It was possible to obtain aldehydes quantitative or near quantitative oxidations under milder, less hazardous conditions. Also, the oxidation of 1-hexanal afforded 2-bromohexanal as by-product confirming the formation of bromine in the catalytic cycle. We have investigated various protocols with respect to the elimination or ehancement of this side product. The conversions have been monitored using ^{1}H NMR spectroscopy and GC-FID.



Air oxidation of 1-hexanol in the presence of KBr and TEMPO to afford hexanal and 2-bromohexanal

SERMACS 930

Photopolymer suitability for a 3D printed model of the bile ducts

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Efficient and accurate *in vitro* testing of biomedical device prototypes can decrease device development costs. 3D printing is a relatively inexpensive and timely means to fabricate parts and models for *in vitro* testing systems. An anatomically accurate 3D printed model of the bile ducts will enable rapid evaluation of novel and/or custom biliary stent designs. The printed model must be elastic, pliable, and unaffected by bile to be suitable for an *in vitro* system. In this study we evaluated the tensile strength, elasticity, and surface characteristics of 3D printed samples of Formlabs Elastic, Flexible and Durable resins or a combination thereof that were exposed to water, saline, or bile at 37C for up to one week. All samples were generated with a Peopoly Moai stereolithography printer; print parameters (e.g. laser power, print speed, tilt, etc) were adjusted as necessary to ensure adequate photopolymerization of the resins. Samples for material testing ($N \geq 6$ per resin or resin combination) were cut with an ASTM-D1708 microtensile die. Tensile test samples were stretched to failure on a Mark10 ESM303 to determine percent elongation and tensile stress. Scanning electron micrographs will be taken of liquid-exposed samples to identify any changes in surface characteristics due to exposure duration and/or liquid composition. Preliminary results show that our elastic resin samples are markedly less elastic than expected based on the Formlabs material datasheet. We found percent elongation to be 75.4% ± 3.4% versus the predicted value of 160%. It followed that tensile strength for our samples, 1.18 ±0.11 MPa, was also less than the predicted value of 3.23 MPa. We will confirm if these differences are due to print settings or post processing upon testing of additional samples but we still anticipate the most suitable resin or resin combo for our bile duct model will be highly elastic.

SERMACS 931

Incorporation of hybrid gold nanoparticles to investigate differences in plasma protein biomarkers of chronic obstructive pulmonary disease (COPD) in a population of smokers

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Chronic Obstructive Pulmonary Disease (COPD) is the fourth leading cause of death in the United States. It is mainly caused by cigarette smoking and specific environmental factors. The overall goal of this research project is to identify potential proteomic markers that may explain the differential susceptibility and increased prevalence of COPD amongst African American smokers. We incorporate various nanoparticles to deplete abundant proteins found in serum and various proteomic techniques to shed insight into the disparity in COPD research and identify markers that will enable researchers to: (1) predict risk of progression, allowing early intervention studies; (2) predict response and outcome; so that treatment decisions can be individualized; and (3) identify novel pathogenic pathways as targets for therapy; (4) incorporate nanoparticles as a low cost efficient strategy for immunodepletion of abundant serum proteins. Using our strategy and high resolution mass spectrometry, we have identified several proteins that are differentially expressed amongst African American and Caucasian smokers.

SERMACS 932

Secondary metabolites in *Abies fraseri*: Protective and regenerative properties

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Compositional differences in terpene concentrations in *Abies fraseri* are possibly due to progressive herbivory patterns by various insects. In collected data, it is evident that without elevated levels of primary terpenoids, herbivory continues, as described in literature regarding *Abies grandis*. Current data suggest that elevated concentrations of pesticidal terpenes are signals of direct herbivory and that over time these concentrations decrease and are replaced by resins that contain compounds that are used to help seal the wounds and promote regrowth in infected areas. Oleoresin that is produced in woody growth is stimulated through herbivory patterns to help curb further infestation.

SERMACS 933

Expedited microwave assisted synthesis of 1,2,3-triazoles for ion sensing

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Due to their unique structural properties, 1,2,3-Triazoles have a crucial role in ion sensing in the field of chemistry. Triazoles also have the ability to be a key Component in pharmaceutical drug therapy. The synthesis of these 1,2,3-triazoles is accomplished with the aid of microwave irradiation in a closed vessel. The effective practice of microwave irradiation allows us to increase the rate of the reaction and give good reaction yields in a short reaction time. Herein we are successfully able to report the synthesis of 1,4-di-substituted triazoles and eliminate any hazardous by-products generating a safer chemistry. The products are characterized and confirmed by the proton and carbon Nuclear Magnetic Resonance spectroscopy's (NMR) and Infrared Spectroscopy.

SERMACS 934

Hydroamination of difunctional maleiimides: Access to polyaminoamides

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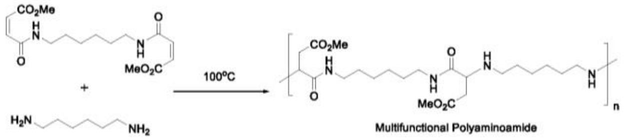
Hydroamination is an attractive, atom-economic synthesis for the formation of C-N single bonds. Due to its limitations, such as the small substrate range only including electron-poor alkenes and alkynes in combination with mostly primary amines or the need of a catalyst, the synthetic value of this reaction often has been overlooked. We have explored the potential of the hydroamination reaction as a synthetic pathway to novel polymeric materials in an effort to produce new, highly functional polymers with potential applications as smart fibers. For this purpose, we have developed syntheses for various dimaleiimide monomers in addition to an aminomaleiimide in straightforward syntheses. The hydroamination of these compounds with diaminanes, namely 1,6-hexanediamine, or the amino groups of the monomer itself, provided access to highly functional polymeric compounds. We are presenting our progress in accomplishing high conversions and hence, high molecular weights with this new polymerization technique.



Hydroamination polyaddition reaction with dimaleates and a diamine

SERMACS 935

Effect of dimerization and interaction with nanoparticles on the absorption and emission spectra of 2,7-dichlorofluorescein

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Absorption and fluorescent emission spectra of 2, 7-dichlorofluorescein (DCF) were obtained and compared for studying the effect of molecular interaction. The concentrations of DCF were varied from $1x10^{-6}$ M to $1x10^{-3}$ M. The emission spectrum showed a peak at 530 nm at $5x\ 10^{-5}$ M concentration with a shift in wavelength with the change in concentration. Further, an initial increase in peak height up to concentration $5x\ 10^{-5}$ M followed by a gradual decrease in peak height above this concentration indicated an onset of dimerization of DCF at this intermediate concentration. Although a red shift of the peak position was observed as the concentration increased, the shift was significantly larger above $5x\ 10^{-5}$ M when compared to the shift below $5x\ 10^{-5}$ M. Absorption spectra also showed a similar behavior. Both absorption and emission peak intensities peaked at an intermediate concentration. When the monomer dominates at relatively lower concentration, the absorption and emission intensities exhibited dilution effect. The presence of nanoparticles and the solution pH had significant effect on the absorption and emission spectral characteristics of DCF.

SERMACS 936

Monosaccharide lithium affinities and how they relate to water adduction to the lithium cationized molecule

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It is important to differentiate the eight stereoisomeric aldohexoses ($C_6H_{12}O_6$); however, their varying chiral centers that have hydroxyls in axial or equatorial orientations are difficult to determine with mass spectrometry. During electrospray ionization, a lithium cation coordinates to hydroxyls in different positions around the pyranose to form gas-phase $[\text{Hexose+Li}]^+$ which can be subsequently analyzed with mass spectrometry. Hydroxyl stereochemistry determines possible lithium coordination sites that can be bi-, tri-, or tetradentate (as determined by density functional theory calculations). $[\text{Hexose+Li}]^+$ can adduct a neutral water molecule in an ion trap mass spectrometer; the reaction rate and amount of $[\text{Hexose+Li}]^+$ that does not adduct a water are unique to a given hexose. The abundance of each type of multidentate structure dictates hexose gas-phase lithium affinity and hexose water adduction reactivity in the mass spectrometer. Hexose relative lithium affinities were determined to better understand their relation to multidentate structures. Relative lithium affinities of aldohexoses and monodeoxyglucoses were found by collisionally dissociating lithium-bound heterodimers of $^{13}C_6$-labeled glucose and unlabeled sugars in the mass spectrometer (Cooks' kinetic method). The sugar that retained the lithium most often in the product ion spectrum had a higher lithium affinity. Hexose lithium affinity and water adduction reactivity are related to the types of lithium-oxygen coordinations formed. Correlations between the two phenomena are discussed herein.

SERMACS 937

Preliminary crystallization results for poly(aspartic acid) hydrolase-2 (paaH-2)

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Poly(aspartic acid) (PAA) is a polymer with industrial and biological applications and is currently an attractive material due to it characteristic of being biodegradable. To date, there are only three known enzymes that are capable of breaking down PAA. We have focused on determining the three-dimensional structures of these enzymes and recently succeeded in determining the structure of poly(aspartic acid) hydrolase-1. This project aims to further build upon these experiments, with the enzyme PAAH-2. Interest in this enzyme resides in its distinctive property of degrading PAA at multiple different linkages. Following optimization of expression conditions and purification, PAAH-2 was initially screened for crystal growth at the Hauptman-Woodward Medical Research center. Based on those crystal hits, in-house crystallization experiments were performed and diffraction quality crystals have been grown. The expression, purification, crystallization, and current progress will be discussed.

SERMACS 938

Multifunctional polyacrylates containing TEMPO, PEG and a hemoglobin binding group

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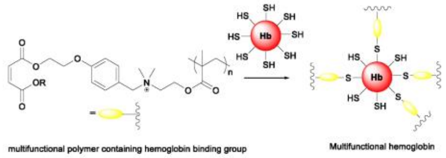
There is a need of hemoglobin-based oxygen carriers (HBOCs), particularly for victims suffering from traumatic brain injuries compounded by hemorrhaging. The most recent generation of HBOCs, polynitroxyl-pegylated hemoglobin (PNPH), is a bovine hemoglobin adorned with radical nitroxides and polyethylene glycol chains on the surface of the protein. In our research, we have synthesized polydimethylaminoethyl (meth)acrylate [poly-DMAE(M)A] via reverse addition-fragmentation chain transfer (RAFT) polymerization. The dimethylamino groups were modified simultaneously with TEMPO and PEG derivatives plus a reactive maleic acid or ester functionality. These groups introduced via postpolymerization modification allow for the detoxification of cell-free hemoglobin plus they provide a covalent attachment to the available cysteine mercapto group of the hemoglobin protein. The binding groups have been synthesized in a three or four step procedure combining a benzylic bromomethyl group for the polymer linking with a maleic acid/ester endgroup for hemoglobin binding.



Binding of TEMPO and PEG functionalized polyacrylate to hemoglobin via a maleate binding group

SERMACS 939

Synthesis of multifunctional polyacrylates via rerversible addition fragmentation chain transfer (RAFT) polymerization

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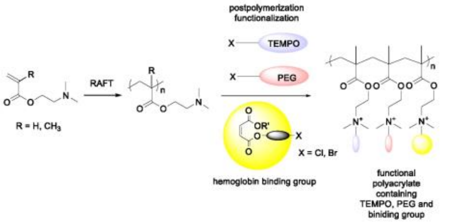
The emergence of Polynitroxyl Pegylated Hemoglobin (PNPH) based on modified cell-free hemoglobin containing 2,2,6,6-tetramethylpiperidine-1-oxidyl (TEMPO) and polyethylene glycol (PEG) groups has initiated a strong interest in these materials as potential blood substitutes in the treatment of severe traumatic brain injuries. Our research is focused on synthesizing multifunctional polymers containing a well-defined number and ratio of PEG and TEMPO groups and their covalent attachment to cell-free hemoglobin. For this purpose, we synthesized functional poly(meth)acrylates containing a dimethylamino groups via Reversible Addition Fragmentation chain Transfer (RAFT) polymerization in a controlled fashion with average molecular weights between 1500-8000 g/mol. The ancillary NMe_2 groups were functionalized with chloroacetate end groups of TEMPO and PEG derivatives in quantitative fashion allowing for the control of functional group density and composition on the polymer as proven via ^1H NMR analysis.



Synthesis of a multifunctional polyacrylate via RAFT and postpolymerization functionalization

SERMACS 940

Mitotropic liposome for targeted delivery of antifibrotics in IPF

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Rationale: Idiopathic Pulmonary Fibrosis (IPF) is a fibrotic interstitial lung disease characterized by abnormal wound repair, excessive collagen deposition, and improper gas exchange. Emerging research has indicated inherent dysfunction of IPF mitochondrial fibroblasts, which is categorized by a hyperpolarized mitochondrial membrane potential. Therefore, selective targeting of dysfunctional mitochondria in fibroblasts is a potential strategy for IPF. Cationic liposomal nanoparticles were synthesized with the goal of observing an increased attraction to hyper polarized negative mitochondria in IPF fibroblasts. The cationic tag, a positively charged stearyl-triphenyl phosphonium (STPP) molecule, was incorporated into a liposomal nanoparticle. Cells were treated with STPP tagged and untagged nanoparticles. Both the untagged nanoparticles and STPP nanoparticles were loaded with the antifibrotic drug Nintedanib. **Methods:**The liposomal nanoparticle was created using cholesterol, lethicin-L-alpha-phosphatidylcholine, mPEG-DSPE and STPP. The lethicin molecule creates the phospholipid bilayer, and the cholesterol provides rigidity while maintaining fluidity of the structure. The untagged liposomes and STPP liposomes were loaded with drug and delivered to tissue culture plates containing normal and IPF fibroblasts. After 24-hour exposure, RNA was extracted, converted to cDNA, and analyzed by QPCR for markers of fibrosis including collagen 1A1 (COL1A) and fibroblast activation protein (FAP). **Results:**Dynamic light scattering demonstrated an increase in size of STPP nanoparticles as compared to untagged (312.3 ± 5.74 vs 297.140 ± 1.40 nm).Fluorescent microscopy demonstrated significant increased delivery of fluorescent Rhodamine cargo in STPP nanoparticles to hyperpolarized mitochondria (27.45%, $p < 0.05$). Antifibrotic potential was observed through significant ($p < 0.05$) decreased gene expression of COL1A and FAP. **Conclusion:**The addition of an STPP cation tag increases nanoparticle cargo delivery to IPF fibroblasts.

SERMACS 941

Forensic application of GC/MS for identification of drugs in human hair

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A forensic analytical method for detection of drugs of abuse in human hair samples was explored using gas chromatography/mass spectroscopy (GC/MS). An extraction method was developed to extract chemical compounds from the hair samples. Using derivatization to increase detection sensitivity of GC/MS analysis, the extracted chemical compounds were identified using GC/MS. The experimental design, method validation, and preliminary results will be highlighted in this presentation.

SERMACS 942

Design, synthesis and anticancer evaluations of piplartine analogues bearing 1,3,4-oxadiazoles as potential anticancer agents

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Piperlongumine (PL), also known as piplartine is a small molecule alkaloid amide extracted from plants of the genus *Piper* which shows several pharmacological properties, including anticancer activities. It was found to be selectively toxic to cancer cells by increasing the level of reactive oxygen species (ROS) and inducing apoptotic cell death, although the exact mechanisms of action remains unclear. The numerous pharmacological activities against a variety of molecular targets essential in different stages of cancer development and progression, as well as low toxicity make PL a strong potential candidate for use in future anticancer treatments. However, due to a lack of nanomolar potency and low water solubility its applicability is limited. In other hand, several reports have revealed the essential features of 1,3,4 - oxadiazole motif as privileged scaffold in drug discovery. Molecular modeling and pharmacokinetic studies have also demonstrated that incorporating 1,3,4-oxadiazole moiety to drug-like molecules change the polarity, flexibility as well as metabolic profile and ability to engage in hydrogen bonding interaction with receptors. Hence, 1,3,4-oxadiazoles have been widely employed as bioesters for esters and amides in several biological targets. Accordingly, we hypothesized that replacement of the lactam ring of PL by 1,3,4-oxadiazole derivatives might improve the aqueous solubility and retain or increase the anticancer activities. In reference to the aforementioned research goal, we have undertaken the design, synthesis and spectroscopic, In Silico analysis and biological evaluations of a series of piplartine analogs bearing 1,3,4-oxadiazole moieties. Knoevenagel reaction, using 3,4,5-trimethoxyaldehyde and malonic acid afforded 3,4,5-trimethoxycinnamic acid in good yield. The 3,4,5-trimethoxycinnamic acid was copled with hydrazine hydrate using Hyroxybenzotriazole (HOBt) in N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) as coupling agent to produce the hydrazide derivative. Condensation of 3,4,5-trimethoxycinnamic hydrazide with *p*-substituted aromatic acids using phosphorus oxychloride afforded the targeted compounds. The synthesized compounds were screened for antiproliferative effect on prostate and breast cancer celllines. The molecular modeling studies of the active compound was performed to understand the potential anticancer mechanism.

SERMACS 943

Photophysics of two-dimensional organic inorganic perovskites

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The solution-processable, earth-abundant organometallic perovskites are promising materials for photovoltaic applications, offering tunable electronic levels, excellent charge transport and simplicity of thin- film- device fabrication. Two dimensional (2D) perovskites have emerged as promising candidates over three-dimensional (3D) due to their interesting optical and electrical properties. In this work, photophysics of the 2D Perovskite (MA)2Pb(SCN)2I2 using steady state and time resolved absorption and emission spectroscopy. Photoluminescence lifetime of this 2D perovskite is 21 ns compared to 7.0 ns of 3D counterpart indicating the less defect/ traps in the former one. Also using ultrafast pump probe spectroscopy we studied the charge carrier dynamics. Carrier dynamics monitored at ~2.3 eV indicates that charges are depopulated with characteristics time constants of 3.5 ps and 57 ps. This indicates that the charge carrier recombination is finished within 100 ps. This work provides an improved understandings of fundamental photophysical processes in perovskite structures and provides the guideline for the design, synthesis and fabrication of optoelectronic devices including solar cells.

SERMACS 944

Investigation of aroma and flavor compounds generated by various yeast strains

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This investigation involves the use of five different yeast strains in several starting solutions, ranging from a simple sugar solution to an all-grain whiskey mash. Different yeast strains produced different aroma and flavor profiles, and we were able to identify some compounds that were unique to different strains, as well as compounds that were only produced when a certain starting material was present. Gas-chromatography mass-spectrometry was used to identify and quantify the compounds.

SERMACS 945

Designing a zwitterionic conjugation-extended viologen for robust aqueous organic redox flow batteries

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In this work, we present a zwitterionic thiazolo[5,4-d]thiazole (TTz) bridged viologen as a two-electron storage anolyte, which has been functionalized with negatively charged sulfonate groups to allow cation exchange in aqueous organic redox flow batteries (AORFBs). Full electrochemical characterization was performed on the sulfonated electrolyte, with cyclic voltammetry studies revealing two closely spaced reduction waves with highly reversible electrochemical kinetics. Scan rate dependence studies yielded diffusion coefficients and electron transfer rate constants for both reduction processes that were several times higher than typical inorganic compounds utilized in aqueous redox flow batteries. Based on DFT analysis, the conjugation-extended TTz moiety imparts increased electronic delocalization and planarity of the pyridinium rings, leading to enhanced robustness of the redox species compared to typical viologens. The enhanced redox stability elucidated via DFT calculations forms the basis for the decreased reduction potential gap seen in the cyclic voltammograms and leads to stable voltage delivery over long-term cycling in charging/discharging tests. In addition to promising electrochemical performance incorporating cation exchange, the novel molecular material is simple and cheap to prepare, thus appealing as a low-cost option for implementation in aqueous organic redox flow batteries.

SERMACS 946

Impact of solvent and fluorination on aggregation of conjugated polymers

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Both morphology and chemical composition (e.g. fluorination) of charge transfer copolymers impact power conversion efficiency in bulk heterojunction solar cells. Here we used absorption and emission spectroscopy to elucidate the impact of these differences on the aggregation behavior of medium band gap copolymers (PBnDT-XTAZ, where X= F or H). We observed the differences in optical cross section strengths for their 0-0 and 0-1 vibronic transitions. This suggests that intrachain and interchain electronic coupling depends on the choice of solvent used and the molecular chemistry. These differences due to morphological and chemical structure variations can impact the photovoltaic performance of the bulk heterojunction made from these polymers.

SERMACS 947

Structural analysis of RNA elements spanning the ribosome binding site in mRNA transcripts of the streptolysin A associated gene from group A *Streptococcus*

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Group A *Streptococcus* (GAS) is a human pathogen responsible for the release of the cytolytic exotoxin, streptolysin S (SLS), which allows the bacteria to spread and destroy soft tissues as a part of necrotizing fasciitis. A nine-gene *sag* locus is responsible for the synthesis of the protoxin SagA and export of SLS after enzymatic modification. The cytotoxin targets sensory neurons of the peripheral nervous system, which then inhibit neutrophils of the immune system. This ultimately paves the way for invasive streptococcal infections. The *sagA* mRNA is also known as Pel (pleiotropic effect locus), which is a small regulatory RNA that regulates other virulence factors. In this project, our goal is to characterize the RNA structural elements that regulate expression of *sagA* and identify potential interactions with regulatory proteins, such as CvfA, or with small regulatory RNAs, such as FasX. Online bioinformatic tools were used to design RNA constructs of Pel/s*agA*, which included the predicted secondary structures that span the ribosome binding site and coding region of *sagA*. The *sagA* gene was isolated from the HSC5 strain of GAS and cloned into a pUC18 plasmid. The linearized plasmid was used for *in vitro* transcription to produce the Pel/*sagA* RNA transcripts. The structured RNA transcripts were characterized by RNase T_1 digestion and thermal melting assays monitored by differential scanning fluorimetry. Three-dimensional modeling was used to predict stem-loop structures and find possible interaction sites within the RNA structural elements. Crystallization screens will identify conditions for structure determination of the RNA transcripts using X-ray diffraction. Intermolecular binding assays will be used to identify protein-mRNA and sRNA-mRNA interactions that may regulate the translation of the *sagA* mRNA. The results of this project can be used to develop therapeutics inhibiting the release of SLS that leads to the invasive phase of streptococcal infections and necrotizing fasciitis.

SERMACS 948

Synthesis of chiral indanone precursors: Short formal syntheses of indatraline and SB-209670 and SB-217242

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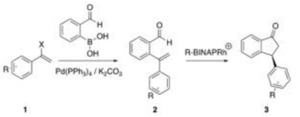
Chiral Indanones can be found in a large number of bioactive molecules and those of importance to pharmaceutical development. In addition, chiral indanones may also serve as valuable intermediates for the synthesis of a large array of compounds, and also may contain inherent biological activity themselves. Kundu, McCullagh, and Morehead developed a highly enantioselective hydroacylation route to chiral indanones utilizing a cationic rhodium BINAP complex to cyclize o-vinylbenzaldehydes. Making this into a general method requires straightforward, high-yielding syntheses of the o-vinylbenzaldehydes and precursors. It is crucial to note that a Suzuki coupling of a vinyl bromide or triflate with 2 – formyl – phenylboronic acid utilizing tetrakis -triphenylphosphine palladium as a catalyst provides a rapid synthesis of the hydroacylation substrate. In this study, two methods for the synthesis of the needed vinyl halide/triflate precursors have been explored. The first employed the method of bromo – boration of an aryl alkyne as the first step, while the second attempted to synthesize the vinyl triflate from aryl ketones. **Formal syntheses of Indatraline, SB-209670 and SB-217242 were chosen to demonstrate the utility of the method.** Past syntheses of these compounds suffer from a low degree of enantioselectivity, a sizable number of steps, and/or low yields. This study aims to seek a more general method for the formation of these vinyl halide/triflate precursors; followed by the proposed Suzuki coupling, and completed by the chiral hydroacylation step which makes use of a chiral Rhodium BINAP catalyst. This short sequence is a significant improvement over established methods for the synthesis of these target compounds.



SERMACS 949

Regulatory RNA structure in *Streptococcus pyogenes*: Terminator of the streptolysin S-associated gene A

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Diseases ranging from simple strep throat to life-threating necrotizing fasciitis are caused by the human pathogen *Streptococcus pyogenes*, also known as group A *Streptococcus* (GAS). The host immune response to necrotizing fasciitis is inhibited by the exotoxin streptolysin S (SLS). SLS is produced by the modification and export of the SagA protein, which is encoded by the *sagA* gene. The *sagA* mRNA has also been identified as a small regulatory RNA, Pel (pleiotropic effect locus), which influences the expression of other virulence factors. The 3' untranslated region (UTR) of the Pel/*sagA* transcript includes a rho-independent terminator, which prevents transcription of the other genes in the *sag* operon. Disruption of the terminator structure through inherent instability or by intermolecular RNA-RNA interactions would allow for transcription of the full *sag* operon required for production of SLS. Our research aims to characterize the structure and interactions of the Pel/*sagA* RNA. Secondary structures of the terminator region were predicted using the programs mfold and RNAfold. Based on these predictions, constructs comprising the terminator were designed. These constructs were isolated from the genomic DNA of the HSC5 strain of *S. pyogenes* and cloned into pUC18 plasmids. Linearized plasmid templates were used for *in vitro* transcription reactions to generate RNA transcripts for each construct. The secondary structures of the RNA transcripts were analyzed using RNase T_1 digests and differential scanning fluorimetry. Three-dimensional homology modeling of the stem-loop structures within each construct was done using the FARFAR program within Rosetta. Further characterization of the terminator structure of Pel/*sagA* will include crystallization screens for structure determination by X-ray diffraction, and RNA-RNA binding assays to identify regulatory interactions. Knowing the structure and interactions of the terminator of Pel/*sagA* will inform the development of therapeutics to decrease the expression of SLS exotoxin.

SERMACS 950

Access to borylated trifluoromethylalkenes via a Boryl-Wittig process

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The unique properties of boron lend themselves to the development of heretofore unknown processes and enable remarkable C-C bond forming events. By devising new methods to generate boryl-containing small molecules, opportunities for the rapid diversification of carbon centers become possible and can be employed by the industrial sector. One simple but fascinating structure is the bis-Bpin methane motif. Although utilized for some elegant reactions, the full potential of this small molecule remains untapped. The goal of this research is to develop new systems to prepare synthetically challenging boryl species from this basic bis-boryl feedstock. Specifically, by combining this reagent with a trifluoromethyl ketone (TFMK) under basic conditions, a boryl substituted CF_3 alkene can be constructed. Diasteroselectivity has also been observed within the products and ongoing work centers on improving the E/Z ratio. Derivatization of the resulting products via cross-coupling or cyclopropanation will enable the construction of challenging trifluoromethylated motifs.

SERMACS 951

Role of solvent when forming palladium nanoparticles on gold nanorods for plasmonic catalysis

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Suzuki Coupling reactions are a form of carbon-carbon cross-coupling reaction used in the synthesis of a wide variety of organic compounds. Prior studies have established the effectiveness of peptide-capped palladium nanoparticles as a catalyst in these C-C

coupling reactions. However, these studies are currently limited to the use of iodine substituted reagents. The use of chlorinated materials in these reactions is coveted due to their relative abundance and cost-effectiveness compared to iodine substrates. Gold nanorods have previously demonstrated unique plasmonic properties which may increase the activity of the palladium nanocatalyst to allow the use of chlorine substituted reagents. The gold nanorods used were functionalized with CPd4 peptide to allow for the attachment of palladium nanoparticles to form a plasmonic nanocatalyst. The peptide attached to the gold nanorods serves as a base structure to which the palladium nanoparticles can attach, which enables the utilization of the catalytic potential of the combined materials for more efficient coupling reactions. Through the use of electron microscopy, it has been found that the dimensions of the palladium nanoparticles vary based on the solvent the nanorods were dispersed in and the concentration of peptide on the surface of the rods. This indicates the catalyst can be manipulated and tuned for use in C-C cross-coupling reactions. The resulting proximity of the palladium to the gold nanorods is expected to enable the utilization of the catalytic potential of the combined materials for more efficient coupling reactions.

SERMACS 952

Raman spectroscopy for the investigation of molecules associated with human decomposition

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The mechanism of human decomposition is not well understood. Thus, there is a need for more effective methods to determine the time since death occurred, or post-mortem interval (PMI). In the past, the most common approach for determining PMI has been the application of different types of mass spectrometry. Mass spectrometry often requires the sample to be in a specific state resulting in sample destruction during the process of acquisition. Raman spectroscopy is a non-destructive technique that is capable of measuring samples in solid, liquid, or gas phases. Here we use both normal Raman and surface-enhanced Raman spectroscopy (SERS) with gold nanoparticles (AuNPs) for the measurement of hypoxanthine, indole, and 3-methylindole, molecules associated with PMI. Our method for measuring these molecules involves normal Raman of solid samples in soil and SERS of dissolved samples in agarose and layered with soil. All analytes were detected in solid-state mixed with soil. More testing is currently underway to optimize the methodology for analyzing the compounds incubated in agarose and layered in soil.

SERMACS 953

Regulating redox and spin state behavior of bis-terpy Fe(II) via steric and inductive influence of ligand substituents

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A series of complexes with the general formula $[Fe(R\text{-}terpy)_2]^{2+}$ where R = Me, OCH_3, OCH_2CH_3, C_2H, $C_2Si(CH_3)_3$, Cl, Br, and I… were synthetically prepared to investigate the steric and inductive influence these substituent groups on the 6’ position of 2,2’:6’,2’-terpyridine (R-terpy) have on the electronic properties of Fe(II). All of the R-terpy ligands were characterized by way of ^1H and ^{13}C NMR followed by coordination onto the metal center in a bis manner. The Fe(III/II) redox couple of each complex was characterized by way of cyclic voltammetry. The redox behavior was observed to correlate well with the substituents inductive influence. NMR methodology was used for measuring room temperature magnetic susceptibilities of each Fe(II) complex under solution conditions. Several of the Fe(II) complexes exhibited spin equilibrium (low and high spin states) that strongly correlated with the 6’- substituents steric influence.

SERMACS 954

Synthesis, characterization and gelation studies of N-(acridin-9-yl)alkanamides based low molecular mass gelators

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N-(acridin-9-yl)alkanamides with dodecyl (9A12) and tetradecyl (9A14) carbon chain have been synthesized. 5 wt % 9A12 and 9A14 have been observed to gelate organic liquids (silicone oil, safflower oil and DMSO) and water. Systematic analysis of gelation properties of synthesized compounds in various polarity liquids, gel melting temperatures and critical gelator concentration will be presented.

SERMACS 955

Design and synthesis of Fe(II) complexes composed of a novel tridentate ligand for studying spin state transition coupled to proton transfer

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The design and synthesis of a tridentate ligand, 2-(1*H*-pyrazol-1-yl)-6-(1*H*-pyrazol-3-yl)pyridine, containing an acidic hydrogen was achieved in a two-step process where one step involves Suzuki Coupling. The ligand was coordinated around an Fe(II) center in a bis-manner. The Fe(III/II) redox behavior of the protonated and deprotonated Fe(II) complex was characterized by cyclic voltammetry under aprotic and protic (aqueous/acetonitrile mix) solvent conditions. Using a modified Evans Method, spin state studies were conducted on the Fe(II) system under solution conditions at room temperature. The study was carried out by shifting the fully protonated to the fully deprotonated Fe(II) complex in incremental steps while maintaining constant overall concentration of the Fe(II) species.

SERMACS 956

Substituted pyrazolines as microtubulin inhibitors under hypoxic conditions

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This research focuses on the synthesis of pyrazolines from readily available chalcones, hydrazine and benzaldehydes in one pot. This one-pot process will allow for a host of pyrazoline derivatives to be synthesized and examined for their bioactivity. The pyrazolines will be designed and synthesized with a sulfate group for future testing on cancer cells in a hypoxic environment. Additionally these compounds will be examined for their cell death proficiencies using MTT assays. Pyrazoline derivatives synthesized containing sulfate groups create a non-toxic prodrug that will be activated once it enters the oxygen depleted environment of a hypoxic tumor cell. The prodrug will be activated to the active drug form by the cleaving of the sulfate group, thereby resulting in the death of the cancer cell by inhibiting the production of microtubulin. The bioactivity of the pyrazolines is very intriguing but their syntheses have received the most attention so far. The early stages of the synthesis suggests the need for a more thermally focused process to generate the pyrazoline from the chalcone and hydrazine. This proof of concept allowed for other chalcones and benzaldehydes to be utilized to develop new pyrazolines. The fascinating design and challenges of this synthetic approach will be discussed.

SERMACS 957

Synthesis of pyrrole molecules as anticancer drug targets

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Leading research in the field of anticancer molecules has focused on antimitotic agents that target the colchicine-binding site of tubulin and halt cell proliferation. The colchicine-binding site has been shown to interact with Combretastatin A4, chalcones, and pyrrole-containing molecules. This research focuses on the synthesis of pyrrole-containing molecules, their ability to inhibit the colchicine-binding site, and their potential to act as DNA cleaving agents. The primary objective of this research project is to create a library of chalcones and pyrrole-containing analogs of Combretastatin A-4 that will be tested against cancer cells to reveal antimitotic effects and structure-activity relationships to the colchicine-binding site of tubulin using an MTT assay. The second objective is to then react the pyrroles to form dienynes that can undergo Bergman-like cyclizations to yield diradicals. These diradical molecules will cleave the DNA of cancer cells, acting in the same way as the enediyne antibiotics. Several chalcones were synthesized in excellent yield (74-99%) and subsequently underwent a 6-pi electrocyclization to form the corresponding pyrrole. The initial attempts in the synthesis of a bromopyrrole molecule while including N-bromosuccinimide using the one-pot, three-step reaction were unsuccessful. However, the last synthesis attempt has shown promising results that a bromopyrrole has been successfully synthesized. The challenges associated with this reaction which will be discussed. This key pyrrole intermediate will undergo a coupling reaction to yield a dienyne substituted pyrrole that will be examined for its potential for antimitotic and antitumor properties and to act as a DNA cleaving agent.

SERMACS 958

Synthesis, thermal properties and gelation studies of anthraquinonylalkanamides as low molecular mass gelators

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Anthraquinone derivatives are well studied compounds because of its pharmaceutical properties as well as its applications as coloring agents. In the present study antrhaquinone derivatives (1-anthraquinonylalkanamides and anthraquinonyl-1, 4-dialkanamides) have been synthesized by varying the *N*-alkyl chain length and gelation properties were examined in various polarity liquids. 5 wt % of 1-antrhaquinonyldodecanamide has been shown to form gel in silicone oil, safflower oil and tert-butanol, whereas 5 wt % anthraquinonyl-1, 4-didodecanamide gelate silicone oil, 1-butanol, tert-butanol, ethanol, isopropanol and cyclohexane. Correlations between antrhaquinone gelators and the properties of their gels, including critical gelator concentrations and gel melting temperatures, thermodynamic properties will be presented.

SERMACS 959

Chemistry in the arts: Identification and documentation of 1920s physicians' kits

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Art and chemistry have been linked since the day the first cave dweller smeared mineral pigments on a rock wall. Today's chemists possess a variety of skills that range from developing pigments and dyes to maintain authenticity of the artifact, while ensuring that they maintain their colors for decades. Chemists, curators, and conservators can authenticate, preserve, and restore artifacts, from present day to 10,000-year-old cave paintings. The Columbus Museum has two collections consisting of 20th Century physicians' kits that they are unfamiliar with and need assistance in identifying the various chemical contents. The 20th century physicians' kits will be will analyzed, identified and the chemical information will be documented to help the museum properly identify, curate, and store the medical collections for an extended period of time. Laboratory analyses will be used to determine the aging of the collections. The historical context of these kits and their contents can provide knowledge of medicine, as well as the use of the items in the twentieth century. Preserving these kits will allow for the evaluation of the evolution of medicine.

SERMACS 960

Synthesis and anti-proliferative activity of ATP-inspired compounds as cancer killing agents

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Cancer, though specific to each individual, invariably expresses its burden by virtue of uncontrollable cellular respiration. Therefore, the majority of anti-cancer medical drugs exert their anti-proliferative activity through cell cycle arrest and induction of apoptosis. Adenosine Triphosphate (ATP) plays a major role in the proliferation of cancer cells owing to the molecule's membrane permeability and function in energy transportation. Recent literature suggests that manipulating the ATP-molecule introduces a natural, site-specific method of combat against cancer stem cells. Incorporating the structural similarity of ATP's base, we hypothesize that the use of purine molecules could offer minimal side effects. Purines, like adenine and xanthines, are naturally occurring molecules and ubiquitously found in human tissue and fluids. A series of purine bases (ie. caffeine, theobromine, etc.) will be investigated to determine the structural components of the xanthine moieties. Additionally, these novel ATP-inspired compounds would be synthesized, characterized and tested for anti-proliferative activity against a panel of breast and prostate cancer cell lines. In theory, a compound with a higher binding affinity than ATP while simultaneously possessing a cell death inhibitor would effectively target and cease tumor development altogether.

SERMACS 961

Embedding multiwalled carbon nanotubes in natural polymer nanofibrous mats

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In recent years, healthcare systems across the globe have begun searching for an alternative to the common wound wrappings and bandages used today. While most of the fibers used to protect open abrasions to the human body perform reasonably well at protecting against infection, emerging superbugs are becoming increasingly able to penetrate and establish themselves in covered wounds. To combat these superbugs and provide a more biocompatible healing patch, natural polymers, such as alginate and chitosan, are being sought for spinning into nanofibrous mats that can be placed over an open lesion. It has also been found that carbon nanotubes greatly enhance the ability of natural polymers to deliver antimicrobial drugs and the ability of natural polymers to remain rigid yet flexible within the body. By performing this experiment, multiwalled carbon nanotubes will be successfully intertwined with both alginate and chitosan polymers by the process of electrospinning. The precise ratio of nanotubes to natural polymer will be determined, and the resulting fibers will be examined using a scanning electron microscope to determine the efficiency of each ratio. Antimicrobial drugs will also be loaded into the nanotubes to assess their efficiency at the delivery of the drug. Also, in doing so, data will be collected for a drug release profile library in order to preserve the rates and efficiency of the carbon-nanotube-embedded natural polymer fibers

SERMACS 962

Progression in the deveopment of an alternative energy synthetic pathway to nylon 6,6 through the use of solar irradiation as the sole heat source

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Due to the acknowledgement of the irreversible damage done to the environment through man-made materials and the desire to circumvent the economic burden of pollution clean-up, scientists have attempted to transform traditional synthetic procedures into ones that are more environmentally favorable. However, since heat is a requirement for the majority of chemical reactions, the amount of electricity required to complete the reactions have become an environmental concern due to depleting fossil fuels. Recently, a technique was developed where satellite dishes were repurposed as solar reflectors capable of providing a focused source of solar irradiation. The ability to use the solar reflector as the sole heat source for synthetic reactions has been analyzed for the synthesis of the commercially important polyaminde, nylon 6,6. Nylon 6,6 is commercially synthesized using a multi-step procedure, in which nearly all of the steps require the addition of heat in order for the reaction to occur. The synthesis also incorporates chemicals that are not particularly friendly to the environment or metals that are considered endangered elements whose supply are in serious danger. The exchange of these reagents with more environmentally friendly, sustainable substitutes has been analyzed. The incorporation of a solar energy heat source and use of environmentally friendly chemicals has provided a new synthetic pathway to nylon6,6 that can be taught in teaching labs as a "green synthesis" experiment or scaled to fit the needs of industrial synthesis.

SERMACS 963

Quantification of Rosmarinic acid in dried rosemary

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Rosemary (*Rosmarinus officinalis*) is a diverse herb that has been used as a culinary spice, preservative in food and for medicinal purposes. It is considered to have anti-inflammatory, antioxidant and anticancer properties. These properties are the result of phenolic properties present. One notable phenolic compound present is rosmarinic acid, which has been shown to exhibit anti-inflammatory and anti-allergy properties. Much research has been done on examining rosmarinic acid in fresh rosemary, but little has been done with dried rosemary. For this research dry rosemary samples compounds were extracted using ethanol and the rosmarinic concentration was determined using high performance liquid chromatography (HPLC) and a standard curve. Concentration of rosmarinic acid in dried rosemary samples were compared to results of rosmarinic acid concentrations found in literature sources for fresh rosemary.

SERMACS 964
Investigation and analytical characterization of *Lavandula angustifolia* essential oils

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As the use of essential oils for natural home remedies becomes increasingly ubiquitous, it is of interest to better understand both the quality and potential hazards of these oils, which may be applied topically and/or ingested. Lavender oil is reportedly one of the most popular oils used by consumers and is readily available for consumer purchase. As such, over 20 samples of lavender oils were procured; the samples varied in price per volume, brand, and growth region of the lavender plant from which oils were obtained (e.g. Bulgaria, France, etc.). The samples were analyzed using FTIR spectroscopy, GC-MS, ICP-MS, and refractometry. The molecular and elemental data from these different analytical techniques was combined along with the consumer information using principal components analysis (PCA) and multivariate analysis.

SERMACS 965
Progress toward the synthesis of paramagnetic luminophores: Mn(II) dipyrrinato complexes

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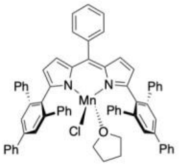
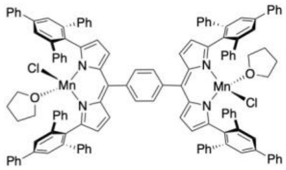
Dipyrrin complexes, including the common BODIPY dyes, are known for their intense coloration and, occasionally, luminescence. Transition metal dipyrrinato complexes are also known for their catalytic activity, most notably in C-H activation processes. Very few open-shell dipyrrinato complexes have been reported to luminesce, but Mn(II) and Cu(II) complexes of very bulky dipyrrins have shown appreciable room-temperature luminescence. We herein report on progress made toward the synthesis of a series of Mn(II) dipyrrinato complexes, in which the metal center is flanked by bulky triphenylphenyl groups.





SERMACS 966
Facile fabrication of pristine nickel hexaminobenezne ($Ni_3(HIB)_2$) metal–organic framework supercapacitor electrodes via electrophoretic deposition

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The use of metal organic frameworks (MOFs) has received increased attention in supercapacitor applications because of their large surface area and controlled porosity. However, MOFs suffer from low conductivity, which hinders their capacitance and rate performance. Herein, we describe a facile and environmentally friendly method for the preparation of nickel hexaminobenzene (Ni3(HIB)2) MOF electrodes using electrophoretic deposition. Both scanning and transmission electron microscopy were used to analyze the morphology of the electrodes. Energy dispersive spectroscopy was used for elemental analysis of the Ni3(HIB)2 electrodes. The electrochemical performance of the Ni3(HIB)2 supercapacitors was characterized using cyclic voltammetry and galvanostatic charge discharge tests. Electrochemical impedance spectroscopy tests were performed over a frequency range from 0.01Hz to 100KHz at an open circuit potential. These supercapacitors displayed an outstanding electrochemical capacitive performance in Na2SO4 electrolyte with an areal specific capacitance of 25.64mF cm-2. Additionally, these supercapacitors exhibited a very low ESR value of 1.28 Ω which can be attributed to both the low contact resistance from the binder free assembly of the Ni3(HIB)2 layers and to the low ion diffusion resistance due to the shortening of the ion diffusion pathway through the electrode micropores. These results demonstrate the potential of pristine MOFs as supercapacitor electrodes and are of great importance to the future of energy storage devices without active carbon materials.

SERMACS 967
Removing copper from aqueous solutions utilizing cotton plant waste

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The purpose of this research was to investigate the copper (Cu) biosorption potential of cotton plant waste (CPW) from aqueous solutions. The CPW were mixed with Cu solutions. Samples were tested unaltered and after HCL treatment. Additional parameters tested include sample dose, contact time, mixing temperature, particle size, and the concentrations and pH of the Cu solutions. Desorption studies were performed to determine if the removed Cu could be recovered. In addition, tests were done to determine if the CPW could be reused for additional Cu biosorption cycles. The results demonstrate that the CPW worked extremely well at biosorbing Cu from aqueous solutions (36-100% removal). Out of all of the parameters tested, only the pH and concentration of the Cu solution had any significant effect on the Cu biosorption capacity of the CPW. As the Cu solution concentration increased, the percent of Cu removed decreased by 18% (100% Cu removal at 1ppm and 82% removal at 30ppm). As the pH of the Cu solution was increased from 2 to 3, the percent of Cu removed increased by 64% (36% Cu removal at pH 2 and 100% removal at pH 3). An explanation could be that, at lower pH, the CPW is positively charged due to protonation, which decreases its Cu biosorption potential. Desorption results showed an 86% Cu recovery rate. Reused CPW was also effective at removing Cu (with or without going through desorption, although 2% more effective without going through desorption). In addition, the CPW that did not go through desorption was still effective at removing Cu from solution when it was reused twice for Cu biosorption (86% Cu removal). Hence, CPW may be reused repeatedly for this purpose without becoming a hazardous waste disposal problem. Overall, CPW demonstrated a great potential for biosorption of Cu from aqueous solutions.

SERMACS 968

Extraction and analysis of the essential oils of fruit rinds and other materials using liquid carbon dioxide

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Essential oils are organic compounds found in plants and other living substances. D-Limonene, the major component of the essential oils extracted from citrus fruit rinds, has a variety of important uses which range from cleaning, to perfumery, to the medical industry. Current methods of extracting essential oils typically involve the use of organic solvents, such as pentane or dichloromethane, or require specialized equipment, such as in cold pressing. This poster describes a study aimed at the improvement and expansion of a previously published method of essential oil extraction using liquid carbon dioxide. This method is greener than typical methods as it does not require the use of typical organic solvents and does not require specialized equipment. A comprehensive optimization of the method, which involves packing and heating a closed centrifuge tube containing dry ice and the extraction material, was performed. The optimized method was then applied to the extraction of essential oil from a variety of different citrus fruits. The composition and yield of oil (typically 1-2%), as determined by GC/MS and IR spectroscopy, was found to be in line with other extraction methods for the citrus fruits. Work scaling the method up to extract larger amounts of oil as well as work aimed at applying this method to the extraction of other materials, such as cannabidiol from hemp products and chlorophyll from spinach leaves, is also described.

SERMACS 969

RTILS as a greener extraction solvent for carbamazepine

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Room Temperature Ionic Liquids (RTILs) were explored as a greener extraction solvent for pharmaceuticals in drinking water. Due to ease of synthesis, 1-methylimidazole (MIM) based ILs were used with varying side chain lengths. Carbamazepine (Tegretol®) was chosen as the drug for extraction based on literature levels found in post-treatment drinking water. [C_7-MIM] [NTF_2] and [C_9-MIM] [NTF_2] were found to have extracted carbamazepine at an average of 83.69% and 98.08% from water, respectively. This was comparable to known extraction solvent, CH_2Cl_2, which extracted 96.15% of the carbamazepine.

SERMACS 970

What is the chemistry behind medicinal plants?

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The purpose of a medicinal garden is not only to study each plant, but to educate students about medicinal compounds in plants and provide alternatives to modern pharmaceuticals. The medicinal garden at Erskine College was established this past summer and over fifteen herbs and plants were cultivated. These are in addition to other medicinal plants that were already on campus. Each plant's chemical composition and medicinal benefits were studied. Ongoing studies of shikimic acid extraction from *Illicium parviflorum* and *Illicium floridanum* will be presented.

SERMACS 971

Comparison of the stereochemical effects on the cyclization of sorbitol and allitol sugars and non-sugar model 1,4-pentanediol utilizing $B(C_6F_5)_3$ and allylsilane CO-catalysis

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Many of the products we utilize every day come from crude oil, including gasoline, plastics, and cosmetics. While it is commonly known that fuels come from crude oil simply through refining, it is less commonly known that crude oil is the main starting material to produce numerous ingredients used in consumer products. Non-renewable resources have simpler chemical structures to renewable resources and are mainly composed of hydrocarbons that function as the backbone for more highly engineered products. Because of their simplistic structure, crude oil requires a series of chemical modifications in order to be used as ingredients. The purpose of this research is to find an alternate way to produce consumer products so that crude oil is no longer heavily relied on. Initial investigations utilized silyl-protected sorbitol and allitol (Si-sorbitol and Si-allitol). These are linear six-carbon sugars that vary in their stereochemistry (the arrangement of groups in 3-dimensional space) which was hypothesized to affect reaction efficiency and selectivity. Reactions were conducted in $CDCl_3$, and a co-catalyst system involving trimethylallylsilane and trispentafluorophenylborane, $B(C_6F_5)_3$, resulted in a five-membered ring via cyclization as determined through NMR analysis (proton, carbon, COSY, NOSY, HSQC). Preliminary optimization of isolation protocols were conducted including purification through silica gel chromatography and subsequent removal of silyl protecting groups. Optimal cyclization occurred when the reactions were performed in the glovebox under nitrogen gas (N_2). Multiple trials were run to screen catalyst loading and to monitor reaction progress over time. Si-sorbitol required lower temperatures and extended reaction times to achieve selective single cyclization, as a second cyclization was discovered to occur at room temperature. Conversely, Si-allitol cyclized at room temperature to exclusively form a

single cyclization product. Exploration of a non-sugar model system, silyl-protected 1,4-pentanediol (Si-1,4-pentanediol; linear five-carbon alcohol), indicates that the sugar scaffold is critical for the observed reactivity due to its failure to cyclize. Future studies will investigate which groups on sugar molecules are responsible for the observed reaction differences.

SERMACS 972

Electrolysis of base hydrolyzed cellulose to oxalate

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Arundo donax is a variety of giant reed which can be used to synthesize secondary biofuels, which are formed from lignocellulosic plants. These sources are being explored as an alternative to primary biofuels due to advantages in terms of supply, but barriers in the efficiency of conversion hold back commercialization of these new fuel sources. Lignocelluloses require a pretreatment to encourage dissolution before they can undergo hydrolysis and additional processing to manufacture useful biofuels. Developing more efficient methods for pretreating and catalyzing this hydrolysis is key to improving the efficiency of the overall process. Here, we have performed a series of electrochemically catalyzed hydrolysis reactions on base-treated cellulose and Arundo donax to form a primary product of oxalate, with acetate and formate also formed. Variations in temperature and pH of pretreatment, as well as in the current and duration of the electrochemical process were performed to observe their effects on the amount of cellulose converted. Additionally, the percent conversion for each set of reaction conditions was found to ascertain the overall efficiency of the method for comparison to other methods of cellulose conversion.

SERMACS 973

Renewable polymers: Towards the ADMET polymerization of plant, animal and fungus alkenes

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With the vast majority of commerical polymers being synthesized from chemicals originating from crude oil, the need to replace them with renewable sourced ones is steadily increasing as the world's oil consumption continues to outpace discovery. The availability of affordable metathesis catalysts that are constantly being improved in terms of functional group tolerance, stability, and activity, provides the opportunity to polymerize natural occurring alkenes via Acyclic Diene Metathesis (ADMET) polymerization techniques. The results of the studies of several renewable acyclic dienes, in combination with commercially available metathesis catalysts will be presented.

SERMACS 974

Formation constants for Cr(III)-DNA binary adducts

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Chromium(VI) is a carcinogen and mutagen, and its mechanisms of action are proposed to involve binding of its reduction product, chromium(III), to DNA. Analysis by this laboratory of self-complementary oligonucleotide duplex DNAs by NMR, EPR and IR spectroscopies in the presence of chromium(III) has recently allowed for the elucidation of the Cr binding sites to DNA to form binary complexes. The metal centers were found to interact exclusively with guanine N-7 positions. No evidence of chromium interactions with other bases or backbone phosphates nor of Cr forming intrastrand crosslinks between neighboring guanine residues was observed. The formation constants for the formation of these binary Cr(III)-DNA complexes have been determined using a series of different sequence self-complementary oligonucleotide duplex DNAs. The binding constants are consistent with Cr binding in a similar fashion to all the duplex DNAs with a slight degree of cooperativity.

SERMACS 975

Redox mediator synthesis for dye sensitized solar cells

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Dye sensitized solar cells (DSSCs) are used as a renewable energy source by converting light energy into electrical energy. Light, a ubiquitous energy source, is used to excite electrons in the dye and then the electrons are injected into the titanium dioxide. Electrons then flow through a circuit to perform work and then the redox shuttle completes the circuit by returning the electrons to the dye. Redox shuttles should be stable in both redox states in order to be an efficient redox shuttle. In this project, new ligand and metal complexes are looked at to form better redox mediators. In current DSSCs, the redox shuttle is not efficient enough, nor is the current solar cell cost effective enough to be put into wide use. This project is meant to look into more efficient and cost effective DSSCs that can deliver greater voltages. Currently, research is being conducted to synthesize the ligands and the metal complexes thereof. After synthesis and characterization, these redox shuttles will be tested by the Delcamp group in a DSSC device.

SERMACS 976

Development of a rapid presumptive test that differentiates between hemp and marijuana

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The passage of the 2018 Farm Bill, legalizing cannabis containing less than 0.3% THC (Hemp), creates problems for law enforcement. Due to the conflicting legality of cannabis across the United States and emerging use of hemp by the public, law enforcement needs to acquire the ability to distinguish between hemp and marijuana using a presumptive test kit. Our approach involves the development of an efficient, mobile, simple thin layer chromatography (TLC) kit that provides presumptive (qualitative) forensic evidence of the chemical extract of a bud or other plant material. The evidence would later be sent to a crime lab for definitive analysis of tetrahydrocannabinol (THC) content, the psychoactive compound in marijuana. Preliminary research has focused on the utilization of TLC plates, a proprietary mobile phase, and commercial stain. The method presented takes no more than five to six minutes to complete. It has successfully differentiated between two lots of commercially available hemp and seven lots of marijuana obtained from the Cookeville City Police.

SERMACS 977

Targeted antibacterial therapeutics for multi drug resistant *Pseudomonas aeruginosa*

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Antibiotics have and are still being used extensively to treat bacterial diseases. However, because of the overuse of these antibiotics in the past, strains of antibiotic resistant bacterial species have emerged. This project is on developing targeted antibiotic delivery system that targets the site of infection in an attempt to reduce the amount antibiotic used for treatment. An engineered nano carrier carries a cargo of antibiotics binds specifically to the surface of the targeted bacterial species and unloads the antibiotic close to the bacteria surface increasing the local concentration of antibiotics. A hollow porous biodegradable nanoparticle is used to store and carry a cargo of small molecule antibiotic. Hollow mesoporous silica nanoparticles (HMSNPs) acts as the nanocarrier. A cationic antimicrobial peptide colistin is electrostatically attracted to the external and internal (pore) surface of phosphonate silane modified HMSNPs. HMSNPs provide a high surface area through the presence of a matrix of high density pores. The bacterial targeting capability to the nanocarrier is offered through a protein (plant lectin) that would bind to the abundant carbohydrate epitopes of the pathogenic species of bacteria.

SERMACS 978

Effect of guest molecules on the hydrogen bonding of water to resorcin[4]arene in supramolecular assemblies

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Hexameric assemblies of resorcin[4]arene monomers form in wet chloroform solution through hydrogen bonding between hydroxy groups on the monomers and water in the molecules. In these assemblies six chloroform solvent molecules are typically encapsulated. We have used molecular dynamics simulations to examine the effect of different guest molecules on the waters that participate in the structure as well as eight additional waters in solution. We consider guests such as additional solvent molecules, neutral trialkylamine molecules, and cationic tetraalkylammonium with a bromide counterion. Given the limited space inside of the supramolecular assembly and necessity of hydrogen bonding for the stability of the structure, the large or charged guests may impact the capsules integrity. This issue is examined based on the simulation data.

SERMACS 979

Studies of the small regulatory RNAS, FASX, and PEL from *Streptococcus pyogenes*

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Group A *Streptococcus* (GAS)/*Streptococcus pyogenes* is a human pathogen responsible for a variety of diseases such as strep throat, scarlet fever, toxic shock syndrome, and necrotizing fasciitis. FasX is a trans-acting small regulatory RNA, which is a crucial factor in regulating GAS virulence factors as well as the expression of streptokinase, fibronectin-binding adhesin, fibrinogen-binding protein and the collagen-binding cell surface pili. Pel (pleiotropic effect locus) is a small RNA associated with the expression of virulence genes in *S. pyogenes*. Based on similar patterns regulating the expression of virulence factors, it is possible that FasX and the small regulatory RNA Pel cooperate in the activation of virulence factors through direct or indirect interactions. To determine potential mechanisms, FasX and Pel were generated by *in vitro* transcription. Nuclease-protection assays combined with differential scanning fluorimetry were used to assess the stability of RNA structure. Results from secondary structure predictions using Mfold and RNAfold were used to predict nuclease-digest profiles. The secondary structure predictions aided in the generation of three-dimensional models of stem-loop structures in FasX by using the FARFAR algorithm in Rosetta. Structural analysis combined with studies of the potential interactions of Pel and FasX will provide an understanding on how GAS virulence factors are regulated during infection. The knowledge gained from this research will provide insight on the design of therapeutics to control GAS virulence in hosts.

SERMACS 980

Development of Pd nanoparticle catalysts supported on carbonaceous ZrO_2 for Suzuki cross coupling reactions

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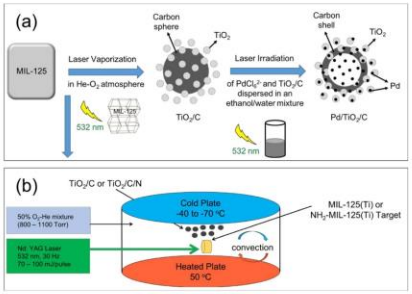
Note: This work is in progress through August 8th, 2019. This work aims to compare the activity of seven Pd nanoparticle catalysts in Suzuki cross-coupling reactions. Pd nanoparticles are loaded via laser irradiation in solution (LIS) onto different support frameworks including: metal-organic framework (MOF) UiO-66, amine-functionalized UiO-66 (NH_2-UiO-66), carbonaceous ZrO_2 prepared by laser vaporization-controlled condensation (LVCC) of UiO-66 and NH_2-UiO-66, reduced graphene oxide (RGO), ZrO_2 prepared by

LVCC, and carbonaceous ZrO_2 containing RGO. These experiments follow recent work with other MOFs addressing many of the same questions about combining the properties of different support materials for heterogeneous Pd catalysts. Additionally, the laser vaporization-controlled condensation (LVCC) techniques offer cleaner and faster routes to the synthesis of optimized heterogeneous catalyst supports. The goal to identify new Zr-MOF and ZrO_2-based supports for Pd catalysts to create more versatile and active catalysts in Suzuki cross-coupling reactions.



Schematic of the laser vaporization-controlled condensation (LVCC) technique used to prepare ZrO_2, carbonaceous ZrO_2, and N-doped carbonaceous ZrO_2 from Zr-based MOFs UiO-66, UiO-66-NH_2, and Zr rod. Schematic shown is taken from another paper and is showing Ti-based MOF MIL-125. Bobb, J. A.; Ibrahim, A. A.; El-Shall, M. S. Laser Synthesis of Carbonaceous TiO_2 from Metal–Organic Frameworks: Optimum Support for Pd Nanoparticles for C–C Cross-Coupling Reactions. *ACS Applied Nano Materials* **2018**, *1*, 4852–4862.

SERMACS 981

Measurement of chlorophyll in green vegetables by fluorescence

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Using fluorescence, the amount of chlorophyll in different green vegetables was determined. Fluorescence was measured both while the chlorophyll was in the vegetables, and after it had been extracted. In order to facilitate the fluorescence measurement from the chlorophyll in the vegetables, a stage was designed and 3D printed. Two different extraction techniques were compared to determine which one extracted more chlorophyll.

SERMACS 982

Comparison of the rates of decay from glow in the dark paints

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Two different brands of glow in the dark paint were investigated with the aid of an emission spectrometer. By measuring the amount of light emitted over time, both the order of the decay and the rate constant was determined for each color. It was found that different colors decay at different rates. Similar colors from the two different brands of paint were compared to see if they had similar orders and rate constants.

SERMACS 983

Changes in enamel surface roughness and *S. mutans* growth after vital bleaching

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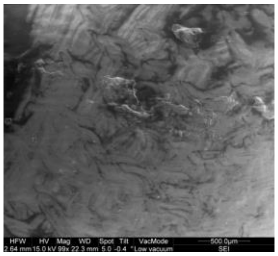
Cavities, gum disease, and heart disease are all linked to the growth of bacteria in the mouth. Scientists have observed that the bacterial genus *Streptococcus* specifically binds to mouth surfaces. The aim of this research was to study and compare how the surface roughness of the human enamel and the growth of *S.mutans* is affected after vital bleaching. Vital bleaching has been used since 1989 for tooth whitening, primarily for the purpose of improving aesthetic dentistry. Current materials used for vital bleaching are hydrogen peroxide and carbamide peroxide, both reactive elements that dispersed into the tooth enamel and dentin. Surface roughness is known to affect the ability of *S. mutans* to bind to tooth surfaces, so it is likely that tooth whitening could affect overall dental health. Statistics have shown that 40.5 million Americans used tooth whiteners in 2018 and this is projected to increase to 40.57 million in 2020. From the results obtained, it was concluded that vital bleaching treatment increased the enamel surface roughness, but showed little effect on S.mutans binding.



SERMACS 984

Computational investigation of the importance of tryptophan to the Myo19 ATPase cycle

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Myosin XIX (MYO19) is a novel actin-based high-duty ratio motor protein involved with the partitioning of mitochondria in anaphase cells. Decreased function of MYO19 has been potentially implicated with a wide range of human diseases where mitochondrial dysfunction is present. This includes neuronal diseases such as Parkinson's Disease and Schizophrenia. The duty-ratio of a myosin motor is determined by nucleotide binding behavior in the ATPase cycle. Subsequent ATP hydrolysis provides the energy necessary for enzymatic function. Unlike most myosin motors, MYO19 contains a tryptophan residue following the phosphate-binding loop (P-loop) in the ATPase active site. This residue is thought to contribute to the high-duty ratio function. While the amino acid sequence of MYO19 is known, currently there is no experimental structure. Theoretical models have been computationally created by threading the MYO19 amino acid sequence onto existing structures of actin-bound MYO2 and actin-unbound MYO5a. Nucleotides ATP, ADP.Pi, and ADP were then bound to both wild-type MYO19 structures as well as glutamate and valine mutants through Glide Docking. These nucleotides were also bound to wild-type MYO5c and a tryptophan mutant. Molecular dynamics (MD) simulations and subsequent energetics analyses were then conducted on these models using AMBER 16 and MMGBSA. A deeper understanding of how tryptophan impacts the ATPase cycle of MYO19 will lead to a greater knowledge of the causation of various mitochondrial diseases.

SERMACS 985

Investigating the *in silico* binding energetics of novel aromatic-substituted POSs and "POCs" HIV-1 protease inhibitors

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Human Immunodeficiency Virus (HIV) is a global pandemic that compromises the immune system by targeting CD4$^+$ T cells. If untreated, HIV can develop into Acquired Immunodeficiency Syndrome (AIDS). HIV-1 is the most prevalent strain and can be targeted by various drug treatments. HIV-1 protease is an enzyme involved in the replication of the HIV-1 virus, making it a viable target for inhibitors. Rapid viral mutation renders many medical treatments ineffective within a short time frame. This necessitates the development of novel drug candidates. Polyhedral Oligomeric Silsesquioxane (POSS) is a cage-like structure consisting of alternating Si-O bonds that can be functionalized with various side chains. Software parameter limitations necessitated the computational approximation of POSS with a POSS-like structure containing alternating C-O bonds. This structure has been tentatively dubbed Polyhedral Oligomeric Carbosesquioxane (POCS). These molecules can be adapted for drug applications with the addition of aromatic side chain substituents. POCS-based inhibitor drug candidates were designed in Maestro and analyzed through Glide Docking to HIV-1 Protease. Molecular dynamics (MD) simulations and subsequent energetic analyses were conducted using AMBER 16 and MMGBSA on candidates that obtained the most favorable Glide Scores.

SERMACS 986

Forced degradation of acetaminophen under high heat, humidity, and radiation

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Acetaminophen tablets were tested using HPLC (High-Performance Liquid Chromatography) methods provided from US Pharmacopeia in order to examine any degradation products found as well as to ensure that potency of the acetaminophen in the tablets was within FDA regulations. Tablets were stored in an environmental chamber with high heat and humidity, and some were exposed to x-ray radiation from the Stanford Synchrotron Radiation Lightsource. Other tablets were kept in storage for several years to be examined as they expired. This is to better understand how these pills will be affected when NASA sends them with astronauts to the moon in 2024 and Mars in 2033. Degradation products have been observed, but are all well below USP Acceptance Criteria maximum percentage.

SERMACS 987

Investigating aged and irradiated meclizine tablets for NASA space mission planning

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This study examined the potency and purity of 4 brands of meclizine tablets exposed to accelerated aging and high energy ionizing radiation using HPLC (High-Performance Liquid Chromatography) and LC-MS (Liquid Chromatography-Mass Spectrometry) methods adapted from the US Pharmacopeia. During deep space travel, including the planned Mission to Mars in 2033, medications aboard the spacecraft may be exposed to conditions, such as high heat, humidity, and radiation, that reduce their potency and that create potentially toxic degradation products. The potency decreased and degradation products were found and identified across all sample sets.

SERMACS 988

DFT study of the Bergman cyclization of several enediynes

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The Bergman Cyclization is a chemical process that rearranges an enediyne to a *p*-benzyne diradical. Many naturally occurring anticancer products contain an enediyne moiety that cyclizes into a highly reactive diradical which can abstract hydrogen from DNA, causing cell death. Most enediynes that function as anticancer molecules are embedded into larger structures 10- or 14- membered rings which cyclize into diradicals closely related to *p*-benzyne. The goal of this project is to utilize density-functional theory (DFT) to study the cyclization and characterize the diradicals of 6-, 10-, and 14-membered enediynes. Though the Bergman cyclization of several enediyne systems have been extensively studied using DFT, these larger systems have not been as well studied and newer functionals such as wB97X-D and M06-2x have not been significantly explored. Initial characterizations using the hybrid DFT functional B3LYP with the cc-pVDZ basis set calculated the activation barrier, energy of the cyclization reaction, and the adiabatic gaps for the singlet and triplet states with the singlet state as the ground state.

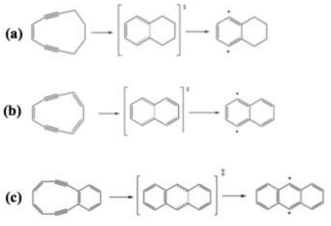

Figure 1. Bergman Cyclization of 10-membered (a-b) and 14-membered enediynes (c).

SERMACS 989

Total phosphorus monitoring in Georgia's Lake Lanier watershed

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When excess nutrients such as nitrogen or phosphorous enter waterways, they can cause harmful algal blooms. The algal blooms are harmful because of the toxins they produce, which affect fish, shellfish, and in turn affect people, birds, and water mammals. Excess nutrients enter the water through various means, including wastewater from sewage treatment facilities, storm-water that carries nutrients and pollutants from cities and towns, and run off and soil erosion from agricultural areas that use fertilizers. It is therefore important to monitor the amount of nutrients in water sources to ensure an excess of one or more nutrients will not cause damage to the ecosystems contained within the water. This study focuses on the precision, limits of detection, and accuracy of the total phosphorus analysis performed by the University of North Georgia Water Lab which has maintained a continuous baseline water quality-monitoring program of the Lake Lanier Watershed since 1987 for The Upper Chattahoochee Basin Group (and its predecessors). Method performance criteria used for the validation process were investigated on standard phosphorus samples: concentration linearity domain (by calibration curve), limit of detection (LOD), limit of quantitation (LOQ), precision and accuracy. Our results demonstrate the method is accurate and precise over the concentration range of 0.032 to 1 ppm P. The validated method was further applied to total phosphorus determination of water samples from Georgia's Lake Lanier Watershed.

SERMACS 990

Spin-flip characterization of the Bergman cyclization of the HEPTA-1, 6-diyne system

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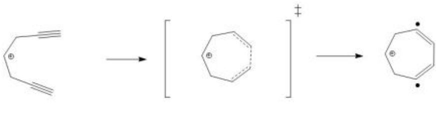
The Bergman Cyclization occurs when an enediyne cyclizes into a highly reactive diradical *p*-benzene. These diradicals are reactive with an affinity for hydrogen abstractions and have the potential to be used as a cancer treatment. However, these diradical based drugs do not differentiate between cancerous and non-cancerous cells. A more thorough understanding of this Bergman structure is critical to create more effective cancer treatments. The cyclization of the hexa-3-ene-1, 5-diyne system has been studied extensively, but the penta-1, 4-diyne anion, hepta-1, 6-diyne cation and octa-1, 7-diyne dication systems have not yet been studied. The cyclization of these three molecules produce enediynes similar in structure and function to that of *p*-benzene and further studying the formation of their diradicals will assist in a greater understanding the character of these diradicals and their potential as anti-cancer agents. The hepta-1, 6-diyne cation system was characterized using the spin flipped coupled cluster (SF-CCSD) method. The activation barrier and energy of the reaction along with the adiabatic and vertical gaps for the singlet and triplet states were calculated using ROHF-SF-CCSD(T)/cc-pVTZ single-point calculations.



Scheme 1: Bergman Cyclization of hepta-1, 6-diyne cation

SERMACS 991

Analyzing conformational changes of steroid response activator RNA (SRA-RNA) bound to sharp suppressor protein using circular dichroism

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The Steroid Receptor Activator (SRA)-RNA is a common target in many diseases including various types of cancer and is important for the diagnosis and treatment. SRA-RNA is used for a response to steroid hormones by tumor cell by increasing nuclear receptor activity. However, the activity is hindered by RNA binding proteins such as the SMRT/HDAC1-Associated Repressor Protein (SHARP). The activity of SHARP is not well understood yet. Nonetheless, this protein binds to the STR7 domain of SRA-RNA and suppresses the activity while forming a ribonucleoprotein complex. We hypothesize that this binding protein will result in a conformational change in the SRA-RNA structure. In this experiment, SHARP2 was purified along with STR7 RNA. A ribonucleoprotein complex was formed and Circular Dichroism was used for analysis. The data was compared to other measurement techniques such as Small-Angle-X-Ray Scattering. Unbound STR7 RNA and unbound SHARP2 was compared to an SRA-RNA SHARP2 Ribonucleoprotein complex. This study is important because the SHARP function will be understood more to improve therapeutic cancer treatments.

SERMACS 992

Synthesis and characterization of new phosphonium ionic liquids

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Our lab has been able to generate an array of phosphonoium compound via a simple S_NAr reaction between triphenylphosphine and an aryl halide. Lithium salts have been shown to promote the halide abstraction, but the phosphonium bromide salts for many derivatives can be synthesised directly from triphenylphosphine and the aryl bromide. The bis(trifluoromethylsulfonyl)imide (Tf_2N^-) anion can be easily incorporated during the synthesis, as well using either the lithium or potassium salt.

SERMACS 993

NacNac: New synthetic routes to a well-known ligand

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NacNac is one of the most widely used ligands in organometallic chemistry, due to its stability, ease of synthesis and tunability. As a monoanionic, bidentate ligand, NacNac can accommodate most metals an geometries. Recently, tri- and tetradentate dertivatives developed, but the syntheses are more complex than traditional NacNac. Our group is working towards developing a greener and more "climate-friendly" synthesis for this next generation of NacNac ligands.

SERMACS 994

Synthesis and analysis of biologically compatible drug-infused polymers

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Polyurethane (PU) materials can be found in a variety of items ranging from paint coatings to insulation foams. More recently, PUs are being utilized in medically implantable devices. Diol prodrug versions of naproxen and nalidixic acid were synthesized to incorporate the drug into a PU backbone. Drug-infused polymers were synthesized with different aliphatic diisocyanates to test the degree of incorporation into the PU backbone. Degradation studies were conducted to determine the degree of pro-drug incorporation as well as the release kinetics of the drugs from the PUs. A HPLC method was developed for the analysis of the degradation studies. A 4 hour pre-wash period and the use of a hydrophobic diisocyanate was shown to exhibit favorable drug release from the PU matrix.

SERMACS 995

Analysis of adonitol as a resource for future sustainable consumer products

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Crude oil is a naturally unrefined source of many consumer products such as fuels, and ingredients in healthcare products and cosmetics. Since crude oil exists in a finite amount, there needs to be a replacement. Renewable resources are an attractive alternative such as readily available sugars, which can be found in nature, in living tissues, and also can be industrially grown. While research has been conducted to transform sugars (e.g., glucose, fructose, etc.) into biofuels, less research has been pursued to access more complex consumer products. The focus of this research is to determine whether various sugars are good candidates for producing the same materials that are currently derived from crude oil. Our initial studies investigated the efficiency of a three-step protocol for using adonitol, which contains five carbon atoms in its molecule, as a building block for the formation of a five-membered or six-membered ring. These rings are a common motif found in consumer products and are challenging to prepare from the molecules found in crude oil, requiring multiple steps. The current project is based on previous studies of six-carbon sugars utilizing tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] and allyltrimethylsilane as co-catalysts. Reaction conditions similar to those involving the six-carbon sugars were applied to adonitol, and results indicate that a five-membered ring is preferentially formed as determined by proton, carbon, COSY, and HSQC NMR spectroscopy. Purification and isolation were performed utilizing silica gel column chromatography. Current efforts are underway to optimize reaction yields and extend these conditions to other five-carbon sugars.

SERMACS 996

Catalytic cyclization of 1-amino-1-deoxy-d-galactitol towards a renewable alternative to petroleum-based medicines

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This research focuses on the development of bio-renewable sugar resources that can be implemented as alternatives to petroleum-based, nonrenewable compounds that are commonly found in many household medicines. With this innovation, the newly formed sugar compound can be used to create a greener medicinal chemistry industry. This project focuses on the conversion of a sugar currently used as a precursor to a cancer therapeutic (1-amino-1-deoxy-D-galactitol or D-glucamine). Our goal is to efficiently transform D-glucamine from its original structure into a form that mirrors petroleum-derived medicinal compounds with ring structures. This will be accomplished using a catalytic reaction, a process where the energy needed to initiate is lowered due to the addition of a compound called a catalyst. Two catalysts, tris(pentafluorophenyl)borane and allyltrimethylsilane, have been shown in prior findings to be necessary to alter similar sugar structures which lack amino groups (e.g., D-galactitol). To prepare the sugar, we have initially altered its structure to make it more amenable to interact with the catalysts, through a reaction that substitutes a portion of the molecule with a group of atoms that can be removed after the desired transition (a protecting group). This temporary group also allows for a more facile analysis of reaction progress and outcome. Preliminary studies combined D-glucamine, pyridine, and chlorotrimethylsilane under room temperature conditions to afford the protected product. Optimization of purification techniques were conducted and toluene was found to be essential. The structure was elucidated by a series of NMR experiments, including proton, carbon, COSY, TOSCY, HSQC, and HMBC. NMR tests are essentially MRIs for chemicals, rather than humans, and use magnetic fields and radio waves to determine the presence of different chemical motifs. Ongoing research entails optimizing the conversion of the silyl-protected D-glucamine using the co-catalysts to form the desired ring structure with respect to reaction efficiency and selectivity.

SERMACS 997

Comparing the efficacy of commerical water filters with homemade water filters using atomic emission spectroscopy

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Since the Flint, Michigan water crisis, clean drinking water and water filtration at home have been on the minds of many. In this poster results will be presented that describe the effectiveness of several different water filters. The filters studied were commercial water pitcher filters and homemade filters. The homemade filters were made using gravel, sand, charcoal and organic material. The organic materials tested were apple, apple peel, banana peel, fresh and dried cilantro, rice and lentils. The filters were tested by filtering water that contained Cd, Cr, Cu, Fe, Pb and Zn through the filters. The metal content of the water was measured before and after filtration using atomic emission spectroscopy.

SERMACS 998

Nickel-catalyzed hydroarylation of alkynes under reductive conditions with aryl bromides and water

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A new method for nickel-catalyzed alkyne hydroarylation is described. This three-component cross-coupling reaction utilizes commercially available alkynes and aryl bromides, along with Zn and water. An air-stable Ni(II) precatalyst is also used. This reductive hydroarylation reaction displays *anti* selectivity, a fairly unusual feature. Optimization data and a preliminary synthetic substrate scope are presented, along with complementary mechanistic experiments including deuterium labeling studies. We believe this report should influence other nickel-catalyzed carbofunctionalization reactions.

SERMACS 999

Ni-catalyzed Larock annulation with *ortho*-bromobenzoates

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A nickel-catalyzed method for indenone annulation is presented. Indenone and indanone moieties are present in a variety of biologically active compounds. The Larock indenone annulation reaction, which has historically been catalyzed by palladium, has been utilized extensively in this field. Still, synthetic methods to make certain classes of indenone products have not been advanced. This procedure employs a nickel catalyst and reductive conditions with Zn. Instead of the previously employed *ortho*-bromobenzaldehyde derivatives, or more elaborate substrates, *ortho*-bromobenzoate esters are used instead. The conditions also expand the substrate scope for the annulation to include a variety of aliphatic alkynes and silyl-protected alkynes. This report constitutes a major advancement compared to the previously reported substrate scope. Moreover, silyl-protected indenone products can be further modified to synthesize more elaborate chemical structures.

SERMACS 1000

Anomalous redox behavior of bis(serinato)copper(II) complex and comparison to closely related bis(homoserinato)copper(II) complex: Update

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Despite being a vital nutrient and having important roles in biological processes, unbound copper ions are toxic when acting as a redox catalyst in the formation of free radicals, which in turn may lead to the oxidation of biologically active molecules. As part of our extended studies on the synthesis and behavior of Cu(aminoacidato)$_2$ complexes, we have continued to investigate the anomalous redox behavior of the cis-bis(L-serinato)Cu complex, which is readily prepared from the reaction of $[Cu(CH_3COO)_2{\cdot}H_2O]_2$ and the appropriate amino acid. This bis(L-serinato)Cu complex is distinctively different from all other known Cu(aminoacidato)$_2$ complexes in that it undergoes a spontaneous redox reaction upon exposure to atmospheric oxygen to yield reduced Cu(I) in the form of Cu_2O. The identity of the oxidized species in the reaction has been elusive. This unusual redox reaction was determined to be a multi-step process. Under slightly acidic conditions in the presence of atmospheric O_2, a significant shift in λ_{max} of the bis(L-serinato)Cu solution (from 625 nm to 704 nm) occurred with no evidence of Cu_2O formation. In turn, this solution rapidly reacts with O_2 bubbled into the solution to yield the previously described red Cu_2O. From a comparison with bis(L-homoserinato)Cu, the primary OH functional group on L-serine was not shown to be the key to the anomalous behavior of bis(L-serinato)Cu; the attempted oxidation of the closely related trans-bis(L-homoserinato)Cu did not occur under the same conditions. We will also report on attempts to compare the bis(cysteinato)Cu complex, which has a primary thiol group, to the bis(L-serinato)Cu with a primary alcohol group.

SERMACS 1001

Characterization of truncated peptides from the novel peptide preptin

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Preptin is a novel, 34-residue peptide that has been isolated from secretory granules of pancreatic β-cells and revealed to be a cleavage product of IGF-11 prohormone. Preptin's therapeutic potential as a treatment for type-2 diabetes or osteoporosis has yet to be fully understood. Truncated peptides were tested for insulin-secreting potential in mouse βeta-TC-6 cells in order to determine the active regions of the peptide.

SERMACS 1002

Stabilization of aβ oligomers using serotonin, indole, and catechol and their effects on DNA

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Alzheimer's disease (AD) is one of many diseases that causes the breakdown of cerebral tissue and subsequent symptoms like difficulty in forming memories, confusion, personality changes, and inhibition of motor function. The amyloid hypothesis states that amyloid-beta (Aβ) peptide aggregates are involved in neuronal death and is one of the most accepted explanations for AD propagation. Small, soluble aggregates of Aβ known as oligomers have oxidative effects on the brain, which can result in the brain damage characteristic of AD. This damage is believed to occur via oxidation-reduction reactions taking place between oligomers of Aβ and biomolecules, such as DNA, lipids, and proteins, within the cell. Based on previous research showing that catecholamine neurotransmitters are able to stabilize oligomers and reduce toxicity, similarly structured catechols were studied to determine if they also have these effects. Experiments assessing the damage to DNA via oxidative effects from these stabilized Aβ oligomers were also conducted. Thioflavin T assays and gel electrophoresis were used to observe the extent of aggregation of Aβ peptides and their ability to oxidize DNA. Immunoblotting assays and NMR were used to determine both structural changes within the Aβ peptide in the presence of small, aromatic molecules, and changes of the aromatic molecules themselves in the presence of Aβ. It was shown that small molecules with catecholic structures stabilize oligomers and may mediate their toxicity more effectively than those small molecules without catechol's ortho-hydroxyl functionalities. Determining how Aβ oligomers are affected by small molecules in the brain will help ascertain the mechanism of AD pathology and lead to more effective treatments against the disease.

SERMACS 1003

Quantitative and colorimetric evaluation of hemoglobin in bloodstains over various time intervals using UV/VIS spectroscopy and chemical enhancements

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The determination and quantification of hemoglobin in bloodstains is an important role in forensic chemistry. In this study, blood stains of known volume and human origin were administered to both white and dark colored t-shirts. After specific time intervals, the preliminary blood tests Bluestar® and Lueco Crystal Violet (LCV) were administered, and blood was extracted from the material. After the specified time intervals, the concentration of hemoglobin was established though the use of UV/Vis spectroscopy. These hemoglobin concentrations were then evaluated to determine if there was a correlation between concentration and the age of the bloodstains. Bluestar® and LCV were used to compare the intensity of colorimetric activity of each stain over the various time intervals and to determine if a greater age diminishes the reactivity of the hemoglobin in bloodstains.

SERMACS 1004

Accessing novel metal organic frameworks using reticular chemistry

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Zeolitic imidazolate frameworks (ZIF's) are a subfamily of porous MOFs mimicking the 145 degree Si-O-Si angle in zeolite minerals. They are prepared using reticular chemistry to form materials that show promise in applications such as gas separation, drug delivery, and catalysis. The purpose of this research is to study the steric and structural directing effects of unexplored disubstituted and trisubstituted linkers such as 4,5-diphenyl imidazole, 2,4,5-trimethyl imidazole and 2,4,5-triethyl imidazole on the formation of zeolitic imidazolate frameworks. These chosen linkers add hydrophobic dynamics to the framework at the 2-, 4- and 5- positions in the form of two phenyl rings (disubstituted) or three carbon chain groups (trisubstituted). Currently, experiments with altering

concentrations, reaction times, and temperature fluctuations of the furnace are being performed using the 4,5-diphenyl imidazole. The reaction was observed to have formed large white urchin-like structures that coagulated together. When the product was observed under an optical microscope, the material had long thin hair-like features. Different metal salts containing cobalt and iron have also been investigated with the 4,5-diphenyl imidazole to study the potential linker to metal coordination patterns. Additional trials, including addition of a variety of strong bases to the reaction mixture to aid in deprotonation of the trisubstituted imidazole linkers and structural identification of the obtained solid/crystalline products are underway.

SERMACS 1005

Designer phonons to sculpt infrared properties

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The optical phonons of many oxides manifest through atomic oscillations at infrared frequencies. Often polar, these oscillations create electric fields that themselves have infrared frequencies. When exposed to IR-photons, the electromagnetic and vibration-induced fields can be of similar energy and momentum causing interactions that dominate the material's infrared properties within the Reststrahlen band bounded by the transverse- and longitudinal-optical phonon modes.Thus, by controlling, modifying, and even creating "designer" polar phonons, a route is opened to induce infrared phenomena. Here, the infrared properties of composite oxides composed of lamellar combinations of common dielectrics and ferroelectrics—MgO/CaO and $SrTiO_3/CaTiO_3$specifically—are examined to this end. Using a suite of vibrational spectroscopies in combination with materials modelling, the optical response of these "Reststrahlen laminates" extends beyond just a summation of the constituents. The resulting optical properties are examined in light of "synthetic" phonon dispersions that emerge with the variations in periodicity implicit in lamellar structures. Together, the work suggests a means of creating arbitrary infrared materials via composite phonon responses. *SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525*

SERMACS 1006

Nano-FTIR correlaction nanoscopy for organic and inorganic material analysis

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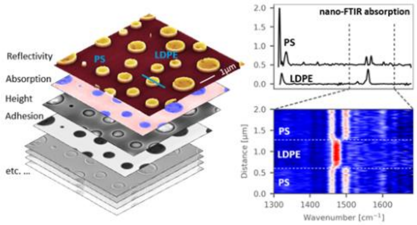
Scattering-type Scanning Near-field Optical Microscopy (s-SNOM) is a scanning probe approach to optical microscopy and spectroscopy, bypassing the diffraction limit of light to achieve nanoscale spatial resolution. s-SNOM employs the strong light confinement at a sharp metallic tip to create a nanoscale optical hot-spot. Analyzing the tip-scattered light enables the extraction of the sample's optical properties directly below the tip, yielding nanoscale resolved images simultaneous to topography[1]. In addition, the technology enables nanoscale-resolved Fourier-Transform Infrared spectroscopy (nano-FTIR)[2] using broadband radiation from the visible to THz spectral range. Recently, the combined analysis of complex nanoscale material systems by correlating near-field optical data with information obtained by other scanning probe microscopy-based measurement methodologies has gained significant interest. For example, the material-characteristic nano-FTIR spectra of a phase-separated polystyrene/low-density polyethylene (PS/LDPE) polymer blend verifies sharp material interfaces by measuring a line profile across a ca. 1 µm sized LDPE island (Fig1). Near-field reflection/absorption imaging at 1500 cm^{-1} allows to selectively highlight the distribution of PS and simultaneously map mechanical properties of the different materials[3,4]. Further, results will be presented that correlate the nanoscale mid-IR and THz response of semiconducting samples like graphene (2D) or functional SRAM devices (3D) to Kelvin Probe Force Microscopy (KPFM) measurements. Thus, s-SNOM systems represent an ideal platform to gain novel insights into complex material systems by different near-field and AFM-based method. [1] F. Keilmann, et al. *Phil. Trans. R. Soc. Lond. A* **362**, 787 (2004) [2] F. Huth, et al., *Nano Lett.* **12**, 3973 (2012) [3] B. Pollard, et al., *Beilstein J. of Nanotechn.* **7**, 605 (2016) [4] I. Amenabar, et al., *Nature Commun.* **8**, 14402 (2017)



Near-field correlation nanoscopy of a thin PS/LDPE polymer film, highlighting the phase separation of the materials by nano-FTIR measurements and the different mechanical properties of the polymers.

SERMACS 1007

Time resolved infrared spectroscopy studies of proton coupled electron transfer

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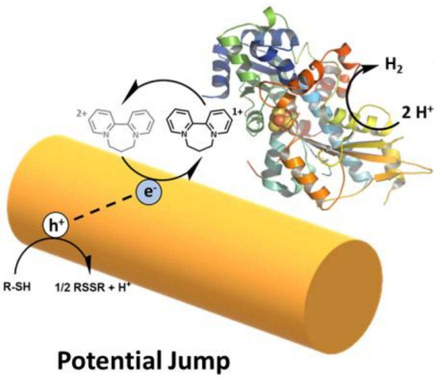
Time-resolved infrared (TRIR) spectroscopy is a powerful approach to study proton coupled electron transfer (PCET) reactions because of its sensitivity to the redox and protonation states of the reacting species. We have developed TRIR methods coupled with the laser induced chemical potential jump to study PCET in redox metalloenzymes. Our approach employs a nanocrystalline semiconductor (NCS) photosensitizer coupled with viologen derived redox mediators as electron relays to achieve efficient interfacial ET to the metalloenzyme as shown in the Figure. Light harvesting and charge separation are accomplished by the NCS material, which can be optimized to efficiently absorb the solar spectrum and to generate long-lived redox equivalents with high quantum efficiency. Pulsed laser excitation of the NCS produces a chemical potential jump that initiates enzyme turnover at a much faster frequency than the steady state turnover rate. Consequently, the fundamental electron transfer (ET) and proton transfer (PT) steps can be resolved with this approach. Hydrogenases catalyze the simplest PCET reactions, the interconversion of H^+/e^- with H_2 and serve as chemically simple model systems. Furthermore, IR spectra of the CO and CN ligands of their active sites are exquisitely sensitive to the different redox and protonation states populated during turnover. We describe the application of the laser induced potential jump coupled with TRIR spectroscopy to study the fundamental mechanisms of the reduction of protons to hydrogen catalyzed by [NiFe] and [FeFe] hydrogenases.



SERMACS 1008

Incorporating primary literature and writing instruction in an upper-level capstone chemistry laboratory course

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Teaching students how to read, search, and utilize primary literature in a field is paramount to training the next generation of scientists. We have utilized an upper-level capstone chemistry laboratory course to introduce students to the primary chemical literature while teaching students the fundamentals of scientific writing. Students were first taught how to read and interpret selected articles from the primary literature using a “three-color-highlighter” exercise, where students visibly represented their understanding of content within the paper. This activity was repeated throughout the semester to demonstrate that students were developing an understanding of a new field. Students were also introduced to the format and purpose of sections within a peer-reviewed manuscript and were required to develop their own laboratory procedures by adapting experimental sections from the primary literature. These skills were used to ultimately convert their procedures into an experimental section in the final assignment. Students were taught how to navigate and search the primary literature, and were required to find their own sources for the laboratory research component and the writing exercises. The final product of the course was a written report in which students were required to author their own primary literature-style manuscript, supporting the interpretations of their data and the significance of their results with primary literature of their own finding. Feedback from students indicated that these exercises allowed them to better understand the science behind their results and to understand the readings from the primary literature; however, the greatest challenge faced by students was communicating how their results fit within the landscape of the primary literature within the field.

SERMACS 1009

Addressing scientific literacy through scaffolded literature review in inorganic chemistry

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This talk will discuss course modifications made in Inorganic Chemistry (CHEM 4610) at the University of West Georgia to address scientific literacy among chemistry undergraduates. CHEM 4610 is one of the few chemistry classes taken by all chemistry majors as upperclassmen. These students’ ability to keep pace with developments reported in scientific journals will be critical for their career success, so I have made critical reading of the scientific literature a key learning objective of CHEM 4610. Within any undergraduate cohort there is a large variation in student experience and confidence engaging with scientific literature, and this has presented a challenge to implementing traditional reading activities. Initial attempts using a semester-long literature review assignment generated poor outcomes in terms of the quality of student writing, the level of scientific comprehension, and student feedback. I have subsequently made a series of modifications that have improved the students’ experiences, writing quality, and critical reading skills. Students’ critical reading skills are now built-up throughout the semester with regular assigned readings, worksheets, and group discussions. These readings introduce students to a range of different techniques for organizing and summarizing complex arguments including tables, concept webs, and elevator pitches. This practice gives students the toolset to engage with the literature such that they can write a review of a series of literature articles at the end of the semester. The scope of this literature review has also been modified to focus on articles published by a single research group. This enables students to track the development of a research question over the course of time and better understand how the scientific method works in practice. These strategies will be discussed in the broader context of teaching critical reading in the experimental sciences to diverse groups of students.

SERMACS 1010

Guiding students to recognize chemical concepts in primary literature

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Primary literature and scholarship represent a rich opportunity to help students understand the importance and utility of basic chemical concepts like bonding, structure, and chemical behavior. However, undergraduate students often find chemical literature dense and difficult to read, and because of this are not able to appreciate that the foundation of current scholarship is built on the same ideas they learn in their 100 and 200 level chemistry courses. In order to effectively use literature to illustrate applications of basic chemical concepts, several considerations must be made which will be detailed in this paper. These include identifying the concept to be illustrated, selecting the paper, guiding students through the reading, engaging them in conversation about the work, and assessing their understanding of the connections between the work and the concepts. Student feedback from literature activities will also be presented.

SERMACS 1011

Connecting diversity to humanity

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Diversity and inclusion are on the minds of everyone as access to a diverse talent pool is a critical component for a company's future growth and success. In the US, Researchers, policy makers, scientific funding agencies, companies, educational institutions and practitioners have invested significantly in the recruitment of women and people from historically underrepresented racial and ethnic backgrounds STEM fields over the past forty-five years. Over this period, some headway has been made in degree matriculation by women and people from underrepresented minority backgrounds. And despite evidence that diversity is good for science and for business, AWIS research has shown that gender and racial gaps remain, and organizations continue to struggle when it comes to evolving diversity practices into thriving cultures of inclusion and equitable work environments. Many problems remain in our STEM educational and workspaces for historically underrepresented groups where, even among fields where degrees earned have reached or neared parity, there is much stratification in movement into senior and leadership roles across sectors. Across the entire length of STEM career pathways, research illustrates myriad cultural biases and barriers for these groups including those that impact scientific identity, self-efficacy, and fit as well as hiring, space and resource allocation, salary and compensation pack composition, evaluation, recognition, promotion, tenure, and more. If women, and people of color are showing up in a way that clearly brings profits to companies, why do we continue to see them less represented at top levels? It is therefore imperative to adopt a framework that can be implemented personally and organization-wide to improve recruitment, hiring and retention efforts. What are the barriers to recruiting and retaining diverse talent in this space? How can we overcome them? This presentation will provide encouraging and actionable evidence about how to effectively and systematically address advancing equity in STEM. Interactive discussions will focus on connecting diversity to humanity by teaching participants how to incorporate an inclusive, intersectional, and intentional lens to their organization's diversity, equity, and inclusion journey.

SERMACS 1012

Characterization of SURMOFs and exploration of patterning techniques

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Metal-organic frameworks (MOFs), which contain metal ions coordinated with organic linkers, are crystalline materials with nanopores that possess extremely high surface areas. MOFs have become extremely valuable in a number of different applications such as gas storage, sensing, and catalysis. Towards the utilization of these worthwhile materials, there is still much to learn about how to integrate MOFs into real-world structures, specifically this research investigates thin films. Surfaced anchored MOFs (surMOFs) can be manufactured by depositing alternating layers of metal ions and organic ligands, which are anchored to a gold substrate functionalized by self-assembled monolayers. Using different instrumentation, such as ellipsometry, atomic force microscopy, FT-IR, and scanning electron microscopy, the surface features can be investigated and the thin film formation of surMOFs can be determined. Current research focuses on patterning surMOFs by methods, such as microcontact printing and chemical lift-off lithography. Both of these techniques involve a polydimethylsiloxane stamp patterned by a master mold. Preliminary results will be presented regarding the use of these methods to define patterned surMOF structures.

SERMACS 1013

Solar-blind ultraviolet-C persistent luminescence phosphors for self-sustained tagging in all lighting conditions

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Visible-light and infrared-light persistent phosphors were extensively studied and are being widely used as self-sustained glowing tags in darkness. In contrast, persistent phosphors for higher-energy, solar-blind ultraviolet-C (UVC) wavelengths (200–280 nm) are lacking. Also, persistent tags working in bright environments are not available. Here we report five types of Pr^{3+}-doped silicates (melilite, cyclosilicate, silicate garnet, oxyorthosilicate, and orthosilicate) UVC persistent phosphors that can act as self-sustained glowing tags in bright environments. These UVC persistent phosphors can be effectively charged by a standard 254 nm lamp and emit intense, long-lasting afterglow at 265–270 nm, which can be clearly monitored and imaged by a corona camera in daylight and room light. Besides thermal-stimulation, in bright environments, photon-stimulation also contributes to the afterglow emission and its contribution can be dominant when ambient light is strong. This study expands persistent luminescence research to the UVC wavelengths and bring persistent luminescence applications to light.

SERMACS 1014

Zirconium and hafnium tritellurides for next generation electronic applications

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The transition metal trichalcogenides have drawn attention as viable candidates to replace aging silicon-based electronics technologies due to their unique electronic properties, including charge density wave states and superconductivity. We report the synthesis and characterization of $HfTe_3$, a promising yet overlooked transition metal trichalcogenide, and its zirconium alloys, $Hf_xZr_{1-x}Te_3$. The preparation of $HfTe_3$ begins with solid-state synthesis from elemental precursors to isolate bulk polycrystalline material. Next, we implement the chemical vapor transport (CVT) method for crystal growth using carbon-coated fused quartz ampules to mitigate oxide formation. For the crystal growth of $Hf_{0.25}Zr_{0.75}Te_3$ (x= 0.25), a direct CVT reaction is used with elemental precursors and a transport agent, yielding millimeter sized crystals. Products are characterized using techniques including powder X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy, and Raman spectroscopy to confirm phase purity, illustrate particle morphologies, determine quantitative elemental compositions, and elucidate crystal structures. These results contribute to reproducible synthetic routes for $HfTe_3$ and $Hf_xZr_{1-x}Te_3$, resulting in crystals that are well-suited for optical and spectroscopic studies, as well as mechanical exfoliation into few-layer/monolayer samples and device fabrication.

SERMACS 1015

Electrodeposition of Photosensitive Metals across Micron-gap Gold Electrodes

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A simple, low cost, and highly parallel electrochemical approach for fabricating nano-scale (metal/metal) or molecular (metal/polymer or self-assembled monolayer (SAM)/metal) junctions that should be useful in preparing working sensors and molecular electronic devices has been reported by Zamborini and coworkers. The fabrication of metal/metal junctions involves metal deposition on one set of electrodes (E1), where the metal grows and becomes connected to a second set of electrodes (E2) of a Gold interdigitated array of electrodes (Au IDA) with a 5 µm separation. Elctrodeposition of silver (Ag) and palladium (Pd) at these micron gap electrodes and their application for H_2 sensing has been reported. However, other metal electrodeposition at Au IDA's has not been explored. Here, we report the electrodeposition of photosensitive materials, specifically Cadmium sulfide at Au IDAs. We are currently investigating the impacts of applied potential and metal ion concentration on the morphology of the cadmium (Cd) electrodeposition on/across Au IDA electrodes. Cd was electrodeposited onto Au IDA electrodes from a cadmium chloride solution. Cd electrodeposition was performed at six different applied potentials and from solution containing three different concentrations of Cd ions. Morphology of electrodeposited Cd was confirmed by scanning electron microscope (SEM). These devices will eventually be used for sensing light.

SERMACS 1016

In situ formation of calcium copper tetrasilicate in Egyptian faience

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Egyptian faience is a quartz-based ceramic encased in an often blue-colored glaze. Faience objects were first made in Mesopotamia and Egypt approximately 6,000 years ago. Calcium copper tetrasilicate is the colored component of Egyptian blue, the first synthetic pigment, which also dates back to the early 4th millennium B.C.E. Both faience and Egyptian blue have similar elemental compositions—calcium, copper and silicon oxides—yet faience is more heterogeneous, and its preparation involves greater complexity. Here we report the in-situ formation of calcium copper tetrasilicate within faience objects made using the efflorescence method. By tuning the concentration of calcium and the calcium/copper ratio, the product can have the characteristics of faience or those of Egyptian blue or contain a combination of these two materials. Visible-induced near-infrared luminescence imaging reveals calcium copper tetrasilicate crystals within both modern faience and ancient samples. Scanning electron spectroscopy shows the morphology of interior stratigraphy: the glaze, interaction layer, and quartz core. Energy-dispersive X-ray spectroscopy shows an overlap between calcium and copper that helps confirm the calcium copper tetrasilicate composition. Additional material analysis includes Raman spectroscopy, powder X-ray diffraction, and optical microscopy. The occurrence of calcium copper tetrasilicate within ancient faience has not been appreciated previously, and its formation provides insight about ancient raw materials and processing techniques.

SERMACS 1017

Properties and nanostructuring of Cr(II) and Cr(II)/Fe(II) containing tetrasilicates

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The chromium-containing alkaline earth metal tetrasilicates, $ACrSi_4O_{10}$ (A= Ca, Sr, and Ba), are noteworthy as examples of rare, high spin Cr(II) in square-planar coordination. Though the synthesis and structure of $ACrSi_4O_{10}$ has been known for several decades, much of the related chemistry remains unknown. Thus, this study describes the nano-structuring of these tetrasilicates, and, for the first time, the preparation of a mixed tetrasilicate containing both Fe(II) and Cr(II). Both high temperature solid-state and alkali borate flux-based synthesis routes can yield $ACrSi_4O_{10}$. In the flux method, reactions are carried out in metal capsules made from folded Cr foil, which serves to hold the oxygen fugacities of the system below the Cr^0-Cr_2O_3 buffer conditions. In addition, mixing different metal sources like FeO, Cr_2O_3 and Cr in a 2:1:1 molar ratio can yield mixed compositions $Ba(Cr,Fe)Si_4O_{10}$ with up to a ~40% incorporation of Fe(II) into the $BaCrSi_4O_{10}$ crystal structure. Nanostructuring of these tetrasilicates was accomplished through the chemical exfoliation of crystals, yielding nanosheet with micron-sized lateral dimensions. The magnetic properties of both $ACrSi_4O_{10}$ and

$BaCr_xFe_{(1-x)}Si_4O_{10}$ crystals were determined by high-field electron paramagnetic resonance spectroscopic techniques. Magnetic data confirms the varied magnetic infrastructure in $BaCr_xFe_{(1-x)}Si_4O_{10}$ crystals is due to the paramagnetic and ferromagnetic nature of Cr(II) and Fe(II) centers, respectively.

SERMACS 1018

Mixed transition metal trichalcogenide materials

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The metal chalcogenides include diverse low-dimensional van der Waals materials, many of which exhibit interesting electronic properties like semiconducting or metallic properties, charge density wave states, and superconductivity. One subset of such materials is the transition metal trichalcogenides (MX_3) consisting of a group IV or V transition metal and chalcogen (X = S, Se, Te). These compositions possess quasi-one dimensional morphology and electronic structure stemming from their chain-like atomic structure built of MX_6 units in trigonal prismatic coordination extending along the *b*-axis. One strategy to tune and manipulate the electronic properties of these materials is metal substitution. We have grown single crystals of $(Ta,Ti)Se_3$ and $(Nb,Ti)S_3$ compositions through chemical vapor transport. The structures of these mixed metal trichalcogenides have been established through single crystal x-ray diffraction, and their properties further characterized through powder x-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy, and Raman spectroscopy. The crystal structure and spectroscopic characterizations of $(Nb,Ti)S_3$ indicate close similarities to NbS_3 (polymorph V) whereas $(Ta,Ti)Se_3$ is similar to a high pressure phase of $TaSe_3$. EDS mapping confirms the uniform distribution of metals within each system. These results suggest that metal substitution in trichalcogenides provides a viable route for structural engineering and potential tuning of electronic properties.

SERMACS 1019

Exfoliation of metal hexaborides via metal ion incorporation techniques

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Metal borides are a type of high-performance materials with various stoichiometries that are known for their properties such as high thermal and oxidative stability, mechanical strength and notably high melting points (above 2000 °C). These unique features, however, are also what make the borides challenging to process for industrial applications where often thin films for coatings are required. Typically, methods such as physical and chemical vapor deposition are employed to form such films, but these techniques offer little control over the thickness and uniformity of the deposited layers. One approach to avoid this issue is converting the bulk borides to nanosheets, which commonly self-assemble and lay flat. Since nanosheets tend to stay suspended in various solvents, different techniques such as dip coating, spray deposition and even inkjet printing can be used to apply them instead. One big deterrence to this approach is that unlike van der Waals materials, whose layers are held together by van der Waals forces, the metal-boron framework is bonded by stronger ionic and covalent interactions. Thus, conventional methods such as the scotch tape method or simple sonication cannot be applied to produce metal boride nanosheets. Our research focuses on a novel top down approach, which involves the incorporation of a small metal ion into the bulk material followed by the boride exfoliation into nanosheets. Particularly, the nanostructuring of metal hexaborides, MX_6 (ex. LaB_6, CaB_6, BaB_6, etc.), will be discussed.

SERMACS 1020

Efficient removal of toxic metal ions from aqueous solutions using micro-porous nitrogen-doped carboxylated activated carbon

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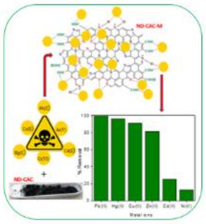
In the present study, the amorphous Melamine Zirconium Phosphate (M-ZrP) was synthesized and used for the extraction of the toxic metal ions Pb(II), Hg(II) and Cd(II) from contaminated water. The synthesis of M-ZrP involves the preparation of melamine phosphate followed by a treatment with zirconyl chloride to yield M-ZrP. Different analytical techniques including FT-IR, XRD, SEM, EDS, TEM, and BET surface area were used to characterize the structure and morphology of the M-ZrP adsorbent. The high adsorption capacity of 681.1 mg/g of Pb(II) indicates that the M-ZrP adsorbent is among the best inorganic adsorbents for removal of Pb(II) from polluted water. Additionally, the M-ZrP adsorbent exhibits maximum adsorption capacities of 117.0 and 56.1 mg/g for Hg(II) and Cd(II), respectively. A 100% removal efficiency of Pb(II) ions by the M-ZrP adsorbent can be achieved within 30 seconds and 5 minutes from starting concentrations of 500 ppb and 100 ppm, respectively. In a mixture of six metal ions at a concentration of 10 ppm and pH of 5.5, the removal efficiencies by the M-ZrP adsorbent are 100% Pb(II), 99% Hg(II), 99% Cd(II), 99% Zn(II), 94% Cu(II) and 90% Ni(II), while at a concentration of 500 ppb a 100% removal efficiency for all the six metal ions can be achieved. The mechanism of adsorption is shown to follow the Langmuir isotherm model by the formation of a monolayer. The kinetics of heavy metal ions' adsorption on M-ZrP follow the pseudo-second-order kinetic model by chemical adsorption through amines, triazine nitrogen's, and hydroxyls active sites on the M-ZrP. Regeneration results show that by using 1.5 M of nitric acid the adsorbed toxic metal ions can be removed from the surface with a desorption efficiency of 100%, for all studied heavy metals.



SERMACS 1021

Sulfur host based on cobalt phosphides-graphitic nanocages for advanced lithium-sulfur batteries

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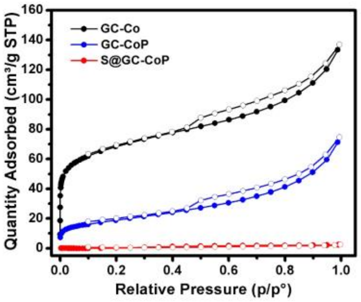
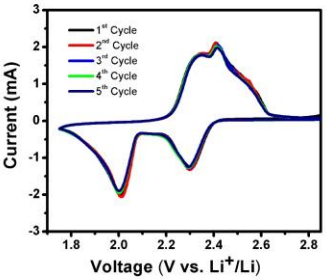
Non-renewable energy sources like fossil fuels have intensified the environmental crises due to the continued emission of greenhouse gases, which could irreversibly damage our ecosystem. Lithium-ion batteries (LIBs) has proven to be successful in the booming electronics industry, and it is predicted to play a critical role in large-scale energy storage. However, the capacity of graphite anode is theoretically limited to 370 mA h g^{-1}, resulting in low energy and power density. To address this problem, there is an *urgent need* to explore alternative battery chemistries to LIBs with low cost, longer life cycle, and high capacity and/or energy density. Lithium Sulfur batteries have generated much excitement in the scientific communities. Sulfur is a low cost, eco-friendly, and is considered one of the most abundant elements in the earth's crust. Also, Lithium has a low redox potential (–3.04 V Vs. S.H.E) which maximize the energy density of Li–S chemistry. Physical and chemical confinement of polysulfides is ought to be the holy grail formula to achieve highly stable Li-S batteries. The specific aim of this work is to deliberately be tailoring specific metal phosphide (Co_2P) inside nitrogen/oxygen doped porous MOFs matrix (i.e., ZIF-67), one can chemically and physically suppress polysulfide migration.





SERMACS 1022

Initial studies of biolubricants obtained from the epoxidation of macaúba (*Acrocomia aculeata* (jacq.) Lood. Ex mart) kernel oil

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The increase environmental awareness creates a need to obtain non-petrochemical products for people's daily lives. Vegetable oils are seem as promising replacements for petroleum as they are versatile enough to be made suitable for many different applications and are renewable. This environmental awareness also triggers the search for more efficient energy consumption; one way to achieve this is using biolubricants. Lubricants are essential for any kind of machine as they not only protect them from friction damage but also from heat, corrosion and make them more energetically efficient. However, about half of the lubricants produced in the world ends up wasted, considering that they are oils of petrochemical origin, which makes them an important source of environmental contamination. Vegetable oils are usually not suitable for most of the lubricant's applications because they are easily oxidized due to the presence of many reactive sites in their composition, like unsaturations. One way to increase their oxidative stability is by epoxidating them. There

are different ways to epoxidate vegetable oils, for example, by reaction with formic acid and hydrogen peroxide under mechanical stirring and heating. The epoxidation made in this work of macauba (Acrocomia aculeata (Jacq.) Lood. ex Mart) kernel oil was confirmed by Fourier transformed infrared spectroscopy (FT-IR) and ^{1}H nuclear magnetic resonance (^{1}H NMR), and the characterization has also shown increases in viscosity, thermal and oxidative stability, which are important properties for lubricants.

SERMACS 1023

Novel semiconductors for dye-sensitized solar cells

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The well-known dye, $[Bu_4N]_2$ *cis*-[Ru(4-carboxy-4’-carboxylate-2,2’-bipyridine)$_2$(NCS)$_2$], N719, was synthesized from 4,4’-dimethylbipyridine (dmb) and ruthenium(III) chloride through four reactions and characterized using ^{1}HNMR and UV-Vis spectroscopy. Then Dye-Sensitized Solar Cells (DSSC) were constructed and tested using novel nanoparticle semiconductors as the anode and N719 as the chromophore. These results were compared with a DSSC made with a titanium dioxide nanoparticle anode.

SERMACS 1024

TiO_2 nanotubes electrode decorated with NiS nanoparticles applied as a photoanode for photoelectrocatalytic degradation of penicillin G

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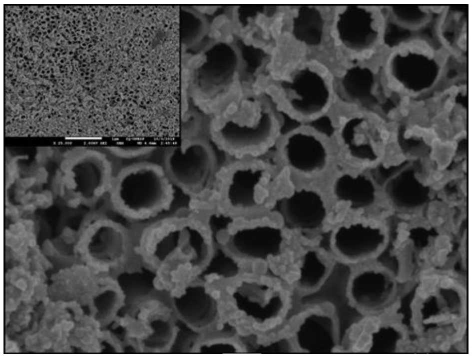
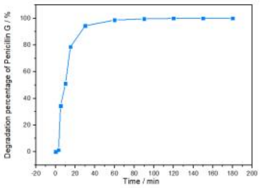
Photoelectrocatalysis has appeared as a promising powerful technique for organic compounds degradation. It is based on the irradiation of a semiconductor by light equal or greater than its band gap and concurrently biased by a gradient potential. Titanium oxide is one of the most used semiconductors on photodegradations, but its absorption is at ultraviolet range. The use of nickel compounds for decoration of TiO_2 increases absorption on a visible range and assists electrons being trapped. The goal of this work is to investigate the modification of the surface of the Ti/TiO2 nanotubes with NiS nanoparticles for photoelectrocatalytic degradation of Penicillin G. The Ti/TiO_2-NiS electrode was electrodeposited, applying −1.20 V vs Ag|AgCl for 120s on an electrochemical cell containing $NiCl_2$ (0.01 mol L^{-1}) in $Na_2S_2O_3$ (0.05 mol L^{-1}). NiS are distributed uniformly and around the edges of TiO_2 nanotubes (Fig. 1). The modification resulted in the expansion of the absorption of the electrode on the visible range and it obtained the band gap energy of 2.90 eV. The complete degradation of 10 mg L^{-1} Penicillin G, in 0.1 $NaSO_4$ mol L^{-1} and pH 7, over Ti/TiO_2-NiS electrode was achieved applying +0.5 V vs Ag|AgCl, on UV-vis light for 90 minutes (Fig. 2). After this treatment, there was a total removal of organic carbon. The photodegradation of Penicillin was monitored by LC-MS and TOC. Therefore, the TiO_2NT electrode decorated with NiS nanoparticles proved to be more efficiency and improve its absorption on visible light.



SEM images of Ti/TiO2-NiS



Photoelectrocatalytic degradation of Penicillin G.

SERMACS 1025

Synthesis, characterization, and antimicrobial studies of silver nanoparticles synthesized using *Annona glabra* plant extract

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Silver nanoparticles have been studied extensively due to their wide applications in nonlinear optics, biolabeling, reaction catalysis, antibacterial products, electrical conductors, and chemical sensing. Use of plant extracts in the synthesis of silver nanoparticles has gained much attention recently as it is very simple, rapid, eco-friendly and cost effective. In this work, a green synthetic method was carried out for the reduction of Ag^+ ions in to silver nanoparticles using the leaf extract of *Annona glabra* as the reducing and capping agent. Reaction conditions including the concentration of the plant extract and silver nitration were optimized. Green synthesized nanoparticles were characterized using dynamic light scattering, scanning electron microscopy, powder X-ray diffraction, UV-Vis absorption spectroscopy, and Fourier transform infrared spectroscopy. Antibacterial property of silver nanoparticles was studied using Gram negative Escherichia coli and Gram Positive Staphylococcus aureus bacteria species. At 20 mg/L concentration of silver nanoparticles, percentage inhibition of E. coli and S. aureus was found to be 61.53 and 84.61 %, respectively.

SERMACS 1026

Carbon dioxide adsorption on a stilbene-based manganese metal-organic framework

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A metal-organic framework(MOF) was synthesized by combining manganese (II) nitrate tetrahydrate with two organic ligands, 2,2'-bipyridine and 2,2'-dinitro-4,4'-stilbenedicarboxylic acid at 200°C for 48 hours. This material was characterized using FTIR, TGA and non-ambient X-ray diffraction analyses with the later indicating a very stable structure up to 200°C, and upon slow cooling from 250°C to 25°C the structure was restored. This was followed by degassing the MOF at various temperatures (25°C, 50°C, 100°C, 120°C and 180°C) under vacuum and CO_2 adsorption at 256 K after each degas temperature. The CO_2 adsorption capacity was highest at the degassing temperature of 180°C. Further analyses and results showed that at 256 K, 273 K and 298 K, the CO_2 adsorption capacities were 1.52 mmol/g, 1.55 mmol/g and 0.77 mmol/g, respectively. The experimental isotherms were fitted using a modified Langmuir-Freundlich isotherm model. The thermodynamic parameters calculated showed that at 256 K and 273 K the adsorption process was spontaneous, while at 298K it was non-spontaneous. With these results, this MOF can be of great interest based on its intriguing thermal stability and its capacity to adsorb CO_2.

SERMACS 1027

Hexacoordinate silicon complexes for OPV and OLED applications

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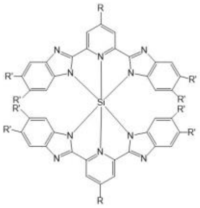
Hexacoordinate silicon complexes containing two pincer ligands often exhibit luminescence and electronic properties comparable and in some ways superior to Alq_3 (tris-(8-hydroxyquinoline)aluminum, a widely used metal chelate for organic electronic devices. A series of $Si(pincer)_2$ complexes, including $Si(bzimpy)_2$, (2,6-bis(2-benzimidazolyl)pyridine = bzimpy), and several synthetic analogs were synthesized. The electronic and optical properties were studied in the solution state, and films of the complexes were grown via thermal evaporation/deposition. Electron mobilities of the thin films were determined in the space-charge limited current (SCLC) regime. Many of the complexes exhibit electron mobilities comparable to that of Alq_3. $Si(bzimpy)_2$ and its analogs have been incorporated into OLEDs, OPVs and OFETs demonstrating the ability for the $Si(pincer)_2$ complexes to be suitable alternatives for electron transport layers in organic electronic devices.



1. R = OMe, R' = H
2. R = OMe, R' = Me
3. R,R' = H
4. R = H, R' = Me

SERMACS 1028

Synthesis and biological investigation of aeruginoic acid and derivatives

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Fluorescent *pseudomonads* produce a wide array of secondary metabolites, many of which have antibiotic activity. Among these metabolites are aeruginoic acid, and (+)-(*S*)-dihydroaeruginoic acid, both of which are produced by *P. fluorescens*. Additionally, aeruginol has been found in the $CHCl_3$ extract of *P. aeruginosa* grown on lard as its carbon source. Despite the antibiotic activities of other *Pseudomonad* secondary metabolites, the biological data reported for any of these compounds is limited, thus motivating more extensive study of them as well as analogs. Both aeruginoic acid and (+)-(*S*)-dihydroaeruginoic acid displayed iron-binding capabilities in liquid and solid CAS assays. Additionally, the activities of the three previously mentioned compounds and five analogs were determined against four pseudomonad species (*P. aeruginosa, P. putida, P. fluorescens, P. syringae*) under normal growth conditions as well as under iron-limited conditions.

SERMACS 1029

One-pot allylsilane synthesis from enolizable aryl ketones

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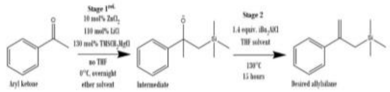
A convenient one-pot synthesis converting methyl aryl ketones to allylsilanes is developed. The protocol is based on the abnormal Peterson Olefination reaction affording products in fair yield. Alkylation of para-substituted aryl methyl ketones (Stage 1) works well using the $ZnCl_2/LiCl/TMSCH_2MgCl$ ate complex. But the method fails to convert ortho-substituted aryl methyl ketone to the corresponding β-silylalkoxides. We are now examining anhydrous $CeCl_3$ to facilitate the alkylation step and in the one-pot synthesis of allylsilanes.



SERMACS 1030

Synthesis of divalent and tetravalent carbohydrates to improve sensitivity of glycosidases synthesis of divalent and tetravalent carbohydrates to improve sensitivity of glycosidases

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β-galactosidase is a glycoside hydrolase enzyme responsible for breaking glycosidic bonds to hydrolyze β-galactosides into monosaccharides.[1] β-gal is a known biomarker enzyme for *in vivo* tumor growth monitoring, transcriptional regulation, gene expression and more importantly characterization of cellular senescence.[1-3] Cellular senescence is a persistent cytostasis that is closely related to oxidative stress and telomere shortening; it is characterized by morphological and biochemical phenotype that includes an abnormally large accumulation β-gal activity called senescence-associated β-galactosidase (SA-β-gal). Successful monitoring and characterization of senescent cells can aid in the development of therapeutics specific to age-related diseases and anticancer treatments.[1] We propose the development of divalent and tetravalent compounds that will improve the sensitivity of β-galactosidase and α-mannosidase significantly. To accomplish this goal, we have synthesized four novel compounds which will release p-nitrophenoxide upon exposure to β-galactosidase or α-mannosidase

SERMACS 1031

Effects of enzymatic treatment on vitamin E and mineral contents of raw peanuts

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Peanut is an important source of vitamins and minerals in human diets. It is an excellent source of niacin and vitamin E, magnesium, phosphorous, and potassium, and a fair source of vitamin B1, B2, B3 (niacin), B6 and B9 (folate), calcium and zinc. Some processing methods usually cause loss of nutrients. This study investigated the changes of different tocophenols and minerals in raw peanut as a results of enzymatic treatment which was used to reduce peanut allergens. Peanut kernels were treated by 4 proteases (Alcalase, bromelain, Neutrase and papain) separately at the optimal pH and temperature of each enzyme. After vacuum dried, peanuts were ground into paste and defatted. The fat/oil samples were analyzed for tocopherol contents by HPLC, while defatted peanut flour were analyzed for mineral contents by ICP-OES. Alph-tocopherol was significantly lower in all enzyme treated samples. Only Alcalase reduced γ and δ tocopherol contents in the peanuts, other enzyme did not show significant impacts. The treatment of peanuts using Alcalase, Neutrase or Papain significantly reduced K, Mg and P, increase Ca and Na contents. Treatment with Bromelain did not reduce Mg and P in peanuts, but decreased K by 11%. The loss of minerals during enzyme treatment is most likely due to the dissolution of mineral ions in the enzyme solution. Overall, the impact of enzymatic treatment on vitamin E content of peanuts is limited, but the impact on some minerals are significant.

SERMACS 1032

Primary amine synthesis of functionalized ketones by reductive amination

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Primary Amines are important pharmaceutical precursors and they comprise a large portion of active pharmaceutical ingredients. Current research shows syntheses that include toxic or dangerous reagents and are not feasible for industrial scale-up. We are investigating novel synthetic organic routes at primary amine synthesis. In the Feske Lab we are proposing a two-step process that includes Lewis Acid-Catalyzed α-Chlorination of the β-ketoester using 1.1 equiv N-Chlorosuccinamide(NCS) and 0.3 equiv Magnesium Perchlorate $Mg(ClO_4)_2$ followed by reductive amination using 5.0 equiv of ammonia in ethanol (NH_3 in EtOH), 2.0 equiv Titanium (IV) Isopropoxide $Ti(oiPr)_4$, and 1.5 equiv Sodium Borohydride $NaBH_4$ to afford the primary amine.

SERMACS 1033

Effects of enzymatic treatment on sucrose content and sensory quality of peanuts

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The major free sugar in peanuts is sucrose which is very important to the flavor and color development of peanuts during roasting and other processing. Because sugars in peanuts are water soluble and the enzymatic treatment of peanuts for allergen reduction is conducted in aqueous solution, therefore, sugar loss is an important issue to be addressed. The objective of this study was to evaluate the influence of enzymatic treatment of peanut on sucrose content and sensory quality of peanuts. Raw and roasted peanuts (2kg each) were treated separately by 3.5% of Alcalase at 50 ºC for 2 hours, then vacuum dried. Untreated peanuts were used as controls. For sucrose analysis, 25g of each sample was ground into paste and defatted. The sucrose was extracted from defatted peanut flour by 80% methanol, purified by SPE using Sep-Pak C18 cartridge and determined by HPLC. Consumer preference/acceptance test was conducted by Quantitative Affective Test method using 9-point hedonic scale and 50 untrained panelists. Results show that enzyme treatment reduced sugar contents in both raw and roasted peanuts. Overall, enzyme treated peanuts had lower sensory score than untreated peanuts, but the sensory quality of raw peanuts was less influenced by than that of roasted peanuts. Although still taste like peanuts, panelists detected weaker sweetness and peanut flavor for the enzyme treated peanut than that of controls. Thus we conclude that reduced sucrose content is a major contributing factor of lower sensory quality of peanuts.

SERMACS 1034

Biologically active tri-substituted pyridazine compounds as anti-cancer agents

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Pyridazines are heterocyclic compounds that are significant in the field of medicinal chemistry and pharmacology. Although pyridazine derivatives have multiple applications, they are very rare in nature compared to one of its isomers, pyrimidines, which also play a crucial role in biological processes. Due to the scarcity of pyridazines, they were often overlooked but research from the last few years has proven their importance with adjacent nitrogen atoms within its ring. Its inclusion within the structure of various pharmaceutical drugs has improved specific properties of those drugs to increase its effectiveness in the body. This particular project will target the synthesized derivatives in cancer research using zebrafish model. Detailed toxicological analysis, melanosome activity and data of potential ephinephrine alternative with the pyridazine compounds will be shared.

SERMACS 1035

3-step synthesis of fluoroflavones as potential neuroprotective agents

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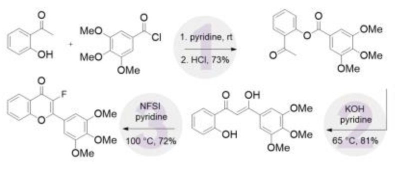
Flavones are secondary metabolites found in many plants that are characterized by the presence of phenol rings. These natural products are well known to have neuroprotective effects against many diseases caused by the formation of reactive species. Flavonoids are subgroup of flavones and they are believed to function as antioxidants. Specifically, they target free radicals and eliminate their harmful effects by acting as radical scavengers. Introducing a fluorine atom into a biologically active molecule is known to produce a significant impact. Having high electronegativity and a small molecular size, makes fluorine atom valuable in drug design. Accordingly, fluoroflavones were designed to improve the potency of the antioxidant activity of flavones and enhance their potential use as neuroprotective agents. Fluorinated flavones were synthesized using the electrophilic fluorination reagent, *N*-fluorobenzenesulfonimide. After isolation and purification, biological testing was conducted on the fluoroflavones and their non-fluorinated counterparts. Antioxidant activity was evaluated by using a DPPH assay, and neuroprotective activity was determined using rat-derived cortical neurons. Generally, the fluorinated flavones are more potent antioxidants compared to their non-fluorinated derivatives, but, the neuroprotective assay showed that both fluorinated and non-fluorinated flavones have potential neuroprotective activity. In addition, ^{19}F NMR experiments were conducted on fluoroflavones to investigate the effect on the chemical shift of the fluorine atom during the radical exchange.



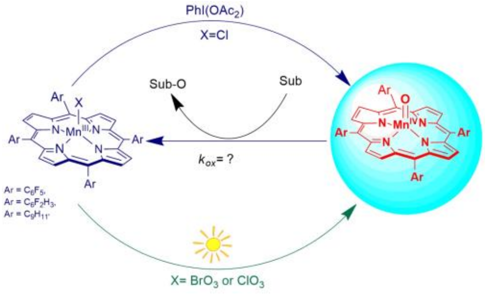
Synthesis of the monofluorinated flavonoids

SERMACS 1036

Oxidation kinetic studies on porphyrin-manganese(IV)-oxo intermediates via chemical and photochemical generation

Seth Klaine*, seth.klaine128@topper.wku.edu, Wentao Ning, Rui Zhang. Chemistry, Western Kentucky University, Bowling Green, Kentucky, United States*

In Nature, cytochrome P-450 (CYP450) enzymes can catalyze an array of oxidation reactions with extraordinarily high reactivity and selectivity through high-valent metal-oxo species as active oxidants. In this regard, our particular focus is to generate and study reactive metal-oxo species involved in sulfide oxidation reactions. Toward this end, two electron-withdrawing and one electron-donating porphyrin-manganese(III) complexes were synthesized and spectroscopically characterized. Manganese(IV)-oxo intermediates, i.e. $[Mn^{IV}(Por)O]$ (Por = porphyrin ligand), were chemically generated by utilizing the mild oxidant iodobenzene diacetate $[PhI(OAc)_2]$. Furthermore, a photochemical approach using visible light irradiation of the photo-labile manganese(III) chlorate precursors successfully generated the identical $[Mn^{IV}(Por)O]$. The kinetics of oxygen atom transfer (OAT) reactions with organic sulfides by these chemically-generated $[Mn^{IV}(Por)O]$ were studied in CH_3CN solutions. The comprehensive kinetic studies will be discussed, providing insights into the transient oxidants in oxidation reactions where physical reactive intermediates are not spectroscopically detectable.



SERMACS 1037

Quinidine and quininine based double salt ionic liquids for liver injury prevention

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Injury caused by medications is the leading cause of death in the United States. Drug induced liver injury (DILI) is any form of liver injury caused by medication, herbs, or dietary supplements. A way to fix this problem is the conversion of the solid state medication into their liquid forms via an ionic liquid (IL) formation: active pharmaceutical ingredients (API) in their cationic or anionic form can be combined into a single ionic compound leading to the formation of new dual active liquid APIs that will retain the pharmaceutical properties of the original APIs. Combining three or more APIs into one single ionic compound, namely a double salt ionic liquid (DSIL), would allow one to add additional properties (such as transdermal delivery) to the final liquid drug. Our research focuses on applying the DSIL strategy to pharmaceuticals that cause liver injury (quinidine and quinine) by combining them with drugs that offer liver protection properties (N-acetyl-L-cysteine or NALC) and with compounds that will increase their permeability (sodium docusate or NaDoc) adding new delivery mechanisms to the drug. Here we discuss the synthesis of six new DSILs formed by combining quinidine or quinine in their cationic form with NALC and NaDoc in their anionic form in different cation to anion molar ratios followed by their spectroscopic characterization.

SERMACS 1038

Synthetic and catalitic studies of metalloporphyrin complexes for biomimetic oxidations

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In Nature, cytochrome P450 (CYP450) enzymes catalyze important oxidation reactions which serve as inspiration for use of synthetic metal complexes as biomimetic catalysts. Several different porphyrin free ligands containing different aryl groups were synthesized according to a well-documented procedure. Metals of iron, manganese, and ruthenium were inserted into the porphyrin ligands and the resulting metalloporphyrin complexes were characterized by ^{1}H-NMR and UV-vis spectroscopies. With $PhI(OAc)_2$ as a mild oxygen source, the catalytic ability of the metalloporphyrin complexes were evaluated in alkene epoxidation and sulfoxidation. High conversions and excellent chemoselectivity without overoxidation of or sulfoxides into sulfones were obtained with various substrates. Of note, visible light irradiation was found to promote the manganese and ruthenium porphyrin-catalyzed oxidation in a significant way, which will be discussed in the presentation.

SERMACS 1039

Characterization of unmodified and bleached peanut hulls for use as an inexpensive biosorbent for waste water treatment

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Treatment of waste water from factories can be costly due to the need for continual replacement of expensive, manufactured filtration media. The use of a readily available natural product, as opposed to synthetic resins and filters, could lower the cost of waste water treatment and allow for larger scale use. Due to their availability and their ability to adsorb heavy metals, peanut hulls have the potential to serve as a cheaper alternative to manufactured ion-exchange resins. Ground peanut hulls have been shown to adsorb copper (II) ions with and without modification to the structure of the material. However, a bleaching process involving sodium hydroxide (NaOH) and hydrogen peroxide (H_2O_2) causes an increase in adsorption capacity. This increase is due in part to increasing surface area by dissolution of alkaline soluble material present in the hull's structure. While similar studies of other lignocellulosic materials attribute an increase in adsorption capacity to the oxidative formation of carboxylic acids, the resulting chemical changes in peanut hulls have not yet been characterized. The goal of this research is to investigate how various oxidative environments chemically modifiy peanut hulls. Identification of changes to the chemical structure may help to elucidate modification and cation adsorption mechanisms. Ground peanut hulls and pure cellulose have been modified with the $NaOH/H_2O_2$ mixture as well as with a strong oxidizing agent, potassium permanganate ($KMnO_4$), and the selective oxidizer, (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO). The pH, temperature and oxidation-reduction potential was monitored throughout the reaction, and the infrared spectra of the products have been compared. Changes in the spectra have been used to indicate which functional groups are being modified in the hulls.

SERMACS 1040

Activity of resveratrol analogues against triple-negative breast cancer (TNBC) cells and LCMS monitoring of molecular isomerization

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Resveratrol is a plant-derived stilbene found mainly in the skin of red grapes, peanuts, and berries. It is a strong antioxidant agent that has been associated with treatments against diabetes, obesity, cardiovascular diseases; moreover, it has been proven to be effective against certain types of cancer. However, its low solubility and bioavailability has posed great problems for researchers seeking to use it as a treatment method. In an effort to discover a more effective alternative, our research group has synthesized and tested resveratrol analogues against multiple breast cancer cell lines. Recent studies have demonstrated the efficacy of resveratrol analogues against estrogen positive (ER+) breast cancer cells and have associated this effect to the structural similarity of these molecules to estrogen, assuming the analogues would act as antagonists to estrogen signaling. Surprisingly, though, some of our analogues have shown high activity against ER+ cell lines, but also against triple-negative breast cancer (TNBC) cell lines despite the lack of the ER-*a* on the surface of these cells. Our compounds inhibit cell growth, induce apoptosis, and even cause morphological changes that indicate a possible reversal of epithelial-mesenchymal transition and thus a potential inhibition and reversal of metastasis. Recently, we have been focusing our efforts toward the expansion of our analogue inventory in an attempt to fit in the missing pieces of the puzzle and delineate a possible structure-to-effect relationship. The integrity of our compounds in the culture media was monitored by means of the LCMS (Liquid-Chromatography Mass-Spectrometry).

SERMACS 1041

Synthetic simplification enables the discovery of a unique biofilm target in *Streptococcus mutans*

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With the rise of antimicrobial resistance, scientists are searching for new methods to eradicate bacterial infections. Bacterial pathogenicity is commonly targeted to prevent emerging resistance development by decreasing the selection stresses that are present with traditional antibiotics. A key contributor to pathogenicity are biofilms, communities of cells that create an economic burden for several industries and are common in many disease states in human health. *Streptococcus mutans* is a Gram-positive microorganism that is used for the study of biofilm pathogenicity and is the causative agent in the formation of dental caries, the most prevalent childhood disease. Our research program has a continued interest in developing novel small molecule probes that specifically target *S. mutans* biofilm growth. Carolacton **(–)-1** is a myxobacterium natural product that was identified to induce cell defects in *S. mutans* biofilms. Unfortunately, carolacton's utility is limited due to the complexity of the structure and the inability of performing quick, prolific biological assays since cells must be imaged to determine effect. Herein, the development and synthesis of a simplified natural product, **(+)-2**, will be disclosed. This compound enables further characterization of biological activity since it exhibits a quantifiable growth inhibition in biofilm cultures. Using this simplified chemical structure we have gathered evidence that our compounds are acting via an acid tolerance mechanism, and have identified a putative biofilm target.

SERMACS 1042

Electrochemical behavior and stability of juglone in buffers of varying pH

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Juglone or 5-hydroxy-1,4-napthoquinone (molecular formula of $C_{10}H_6O_3$ and molar mass of 174.15 g/mol) is a phenolic compound found in black walnuts. Juglone is known for its use as an anti-microbial, anti-fungal, herbicidal substance with observable effects on its surroundings. Due to the inherent presence of several polyphenols, and the possibility of multiple forms of juglone being present in this plant material, it is difficult to rely solely on spectroscopy to argue the presence of juglone in a given extract. Therefore, knowing the electrochemical behavior of juglone in aqueous buffers of different pH is a useful tool for comparing the juglone extracted from plant material with commercially available synthetic juglone and can help better classify it in extracts from black walnut hulls. Electrochemical analysis of cyclic voltammograms was used to observe changes in electroactivity related to possible juglone degradation products. The work presented here focused on (a) the electrochemical behavior using cyclic voltammetry of juglone free acid solutions obtained by dissolving it in buffered ethanol (1:1 ethanol:aqueous buffer ratio) of pH 5, 7, and 9 to simulate soil pH extremes and (b) the chemical stability of the juglone forms in the obtained solutions over given time intervals via UV-Vis Spectroscopy.

SERMACS 1043

Synthesis of a biochemically important aldehyde, 3,4-dihydroxyphenylacetaldehyde (DOPAL)

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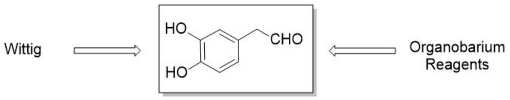
3, 4-Dihydroxyphenylacetaldehyde (DOPAL) is an important intermediate metabolite found in catecholamine neurotransmitter systems. As such, it has an important role in medicinal research directed toward the study of alcoholism, Alzheimer's disease and Parkinson's disease. Despite the immense biochemical significance of DOPAL, attempts to synthesize this compound in pure form has been met with grave difficulty. Various preparations of DOPAL have been reported, but the synthesis of this eight-carbon compound suffers from detailed procedures, physical isolation, full chemical characterization of the product/intermediates and extremely low overall product yield. These published methods also share one common problem, DOPAL is very unstable and is very difficult to isolate and work with. Therefore, considerable effort to produce DOPAL in a higher yield would be of interest. In an effort to mitigate these problems, we have directed our attention toward the synthesis of DOPAL using organobarium reagents. These novel reagents, fundamental to organic synthesis were utilized in the total synthesis of DOPAL. In addition, we also report the synthesis of the protected DOPAL via a Wittig reaction, followed by subsequent hydrolysis/deprotection protocols resulted in the isolation of the free aldehyde. These studies may provide important insight on future drug action to combat PD and, when the scope of this research is expanded, may aid in the treatment of other neurodegenerative disorders.



SERMACS 1044

Two-step synthesis of flavonol-derived ligands for metal-flavonol complexes and CO release

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Our research is focused on the synthesis of novel flavonols, flavonoid compounds consisting of the 3-hydroxyflavone backbone, to further the studies into the use of metal-flavonol complexes as carbon monoxide-releasing molecules (CORMs). CORMs are significant for their use in therapeutics and organic synthesis. Flavonols have the natural ability to release CO, and research has shown that the ability can be enhanced by complexation with metal and additionally affected by the character of the flavonol and its substituents. Presently, we are concentrating on alternate procedures for the Claisen-Schmidt condensation and subsequent Algar-Flynn-Oyamada in order to synthesize novel flavonol-derived ligands with electron-withdrawing substituents at substantial yields. An evaluation of the ability to act as anti-cancer agents and release CO will be conducted on the metal-flavonol complexes.

SERMACS 1045

Development of a 1,2,3-triazole chemosensor for the detection of organophosphate nerve agents

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Development of a 1,2,3-Triazole Chemosensor for the Detection of Organophosphate Nerve Agents Oluwagbotemi Akinsoji[1] Unodinma Ofulue[1] Kayley Yates[1] Debanjana Ghosh[1] Shainaz Landge[1] Karelle Aiken[1] 1-Georgia Southern University Abstract Rapid detection of different classes of organophosphates nerve agents (OP-NA) remains a challenge. One of the most convenient and simplest means of chemical detection is generating a change in absorption or fluorescence intensity or color. Organic-based chemosensors can be used in these types of detection. These molecules can be designed to differentiate between classes of OP-NAs. Previous work by our group has generated hydroxyaromatic 1,2,3-triazole-based chemosensors that are highly selective for the fluoride ion. The current focus will build on prior results by designing sensors that can detect OP-NA G-series agents which release the fluoride anion upon hydrolysis. Groups that can perform nucleophilic substitution at the OP back bones will be introduced while retaining the fluoride receptor site. In order to avoid the direct use of extremely toxic nerve agents in laboratory research, less harmful nerve gas mimics will be studied. This investigation will target the accuracy in detection. Results from this work will be presented.

SERMACS 1046

Structure-activity relationship and anticancer profile of second-generation anti-MRSA synthetic retinoids

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We previously reported the antibacterial activity of CD437, a known antitumor toxin. It proved to be a potent antimicrobial agent effective against both growing and persister cells of methicillin-resistant *Staphylococcus aureus* (MRSA). Herein we report the synthesis of a panel of analogs and their effect on both MRSA and cancer cells. The hydrophobic group of the parent compound was varied in steric bulk, and lipid-mimicking analogs were tested. Biological assessment confirmed that the adamantane moiety is the most effective substitution for antibacterial activity, and some preferential action in cancer over MRSA was achieved.

SERMACS 1047

Spectroscopic characterization of new phenothiazine double salt ionic liquids

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Double salt ionic liquids (DSILs) are complex, pure ionic compounds that melt below 100 oC. Their structure is comprised of more than two types of ions, with varying ratios of cations to anions. DSILs can be prepared by using the traditional methods of synthesis for simple ionic liquids (ILs), and also by mixing and/or melting of ILs. These materials exhibit different chemical and/or physical properties than their single salt counterparts, as the resulting properties (e.g., solubility) depend on the chemical interactions between the individual ions with new coulombic interactions and unique properties being obtained by manipulating the molar ratios between the component ions. Therefore, one can harness this behavior and develop task specific DSILs. We have previously shown that the DSIL strategy can be successfully applied to promazine, a well-known antipsychotic phenothiazine drug. Here we show that by varying the molar ratio between various phenothiazine cations and two anions, ibuprofenate (a NSAID) and docusate (a known penetration enhancer), new DSILs with potential synergistic effects can be synthesized. This presentation focuses on the synthesis and spectroscopic characterization of nine new DSILs obtained by pairing three different phenothiazine drugs in their cationic form with ibuprofenate and docusate anions in different molar ratios.

SERMACS 1048

Synthesis of biased κ-opioid agonist collybolide-A

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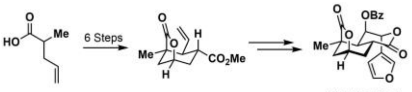
Collybolide A is a furanolactone natural product that acts as a potent biased κ-opioid agonist expected to provide pain relief while minimizing accompanying negative side effects such as sedation, hallucination, and dysphoria. Employing robust enolate chemistry, palladium catalyzed C-H alkylation, and cheap commercially available precursors, we have generated gram quantities of the bicyclic lactone motif of collybolide A advancing toward its concise synthesis. Once completed, our synthesis will allow for systematic structure-activity relationship studies to determine the pharmacophore of collibolide A and generation of analogues of collibolide A with modulated pharmacological profiles.



Collybolide A

SERMACS 1049

Synthesis and characterization of new silica immobilized juglone materials

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Juglone is a naphthoquinone found in walnut hulls. Fresh walnut hulls are a historical source of plant pigments with medicinal and herbicidal properties. Juglone is toxic to many unwanted plant species. To take advantage of these allelopathic properties of juglone, and exploit them for herbicidal use, certain properties must be altered. Juglone has poor solubility in water and is too volatile to ensure effective and safe delivery. Toxicity to common garden crops, landscaping species, and water organisms is a relevant concern when utilizing juglone as an herbicidal component. The unwanted movement of juglone through soils and waterways can be mitigated by creating ionic liquids (ILs) formed from the anionic form of juglone and cationic surfactants while improving the movement through and action on the targeted plant tissues. These properties are improved by combining juglone with tetrabutylphosphonium bromide and can be delivered to target species by adhering to a dispersion medium, namely mesoporous silica materials. The research presented here focuses on loading a new juglone compound, specifically a phosphonium salt, on silica gel with pore size of 90 Å (SiO_2-90). Three wt/wt% loadings, 10%, 20%, and 50%, were compared using infrared spectroscopy, and differences were used to inform future phases of this work.

SERMACS 1050

Swellable organically modified silica facilitated synthesis of biodiesel fuel: Complete story

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Continued dependence on fossil fuels for energy production pose significant challenges. Fossil fuels are non-renewable, limited in supply, and damage the environment when combusted. Biodiesel is a potential alternative fuel that contains approximately 90% of the energy content of fossil derived diesel. In many ways, biodiesel is an advantageous replacement to fossil derived diesel as it is biodegradable, safer to handle and transport, it improves engine longevity, it is compatible with the existing fuel distribution infrastructure, and reduces combustion emissions to near zero. Producing biodiesel is technically and logistically simple - combine a lipid (typically vegetable oil), alcohol (typically methanol), catalyst, and heat at 65 °C for hours. Following purification, biodiesel, suitable for combustion in any compression engine, is obtained. Unfortunately, the cost of the lipid and cost of the energy required to maintain a temperature of 65 °C for the duration of the reaction renders the synthesis nearly financially unviable – so much so that the United States government continues to subsidize biodiesel production. With so little to gain financially, it is no wonder that forecasted contributions from biodiesel remain stagnant. The Shaw Research Group has pioneered the use of SOMS nano-reactors in organic synthesis. Conducting organic synthesis using nano-reactors synthesis seeks to overcome the reactivity challenges of conducting synthesis using traditional methods by ensuring reactivity through the restriction of reactants to nano-sized reactors. In a traditional transesterification synthesis, oil that is diluted with alcohol and stirred in a reactor face the same reactivity challenges that you and I would face if we were trying to find each another while bobbing in an ocean that covers the surface of earth. The oil molecules are magnitudes smaller than the reactors that contain them and even well dispersed oil molecules must navigate a large ocean of alcohol to achieve reactivity. However, the chances of reactivity are greatly improved if the oil molecules are restricted to nano-sized reactors. Restriction of reactants to nano-sized reactors can be achieved with swellable organically modified silica (SOMS). The Shaw Research Group developed a novel procedure for the synthesis of biodiesel using SOMS. This procedure is capable of producing biodiesel is incredibly efficient and high yielding.

SERMACS 1051

Anthelmintic activity of prenylated benzophenones from *Vismia guianensis*

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Vismia guianensis (Clusiaceae) produces a range of phenolic compounds including several structurally intriguing prenylated benzophenones. In our continued study of Clusiaceae, we have revisited the extracts of *Vismia guianensis.* In the preliminary biological evaluation of the crude extracts, significant nematocidal activity was observed. The initial inspections of the NMR and LCMS profile of the crude extracts revealed the presence of several known metabolites, including vismiaphenone D and vismiaphenone F as well as various unidentified metabolites which possess the NMR and MS signature of these prenylated benzophenones. We herein describe the isolation and structure elucidation of several prenylated benzophenones *Vismia guianensis*. The anti-parasitic potential of these metabolites is also discussed.

SERMACS 1052

Ultra-stretchable polymer wearable strain sensor with excellent linearity and repeatable autonomous self-healing ability

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Wearable strain sensors are essential for the realization of applications in the broad fields of remote healthcare monitoring, soft robots, immersive gaming, among many others. These flexible sensors should be comfortably adhered to skin and capable of monitoring human motions with high accuracy, as well as exhibiting excellent durability. However, it is challenging to develop electronic materials that possess the properties of skin—compliant, elastic, stretchable, and self-healable. This work demonstrates a new regenerative polymer complex composed of poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAAMPSA), polyaniline (PANI) and phytic acid (PA) as a skin-like electronic material. It exhibits ultrahigh stretchability (1935%), excellent repeatable autonomous self-healing ability (repeating healing efficiency > 98%), and exceptional linearity (R2 > 0.995) — outperforming current reported wearable strain sensors. The deprotonated polyelectrolyte, multivalent anion, and doped conductive polymer, under ambient conditions, synergistically construct a regenerative dynamic network of polymer complex crosslinked by hydrogen bonds and electrostatic interactions, which enables ultrahigh stretchability and repeatable self-healing. Sensitive strain-responsive geometric and piezoresistive mechanisms of the material owing to the homogenous and viscoelastic nature provide excellent linear responses to omnidirectional tensile strain and bending deformations. Furthermore, this material is scalable and simple to process in an environmentally-friendly manner, paving the way for the next generation flexible electronics.

SERMACS 1053

Charge effects and their role on particle transport in polyampholyte gels

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Biological hydrogels are known to fulfill a number of important physiological functions, serving as lubricants in joints, acting as barriers against pathogens and serving as selective filters for nutrients, proteins, ions and drugs. All biogels are heterogeneous with varied biophysical properties arrayed on spatially disordered polymer networks. Nanoparticles diffusing in such biogels experience a mixture of complex attractive and repulsive interactions. Using fluorescence correlation spectroscopy (FCS), we have systematically examined the role of probe charge with respect to filtering capability of polymer networks on transport and dynamics of probe molecules in polyampholytic gels. Using mixed cationic and anionic dextran gels as a model system, we show the asymmetric transport of varied charged dyes. Translational diffusion coefficients in mixed attractive and repulsive interactions reveal the probe filtration is primarily attractive with strong trapping between oppositely charged probe even in mixed gel systems. Initial results on probe transport in succinylated amino dextran gels and subsequent comparison of the effect of electrostatic interactions in polyampholytes with mixed charged gel system will also be presented. Knowledge of polymer-probe interactions may serve as a guideline in the rational design of promising therapeutics that must overcome the significant work required to navigate biological hydrogels in vivo to successfully deliver their payloads.

SERMACS 1054

Investigations of succinylated polyethylenimine derivatives for enhanced transfections in serum

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Although gene therapy has promise to treat serious inherited and acquired diseases, its clinical success has been hindered because of safety concerns or lack of efficiency and biocompatibility of various gene delivery agents. Currently, viral vectors account for roughly 70% of clinical trials due to their inherent gene delivery activity, but, they suffer from substantial safety concerns including immunogenicity and oncogenicity as well as concerns for commercial production. In contrast, synthetic polymeric materials are an attractive platform due to ease of production as well as reduced immune responses, but to date, have lacked the efficiency and

biocompatibility to be clinically relevant. Addressing these issues, we have produced zwitterion-like derivatives of polyethylenimine (zPEIs) via succinylation of primary and secondary amines. Evaluation of polymer/DNA interactions revealed these polyampholytes decreased buffering capacity, increased serum stability and created tunable particle stability in the resulting PEI/DNA polyplexes. In vitro gene delivery in the absence of serum was moderately improved, however transgene expression in the presence of serum was increased 51-fold compared to unmodified bPEI/DNA. Lastly, we'll discuss more recent results focusing on low percent modified zPEIs to more fully comprehend the correlation between enhancement of transfection in serum-containing media and succinylation.

SERMACS 1055

Surface modification of titanium surfaces for improved tendon adhesion

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Titanium implants have proven to be appealing and successful for orthopedic surgery due to surface modifications that allow for effective osseointegration. Titanium is highly biocompatible, however, such metal prosthetics are not conducive to soft tissue and tendon adhesion. Here, we address this problem with thin films composed of a gradient of polypyrrole (PPy), polydopamine (PDAm) and collagen, which were used to coat the surface of titanium or tantalum plates. PPy films were grown through an electrochemical oxidative polymerization. PDAm is formed through electrochemically induced self-polymerization of dopamine (DAm). The two monomers can be copolymerized electrochemically. This copolymerization produces a film with both conductivity and better adhesion than just the PPy films. Collagen, a cell adhesive protein, will then be incorporated. The PPy-PDA-collagen coatings were characterized by scanning electron microscopy, contact angle measurements, four-point probe conductivity measurements and the sticky-tape method for adhesion.

SERMACS 1056

Cationic tricyclic natural product-derived polymers as antimicrobial agents

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Antimicrobial Resistance (AMR) has recently become an urgent public health concern worldwide. To combat AMR, living organisms develop natural antimicrobial peptides (AMPs), an essential biological material, as a part of their innate immune response. AMPs work as antimicrobial agents by utilizing an amphiphilic structure. Cationic charges provide electrostatic interactions with the negatively charged bacterial membranes, while hydrophobic parts penetrate through membranes. In this study, we utilized a multicyclic natural product derived from rosin to mimic AMPs for antimicrobial applications. Various functional groups present in the natural product allow for the preparation of monomers and polymers, while subsequent post-polymerization modification produces an amphiphilic structure through the incorporation of cationic groups. Overall, the resulting amphiphilic structure of these polymeric materials should lead to better electrostatic and hydrophobic interactions with bacteria, resulting in enhanced antimicrobial properties.

SERMACS 1057

Modification of polymeric carbon nitride films for increased photoelectric density

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In recent decades, consumption of nonrenewable resources has increased at an unprecedented rate, creating more frequent energy crises and environmental pollution concerns. Hydrolysis reactions have shown potential in solving these issues by utilizing naturally evolved hydrogen as a clean fuel source, but to make an industrially practical system, it must be optimized with a catalyst photoelectrochemically. A modified-precursor version of a well-known polymeric carbon nitride film (PCN) has been proposed, containing various ratios of nitrogen- and sulfur-containing compounds to create a viable form of the necessary catalyst with an increased photocurrent density compared to more costly transition metal catalysts. Films were synthesized through the molten mediate method, achieved by annealing an ITO glass in various ratios of precursors at 500 °C under nitrogen flow. The resulting ITO glasses with films could then be used directly as photoanodes. Control films containing melamine, thiocyanuric acid, thiourea, and urea have been synthesized, and analyzed for light transmittance and for photocurrent efficiency. All photocurrent densities are in the range of 2-10 µA/cm2. Future work includes synthesizing PCNs using other precursors, and using SEM imaging to characterize the morphology of the films created and link trends to efficiency.

SERMACS 1058

Preparation of metallopolymer hydrogels

Jihyeon Hwang, *jihyeon@email.sc.edu, Tianyu Zhu, Yujin Cha, Chuanbing Tang. Dept of Chemistry Biochemistry, University of South Carolina, Columbia, South Carolina, United States*

Hydrogels have been widely applied for biomedical applications, such as drug delivery and tissue engineering. Compared to traditional hydrogels, charged hydrogels have been extensively exploited in various fields because they could provide additional functions like antifouling. Moreover, charged hydrogels based on cationic metallopolymers can further embed antibiotics via ion-complexation with metal cations, which have exhibited robust antibacterial activities with the synergistic effects of antibiotics and metal-building blocks. Herein, I will present the synthesis of cobaltocenium-containing hydrogels with diverse macromolecular structures and their potential applications as antimicrobial agents.

SERMACS 1059

Controlling topologies of biobased copolymers from renewable rosin and soybean oil

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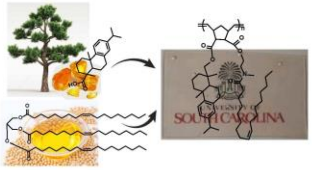
Sustainable polymers from biomass have recently gained a lot of attention [1, 2]. Our group have demonstrated that macromolecular engineering could play a critical role to tune properties of biobased polymers. In this presentation, we report a method to control topologies of copolymers, which were prepared by ring-opening metathesis polymerization. These copolymers exhibit structure-dependent thermal and mechanical properties. [1] YUAN, L, WANG, Z, TRENOR, N M, *et al.* Robust amidation transformation of plant oils into fatty derivatives for sustainable monomers and polymers. Macromolecules, 2015. 48(5):1320-1328. [2] GANEWATTA, M S, DING, W, RAHMAN, M A, *et al.* Biobased plastics and elastomers from renewable rosin via "living" ring-opening metathesis polymerization. Macromolecules, 2016. 49(19):7155-7164.



SERMACS 1060

Optical and electronic properties of benzodithiophene-based conjugated polymers with nucleobase side chain functionality

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The optical properties and charge-carrier mobilities of conjugated nucleobase side chain containing polymers are reported. Variations between adenine and thymine along with alkyl side chains on benzo[1,2-b:4,5-b']-dithiophene (BDT) gives rise to subtle variations in the electronic structure of the copolymers in solution, with absorbance of copolymers containing thymine functionality strongly red shifted in thin films. Differences in absorbance suggest a strong tendency of the nucleobase to increase organization, which is consistent with a significantly higher hole mobility for the thymine-functionalized copolymer containing branched ethyl hexyloxy side chains on BDT repeating units. In the case of the ethyl hexyloxy side chain BDT, the addition of an adenine side chain to the thiophene unit also increased hole mobilities. When heating the polymers before casting, adenine side chain polymers are less affected than non-nucleobase containing polymers, which was observed in both optical and hole mobility measurements. The adenine side chains are believed to promote similar organization observed when heating the non-nucleobase polymers.

SERMACS 1061

Polymer from pine rosin and tung oil

Allen Hulette, *ah10963@georgiasouthern.edu. Chemistry, Georgia Southern University, Atlanta, Georgia, United States*

As fossil fuels become more finite, research within polymers is driven towards renewable bio-based materials. This aspect drives home the need for more plant derived polymers. The purpose of this research project is to determine if pine rosin can be used to manufacture polymers. Pine rosin is made up of abietic acid and can be distilled from pine sap. From past research, tung oil has shown co-polymerization with free radical molecules so it was used in the first step of modifying the glycerin molecule. It was calculated that a 3:2:1 ratio of abietic acid, tung oil, and glycerin was needed to create the desired monomer that could later be manipulated into a polymer through a free radical chemical process. Sodium hydroxide is used to modify the glycerin molecule before two tung oil fatty acid chains are attached. Nuclear Magnetic Resonance, Fourier Transmission Infrared Spectroscopy, and Raman spectroscopy were all used to characterize the modified glycerin molecule with fatty acid chains. The next step is to modify the abietic acid to be able to attach it to the remaining available hydroxyl group of the glycerol abietate through . The best candidates for the (co-)polymerization once the monomer with abietic acid has been manufactured would be Azobisisobutyronitrile (AIBN) and peroxide based Luperox DI polymer initiators. After the monomer has been synthesized, the prior mentioned free radicals will be used to produce a polymer that can be used to make plastics.

SERMACS 1062

Elements of alchemy

Clifford W. Padgett, *cpadgett@georgiasouthern.edu. Chemistry and Physics, Armstrong State University, Savannah, Georgia, United States*

This talk will present an overview of the elements (chemical and other) used in alchemy and how these laid the foundation of modern chemistry and its periodic table. A brief introduction to the alchemical process will be presented and how this process compares to the process used by chemists today. We will also explore the symbology used to represent elements currently found on the periodic table and compounds made from those elements.

SERMACS 1063

Elemental name game

Catherine E. MacGowan*, cmacgowan@georgiasouthern.edu. Chemsitry & Biochemistry, Georgia Southern University, Savannah, Georgia, United States*

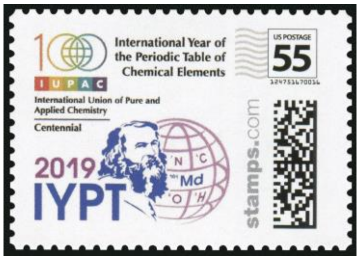
One of the first lessons learned in an introductory chemistry course is the names and symbols of the chemcial elements. Our discipline revolves around the elements. For chemists, the elemental symbols are our alphabet. We make words (chemical compounds) from these symbols, and from these words compose sentences (balanced reactions) to describe our work. But have you ever wondered how the elements acquired their names and subsequent symbols? The story behind the names and symbols of the elements is the premise of this presentation. This talk will focus on elemental name groupings as well as how their discoveries and at times world politics lead to their names.

SERMACS 1064

Law & order: Periodic table

Daniel Rabinovich*, drabinov@uncc.edu. UNC Charlotte Chemistry, Charlotte, North Carolina, United States*

The International Year of the Periodic Table of the Chemical Elements (IYPT) celebrates the sesquicentennial of the development of the modern periodic table, first disclosed in 1869 by the Russian chemist Dmitri Mendeleev. The IYPT presents a unique opportunity to highlight the value of chemistry to society and the history of its most recognizable source of information. One of the key features of Mendeleev's elemental arrangement was its predictive power since empty spaces were reserved for elements unknown at the time. The fact that scandium, gallium, and germanium were all discovered within a few years, and showed many of the physical and chemical properties anticipated by Mendeleev, led to the success of his proposal. In this regard, this talk will use postage stamps and related philatelic materials to outline the discovery of several elements and the development of the modern periodic table, from the four classical elements in Greece to the synthesis of superheavy elements.



SERMACS 1065

Musical tables: Two early periodic arrangements of the elements

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The chemist most closely associated with the discovery of the periodic law and the establishment of the periodic system of elements, Dmitri Mendeleev, was not the first to notice chemical periodicity. This presentation examines two periodic arrangements of the elements from more than 150 years ago. The French geologist Alexandre-Émile Béguyer de Chancourtois devised the first periodic arrangement of elements in 1862, which he called the Vis Tellurique. British analytical chemist John Alexander Reina Newlands made several arrangements of the elements, the best of which he called the Law of Octaves (1865). Although both of these scientists made analogies to musical scales, the musical aspect will be treated only lightly in the presentation, which will emphasize both strengths and weaknesses of the arrangements. Neither arrangement earned much attention from other scientists, though, until periodic systems of Mendeleev and Lothar Meyer were widely known in chemistry.

SERMACS 1066

South Carolina: Wonderful iodine state

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WWI medical examiners observed a much lower incidence of goiter (thyroid enlargement typically associated with iodine deficiency disease) in soldiers from South Carolina and other southern states, as compared with those from other parts of the country, particularly the upper mid-western states.1 Dr. William Weston, a pediatrician from Columbia, South Carolina was one of these examiners, and working with Dr. A. Bethune Patterson, a physician and state senator from Barnwell, South Carolina, he convinced the SC legislature to commission a study of South Carolina produce to determine its iodine content. This led to a successful, but short-lived campaign to market South Carolina grown fruits and vegetables to consumers in the goiter belt region of the country. Despite initial success, the campaign succumbed to the Great Depression. By the time the Depression was over, iodine supplementation had been installed as a cheap and effective method to address the problem. Despite it's demise, vestiges of its existence are still present in South Carolina. 1. Katherine D. Cann, Proceedings of the South Carolina Historical Association 1995, 67-76.

SERMACS 1067

History of the valence electronic structure of the actinides

Henry S. La Pierre, *la_pierre@chemistry.gatech.edu. School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, United States*

This lecture will follow the historical isolation and identification of the elements now characterized as the actinides from the perspective of the theory of the valence electronic structure of the actinides. This perspective on the intellectual development of the field will highlight how the actinides challenged the understanding of the structure of the periodic table and how contemporary problems in actinide electronic structure continue to challenge our fundamental understanding of bonding. The physical techniques that have been developed to address these challenges have significant implications for our understanding of chemistry and physics across the periodic table.

SERMACS 1068

History Pu-238 production at the Savannah River Site

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The Savannah River Site was named a National Chemical Historical Landmark (NHCL) by the American Chemical Society in 2018 for the production of Pu-238 for space exploration. This presentation will highlight the production of the isotope, how it was vital to space exploration, and how our scientific knowledge of the universe has expanded as a direct result of its use in satellites. In addition, the NHCL process will be discussed in an effort to encourage other ACS local sections to seek the designation for their important local chemical history.

SERMACS 1069

Future of new superheavy element discoveries

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From 1981-2010, scientists worldwide discovered 12 new elements at a rate of approximately one new element every 2.5 years. This was an incredible period of widespread success and was driven by new developments in accelerator technology, separator design, and the availability of appropriate target materials. However, no new element has been discovered since 2010, even though there have been multiple attempts by several highly skilled groups utilizing very sensitive equipment. This lack of success has led to theoretical investigations of the nuclear reactions, and these suggest that the reaction probabilities may be much lower than those for previously utilized reactions. This talk will discuss the theoretical basis for new element production, recent experiments to synthesize new elements, and the prospects for discovering new elements in the next few years.

SERMACS 1070

Dinitrogen coordination and activation by weak-field ligated multimetallic complexes

Leslie J. Murray, *murray@chem.ufl.edu. University of Florida, Gainesville, Florida, United States*

Here, our ongoing work in the area of dinitrogen activation by multimetallic compounds will be discussed. In particular, recent results on catalytic silylation of dinitrogen, kinetics for dinitrogen binding, and employing metal-metal bonds as N_2 reactive functional groups will be presented.

SERMACS 1071

Napthylsalophen lanthanide(III) complexes with tunable emissions

Emily E. Hardy, Ethan A. Hiti, John D. Gorden, ***Anne E. Gorden***, *gordeae@auburn.edu. Department of Chemistry, Auburn University, Auburn, Alabama, United States*

Multi-nuclear lanthanide complexes are of interest for their potential applications in imaging, quantum computing, in energy transfer, or as single-molecule magnets (SMMs). Synthesizing such species can be difficult because of the large coordination numbers and the flexibility in coordination geometries and of the lanthanide ions. Multidentate ligands have been employed to prepare multinuclear species; however these can be very sensitive to changes in pH, solvent effects, or affected by counter anions. Here, we describe a series of Schiff- base ligands based on 1,1’-((1E,1’E)-(1,2-phenylenebis (azanylylidene)) bis(methanylylidene))bis(naphthalen-2-ol) or “napthylsalophen.” These were then used to prepare a series of metal complexes with Th(IV), Ce(IV), and U(VI) as well as with lanthanide(III) metal salts. While the Th(IV) and Ce(IV) complexes were found to form as M1L2, the resultant Ln(III) complexes were found to self-assemble as triple decker sandwich complexes of the type (M2L3). Structural differences found can be attributed to the decreasing ion size across the lanthanide series. The spectra were found to be somewhat tunable through changing metal ion, substitution, or solvent. Comparisons of the structure and emission provide some insight into metal coordination characteristics and tenability of properties.

SERMACS 1072

Sustainable synthesis of organometallics through mechanochemistry

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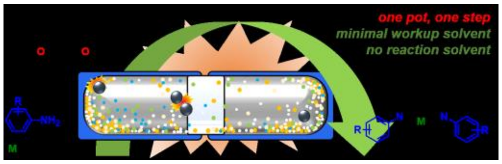
The development and implementation of organometallic precatalysts has played an important role in modern molecular and macromolecular organic synthesis. However, while the use of such species as precatalysts greatly improves sustainability, their preparative routes often rely on multiple time-, energy-, and solvent-intensive steps. These factors can impact overall reaction-system sustainability but are often ignored/justified due to the precatalysts being highly value-added. By leveraging solvent-free mechanochemical synthesis through vibratory ball-milling, we report the one-pot, one-step synthesis of a range of first-row transition-metal bis(imino)pyridine complexes, where both the ligand and coordination complex are assembled in-situ. Bis(imino)pyridine complexes of the first-row transition-metals have an extensive history of application as precatalysts for numerous bond-forming transformations and serve as a starting point for our efforts of increasing sustainability of precatalyst preparation. Our method facilitates access to such species in a time-, solvent-, and space-saving manner which can easily be adapted to any laboratory setting regardless of pior experience with organometallic complex synthesis.



SERMACS 1073

Metal-organic frameworks: Perspectives and applications

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Self-assembled materials such as metal–organic frameworks (MOFs) could add a new dimension to a wide number of applications including supercapacitors, electrodes, or thermoelectrics. From this perspective, the understanding and tailoring of the electronic properties of MOFs are key fundamental challenges that could unlock the full potential of these materials. For instance, materials with a predesigned pathway for energy transfer (ET) can address the urgent needs in fast enhancement of material performance in areas ranging from optoelectronic devices to photocatalytic systems and, thereby, drastically modify the existing energy and material landscape. MOFs have significant advantages to achieve directional ET. For instance, they provide a high level of control for chromophore arrangement, structural parameters, and photophysical properties, through rational chromophore design and synthetic conditions unprecedented for large light-harvesting ensembles and extended structures. In this presentation, mechanistic and structural aspects of directional energy transport will be discussed on the examples of photochromic, fulleretic, and biomimetic systems in order to harness MOFs as a versatile platform for energy utilization enhancement. These studies unveil the possible pathways for transforming the electronic properties of MOFs from insulating to semiconducting, as well as provide a blueprint for the development of hybrid porous materials with desirable electronic properties.

SERMACS 1074

Metal organic–frameworks for noble gas adsorption

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Metal-organic frameworks (MOFs) have recently attracted enormous interest over the past few years due to their potential applications in energy storage and gas separation. Like zeolites, MOFs consist of open frameworks that can accommodate several different gas molecules in a cage structure. Different than zeolites, MOFs represent a new class of functional materials consisting of metal centers linked with organic building blocks to produce diverse structural frameworks. These metal centers and organic linkers readily self-assemble into materials with open framework structures, where all the porosity is accessible. Several porous materials (zeolites, activated carbons) were reported for applications in separation, catalysis but MOFs have received considerable attention over the past few years because of the high mass flux, thermal stability, adjustable chemical functionalities and availability of hundreds of well characterized materials reminiscent to zeolites. However, very few reports on MOFs for adsorption of noble gases have been reported. In this regard, Pacific Northwest National Laboratory (PNNL) is exploring MOFs for noble gas adsorption and separation at near room temperature. Subtle changes in pore size, functionality and metal cluster found to have huge impact on noble gas separation. I will present the role of metal and temperature play in noble gas adsorption in various MOFs synthesized at PNNL.

SERMACS 1075

Investigating bonding and catalytic activity of TpCu(Co) complexes

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Copper(I)-CO complexes are relatively unstable under standard conditions primarily due to the lability of the Cu-CO bond. Examples of stable copper carbonyls belong to the family of LCu(CO) complexes where L is a trispyrazolylborate (Tp) ligand. The rationale for the stability of these complexes is the presence of the electron donating Tp ligand that allows for back donation from the relatively electronegative Cu(I) metal to CO. In this study we explore the effect of the L ligand on Cu-CO backbonding for a series of LCu(CO) complexes using DFT. The reactivity of a TpCu(CO) in the alkyne azide cycloaddition (CuAAC) reaction was also investigated. The TpCu(CO) complex exhibits catalytic activity at room temperature under neat conditions as well as at elevated temperatures when using a solvent.

SERMACS 1076

Catalytic two-electron oxidation of a cobalt(II) complex supported by a redox-active ligand scaffold: Synthesis, characterization, and catalytic activity

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Cobalt(II)-catalyzed chemical transformations using dioxygen as a terminal oxidant have received rigorous attention over the past decade as an earth-abundant alternative to the use of precious, second and third-row metals in these reactions. While the use of more naturally abundant metals in place of the precious metals is an attractive option, there are a variety of challenges in first-row transition metal catalysis. One key challenge arises from the tendency of first-row transition metals to favor one electron redox chemistry while second- and third-row metals favor two-electron processes. The use of redox-active ligands in conjunction with cobalt(II) is of particular interest for green catalysis because the ligand scaffold can serve as a radical reservoir and promote the multi-electron chemistry necessary to activate dioxygen at a first-row transition metal center. We have previously reported a modular, redox-active ligand scaffold, bis(2-isobutyrylamidophneyl)amine, as well as its complexation with Co(II) in both a mono- and binuclear fashion. Both complexes were shown to be active catalysts for dioxygen activation and two-electron aerobic oxidations. This presentation will describe a modified ligand scaffold that incorporates secondary-sphere H-bonding moieties. This ligand supports a mononuclear Co(II) complex that is capable of catalyzing aerobic, two-electron oxidations of alcohols. Efforts to understand the mechanism of this transformation, including the isolation and structural characterization of the two-electron oxidized Co complex will be discussed.

SERMACS 1077

Mechanism of frataxin “bypass” in human iron–sulfur cluster biosynthesis with implications for Friedreich’s ataxia

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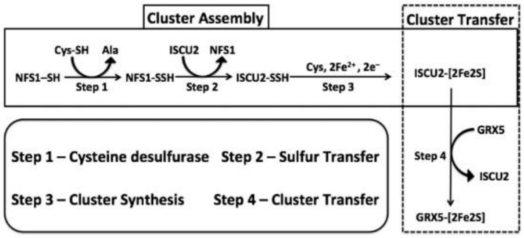
In humans, mitochondrial iron–sulfur cluster biosynthesis is an essential biochemical process mediated by the assembly complex consisting of cysteine desulfurase (NFS1), LYR protein (ISD11), acyl-carrier protein (ACP), and the iron–sulfur cluster assembly scaffold protein (ISCU2). The protein frataxin (FXN) is an allosteric activator that binds the assembly complex and stimulates the cysteine desulfurase and iron–sulfur cluster assembly activities. FXN depletion causes loss of activity of iron–sulfur-dependent enzymes and the development of the neurodegenerative disease Friedreich’s ataxia. Recently, a mutation that suppressed the loss of the FXN homolog in yeast was identified that encodes an amino acid substitution equivalent to the human variant ISCU2 M140I. We developed iron–sulfur cluster synthesis and transfer assays and determined that the human ISCU2 M140I variant can substitute for FXN in accelerating the rate of iron–sulfur cluster formation on the monothiol glutaredoxin (GRX5) cluster acceptor protein. Incorporation of both FXN and the M140I substitution had an additive effect, suggesting an acceleration of distinct steps in iron–sulfur cluster biogenesis by each protein. Together, these results reveal an unexpected mechanism that replaces FXN-based stimulation of the iron–sulfur cluster biosynthetic pathway and suggest new strategies to overcome the loss of cellular FXN that may be relevant to the development of therapeutics for Friedreich’s ataxia.



FXN and M104I ISCU2 in Fe-S Cluster Biosynthesis

SERMACS 1078

Flux crystal growth and magnetic properties of new f-element chalcogenides

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Lanthanide elements offer a versatile platform for the design of new magnetic and optical materials. The use of soft chalcogenide ligands introduces tunability of the crystal electric field of the lanthanide cations, which can result in new classes of materials with various potential applications. Exploratory crystal growth of these compounds is an important tool for creating new compounds, and the development of new synthetic routes is highly desirable to achieve the intentional synthesis of new chalcogenide materials. One well-developed technique for obtaining crystals is flux crystal growth. Unlike solid state synthesis, which is usually performed at higher temperatures and which typically results in thermodynamic products, flux crystal growth enables access to kinetically stabilized phases by using fluxes with low melting points. Focusing on the synthesis of new magnetic materials, specifically those containing f-elements, we employed alkali iodide fluxes to obtain single crystals of new thiophosphate and thiosilicate compounds with incorporated lanthanide and uranium cations.

SERMACS 1079

Nature-inspired molecular sensors for the selective detection of metal ions

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The Wallace group is focused on designing molecular sensors that are selective for metal ions that are considered toxic above the allowable daily intake concentrations defined by the World Health Organization. To design these sensors, we utilize the Pearson acid-base concept and pay attention to metal binding motifs that are present in nature, such as siderophores. We have synthesized and characterized a library of rhodamine-based molecular sensors and monitored the optical responses of each sensor to various metal salts in a range of solvent systems. The extent of complexation between the molecular sensor and each metal ion was studied using spectroscopic and/or spectrometric analysis. By analyzing the complexation between the molecular sensors and the metal ions that they are selective for we have determined that the counterion plays a crucial role in host-guest binding ratios, a factor that is often ignored during solution studies. We also concluded that the presence of oxygen containing solvents can disrupt the ability of the metal ions to coordinate to ligands, as the metal ions will instead coordinate to the solvent if the affinity for the ligand is less than that of the solvent. To minimize interference induced decomplexation we have recently designed a siderophore inspired molecular sensor. Siderophores are small, high-affinity iron-chelating compounds that are secreted by microorganisms such as bacteria and fungi and serve as ferric and ferrous transport agents across cell membranes. By using this approach, we hope to not only improve the selectivity and sensitivity of our sensors towards ferric ions but to also improve the ability of our sensor to permeate cellular membranes for use as a biosensor.

SERMACS 1080

Bio-molecule course-based research experience for sophomores

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Course-based research experiences (CURE) are powerful and inclusive ways to expose a larger number of students to research, and to aid their development as scientists. We have used our experience in CURE development to backward-design our chemistry laboratory curriculum to allow students to develop the cognitive and affective processes necessary to engage in a second-year course-based research experience involving understanding and characterizing bio-molecules. We will discuss the challenges and lessons learned by detailing the current progress of the development the research-based Macromolecules laboratory course, and how the course fits into Oxford College's discovery-based chemistry laboratory program.

SERMACS 1081

Cures beyond the classroom: Student's perspective

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Course based undergraduate research experiences (CUREs) have become an increasingly popular method of instruction, excelling at providing a meaningful research experience to all the students in a course. In addition to helping expand research opportunities during a course, CUREs prove an opportunity for dedicated students to go beyond on what is possible in a lab session by using the CURE as inspiration for independent research. Students in the Biochemistry Authentic Scientific Inquiry Lab (BASIL) work to elucidate the function of unknown proteins using a combination of wet and bioinformatic labs. Assessment of students in a research-based lab has been identified as one of the significant hurdles towards the wider adoption of CUREs (1). Irby and colleagues at Purdue university have identified anticipated learning outcomes (ALOs) specific to BASIL based on instructor needs (2). Using these ALOs, questions were developed, and student assignments analyzed to determine whether the students are learning and applying the knowledge and skills essential to strong biochemical knowledge and rigorous experimental analysis. Students who have previously participated in the biochemistry lab continue their work as research assistants, developing assessments and analyzing responses. This presentation will showcase the role of CUREs as a path to increasing research in and out of the classroom. Brownell, S. E., Kloser, M. J. (2015) Toward a conceptual framework for measuring the effectiveness of course-based undergraduate research experiences in undergraduate biology. Stud. High. Educ. 40, 525–544. Irby, S. M., Pelaez, N. J., Anderson T. R. (2018) Anticipated Learning Outcomes for a Biochemistry Course-Based Undergraduate Research Experience Aimed at Predicting Protein Function from Structure: Implications for Assessment Design. BAMBED. 46, 478-492.

SERMACS 1082

Using spectroscopy to identify a forgery: Inquiry-based, hands-on experience for non-majors

Christine Theodore, *ctheodore1@gmail.com. University of Tampa, Tampa, Florida, United States*

Engaging non-majors and instilling an appreciation for the scientific method can be a challenge. Our Chemistry and Art course allows students to explore chemistry in a more tangible way by extracting the key concepts we hope our non-majors take away from a chemistry course and reframe them through the lens of art and art history. Hands-on activities are completed throughout the semester, culminating in a final inquiry-based experiment. Students are presented with a scenario. They work in an art museum and are asked to help their fictional boss determine whether a newly discovered piece of art by a well-known artist should be acquired for the museum's collection. Students are given "historical" documents to analyze and extract clues from, a "piece of art" by the same artist as comparison, and access to various spectroscopic instrumentation. At the conclusion of the class period, students develop a final analysis and their official recommendation on the acquisition of the art piece. The overall goal of the final activity is to not only give our students the opportunity to experience collecting and analyzing spectroscopic data but to challenge them to think in a way that they might not otherwise have the opportunity to do. Collecting "clues", making connections, and arriving at a conclusion are the relatable and applicable parts of the scientific process. Students reported positive experiences with the final experiment and the ability to collect spectroscopic data. They compared the activity to an escape room because they had to collect all the clues before solving the puzzle at the end. The course and the final project have proven to be a relatively inexpensive and interactive way to engage non-majors in the scientific method.

SERMACS 1083

Incorporating an unexpected procedural flaw in a traditional undergraduate organic laboratory into a discovery-based laboratory experience

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The separation of a mixture of starch, acetylsalicylic acid, and acetanilide is a standard undergraduate organic laboratory used to instruct students in a variety of techniques including liquid-liquid extractions, gravity filtration, vacuum filtration, and recrystallization. Recently, a procedure used for decades at Mercer University was modified, requiring students to analyze recovered acetanilide and acetylsalicylic acid via ^{1}H NMR. To the surprise of both faculty and students, the hydrolysis product of acetylsalicylic acid, salicylic acid, was recovered. This unexpected outcome necessitated an immediate reaction from faculty in order to salvage the learning experience. However, minor modifications to the laboratory have led to a new, discovery-based laboratory sequence that allows students to observe and analyze the unexpected result. The four-week laboratory sequence places students as new employees of a fictitious pharmaceutical company and leads them through the discovery of a flaw in the company's quality assurance process, while simultaneously introducing organic separations techniques such as TLC, filtration, extraction, and recrystallization, along with melting point and ^{1}H NMR analysis. The laboratory sequence demonstrates to students the value of interpretation of experimental results.

SERMACS 1084

Assessing meaningful learning through thematic analysis of creative exercises in inorganic chemistry

***Janet Shaw**, jshaw22@kennesaw.edu. Kennesaw State Univ, Kennesaw, Georgia, United States*

Creative Exercises (CEs) have been incorporated into the upper-level inorganic chemistry foundation course in order to promote meaningful learning. CEs are open-ended, student-centered assessments that reward multiple correct answers and do not penalize for incorrect statements thereby inspiring creativity. By rewarding relevant statements from content in any pre-requisite course, students are encouraged to establish connections between course materials thereby reinforcing concept retention and promoting meaningful learning. CEs that follow content in Miessler, Fischer and Tarr's Inorganic Chemistry textbook have been developed and assigned in-class, as homework, and on midterm examinations. Thematic analysis of student responses is used to determine which pre-requisite course materials they are connecting to inorganic chemistry concepts. Common student misconceptions are also elucidated during the process of thematic analysis and will be reported. A qualitative survey is employed to assess student opinions of CEs, and student performance on CEs is correlated to examination performance. Preliminary findings will be presented along with implications for future inorganic teaching practice.

SERMACS 1085

Teaching proteomics without instrumentation: Novel undergraduate curriculum

***Suzanne Robertson**, suzyrobertson900@gmail.com. Elon University, Durham, North Carolina, United States*

Proteomics is a highly interdisciplinary field, making it ideal for engaging upper-level undergraduates. However, proteomics is usually studied in the setting of graduate programs, utilizing expensive chromatography and mass spectrometry instruments. Use of such resources is often infeasible in undergraduate curricula. Therefore, a curriculum was developed at Elon University designed to engage undergraduate students in the topic of proteomics without requiring the use of analytical instrumentation. The premise of this 25-hour course is that students are interviewing for a job with a proteomic company. The central learning outcome is that students will gain an understanding of core concepts in proteomics sufficient to converse with an expert in the field. To promote active learning, hands-on activities covering trace analysis, chromatography, ion source mechanisms and ion motion are used. Learners are given writing assignments requiring them to evaluate and apply concepts from articles out of the proteomics literature. The final exam is an oral interview in which students are presented a scenario in which proteomic techniques may be used to answer a scientific question. They are asked to describe and justify an experimental design to address the scenario they are given. In this course, students gain an understanding of proteomic sample preparation, chromatography, mass spectrometry, bioinformatics, data analysis and experimental design. This approach is a novel course design as it does not require access to a mass spectrometer. The curriculum was successfully implemented with seven undergraduate students in an intensive seminar format over a four-week timeframe. It could easily be adapted for larger groups and to a full-semester format.

SERMACS 1086

TIME 4 Real Science: Unique high school CURE

***Jennifer S. Williams**, jwilliam@tcsnc.org. Science, Brevard High School, Brevard, North Carolina, United States*

T.I.M.E. 4 Real Science is a unique grassroots STEM initiative that turns the preparation of tomorrow's scientists upside down. Traditionally, students learn science concepts in high school, learn more science concepts in college and then finally get to do real science in graduate school. Most students never find out what it is to do real science, and opportunities are lost. In the T.I.M.E. program, 9th - 12th graders spend over 180 hours during the school day, after school and in the summer conducting real research into questions of their own choosing that matter to them and our community as they contribute to the greater scientific knowledge base. In the process they are supported by educators and volunteer scientists as they learn techniques and content necessary to answer their questions. They develop critical thinking and problem solving skills, learn to create, innovate, plan, communicate, use their resources and persist in their work. The T.I.M.E. program develops scientific entrepreneurs with a love for their community. Over the past 12 years, 136 different Transylvania County, North Carolina high school students (57% female) have conducted innovative, authentic research on local topics including kudzu bug control, chestnut tree restoration, isolation of endophytes from local medicinal plants, and investigation of microbial competition on salamander skin. Thirty-five students have participated in the program for two or more years. Scientists say that student work is on par with that of graduate students. Over the years, 46 different T.I.M.E. students (63% female) have been awarded trips to represent North Carolina in at least one national or international science competition. The T.I.M.E. program has been essential in connecting students from successful elementary and middle school STEM programs to the greater STEM pipeline that spans high school and into college, keeping kids interested in science as a career. A recent study of North Carolina 9th graders found that only 4% go on to study STEM after high school. In the T.I.M.E. program, 70% of the students pursue STEM majors in college and careers after college.

SERMACS 1087
Crossing floors: Developing an interdisciplinary cure between an environental toxicology and analytical chemistry course
Kristina R. Roth, *kroth1@radford.edu, Jamie Lau. Radford University, Radford, Virginia, United States*

We designed a collaborative course-based undergraduate research experience (CURE) between an Analytical Chemistry and Environmental Toxicology course to engage students in a research project that cannot rely on one discipline alone. This study reports on 47 students' self-reported experience with course outcomes and their opinions of the CURE project. Students in both courses increased in the level of experience in skills related to the CURE project, including the ability to design a project where the outcome was unknown. Further, most students felt a sense of project ownership, but their ownership was attributed only to the positive aspects of the CURE. At the end of the CURE, the students in both classes demonstrated an ability to connect ideas and techniques learned in the course to a broader environmental research question. We also suggest several tips for developing collaborative CUREs in undergraduate courses.

SERMACS 1088
Undergraduate research at scale: What if the treatment is a cure?
Erin L. Dolan, *eldolan@uga.edu. Biochemistry & Molecular Biology, University of Georgia, Athens, Georgia, United States*

Undergraduate research experiences are championed for their potential to promote students' personal and professional development. Yet, there are many more science majors than can be accommodated in traditional, internship-style research experiences. Faculty across the country have responded to the need for scalable approaches to engaging undergraduates in research by developing Course-based Undergraduate Research Experiences, or CUREs. CUREs involve all students enrolled in a course in addressing research problems or questions of interest to the broader community. This talk will present data in CURE effectiveness and highlight the features that make CUREs distinctive from other learning experiences.

SERMACS 1089
How do middle grade students interpret particulate level animations?
Tyler Kinner, *tyler.kinner@gmail.com, Kimberly Linenberger-Cortes. Kennesaw State University, Kennesaw, Georgia, United States*

Animations are becomingly increasingly present in the chemistry classroom, in large part due to the ubiquity of technology and the adoption of NGSS-aligned state standards. Before teachers ask students to watch an animation using a phone or tablet, how sure are we that students will interpret the animation correctly? Previous research indicates that students often interpret chemical representations in ways that are not aligned with the "expert interpretation". This talk will share findings from a qualitative inquiry into the nature of student interpretations of particulate level animations of chemical and physical processes. We will identify implications and share potential solutions for K-16 educators.

SERMACS 1090
Transcription through roadblocks
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Transcription factors (TFs) bind one or more recognition sites perhaps with differential affinities and/or cooperatively to modify DNA topology and regulate promoters. However, many genes overlap and TFs regulating one may obstruct the transcription of another. Conversely, transcriptional elongation that displaces TFs along one gene might compromise the regulation of other overlapping genes. Transcription by RNA polymerase (RNAP) in the presence of topological roadblocks was monitored using either tethered particle microscopy (TPM) or magnetic tweezers (MTs). The lac repressor protein (LacI) was used as a model roadblock. Results indicate that: i) In the presence of a roadblock, after reaching the terminator (or the template's end), RNAP often abruptly translocated back to the obstacle and recommenced elongation. ii) Very small differences in the DNA tensional state significantly increased the duration of RNAP pausing at a LacI-occupied O1 site. iii) Elongating RNAP might induce a conformational change in the LacI protein securing a loop which gives rise to two different loop states. iv) LacI-mediated looping between the near, weak O2 and the far, strong O1 operators lengthened the pausing by RNAP at O2 relative to O1, and lengthened the aggregate time RNAP paused in front of an operator. Thus, looping seems to turn O2 into a stronger roadblock, as independently found by AFM. These findings indicate new features of regulation.

SERMACS 1091
Probing chemical biology of DNA damage using NMR
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We have utilized NMR to delineate the chemistry and biology of complex DNA damage arising subsequent to N7-alkylation of dG by environmental mutagens and chemotherapeutic agents. One manner in which N7-dG adducts rearrange is to form N^6-(2-Deoxy-Derythro-pentofuranoysl-)-2,6-diamino-3,4-dihydro-4-oxo-5-*N*-alkylformamidopyrimidine (AlkylFapy-dG). Using NMR, we probed the equilibrium chemistry of the Me-Fapy-dG and the AFB_1-Fapy-dG adducts in DNA. These lesions equilibrate between α or β anomers, and for each anomer, atropisomerism may occur around the MeFapy-dG C^5-N^5bond to produce $R_a$and$S_a$atropisomers. Each atropisomer also exhibits geometrical isomerism about the MeFapy-dG formyl bond yielding *E*and *Z*conformations. The relative abundances of these species have been determined in single strand and duplex DNA. These may be differentially recognized during DNA processing, providing a mechanistic basis for the generation of sequence-specific repair and replication processing. Initially formed N7-dG adducts also depurinate to form apurinic sites (AP sites) in DNA. AP sites, once formed, epimerize via a reactive aldehyde intermediate, which may conjugate with anthracycline anti-tumor agents such as doxorubicin, or form DNA interstrand cross-links (ICL), both of which are potential cytotoxic endpoints. Progress in utilizing NMR to examine the chemistry and biology of AP sites, including an ICL involving the conjugation of AP sites with the N^6-dA in the complementary DNA strand will be presented.

SERMACS 1092

Structural micro-heterogeneity of DNA and DNA bound peptide and protein complexes

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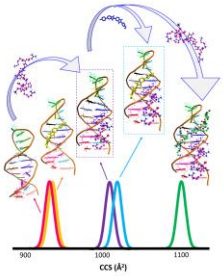
Native mass spectrometry (MS), and more recently in combination with ion mobility spectrometry (IMS), can provide unique insights in structural biology for the description of kinetic intermediates of biomolecules. The IMS-MS coupling provides two dimensional separations: i) separation based on the size/charge, and ii) separation based on their m/z. IMS-MS has addressed several shortcomings of conventional methods by reducing the analysis time (millisecond timescale), sample consumption (ng) and sample purity requirements. In addition, the recent implementation of trapped IMS (TIMS) has shown better potential as compared to other IMS technologies, for the separation and structural elucidation of biomolecules by providing high mobility resolving power (R up to 500) in short time scales (50-500 ms). Due to the higher trapping efficiency and mobility resolution advantages, TIMS-MS has gained significant attention for the investigation of proteins and DNA dynamics in their native and denatured states. When complemented with molecular dynamic simulations, IMS-MS allows for the identification of specific intramolecular interactions that stabilize the kinetic intermediates.In this study, recent applications of TIMS-MS for the structural investigation of peptide - DNA and protein - DNA complexes will be shown.



SERMACS 1093

DNA in tight spaces: Linking structure, stability and protection in sperm chromatin

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Packaged DNA is ubiquitous in nature and the laboratory with examples ranging from chromatin, viruses, sperm cells, bacterial nucleoids, artificial viruses and gene therapy constructs. Sperm nuclei are one of the best examples of in vivo maximum DNA compaction and therefore an ideal model system to study biophysically. Despite intense research, the physical mechanisms underlying tight packaging of DNA remain poorly understood especially at the molecular level. Spermiogenesis is a unique multi-step process resulting ultimately in the replacement of histones by protamines in sperm nuclei to a final volume roughly 1/20th that of a somatic nucleus. The near crystalline organization of DNA in mature sperm is thought crucial for both DNA delivery and the protection of genetic information due to the absence of DNA repair. Using osmotic stress coupled to small-angle X-ray scattering(SAXS) to directly measure intermolecular forces, we have done extensive work to understand how cations modulate DNA-DNA forces in the condensed phase and the interrelationships between cation chemistry, packaging densities and compaction. Recent experiments aimed at understanding the various biological implications for both protamine-DNA packaging and correlations to infertility and oxidative stress in sperm chromatin will be discussed.

SERMACS 1094

Replication of an RNA duplex containing an active ribozyme: Exploring the possible role of viscous solvents in the emergence of functional nucleic acids

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RNA has the ability to store genetic information and to catalyze chemical reactions. Accordingly, it has been proposed that RNA was the first polymer of life to achieve self-replication and to evolve functional sequences (the RNA World hypothesis). However, there are multiple unsolved challenges facing enzyme-free nucleic acid replication. First, structured RNA sequences, which are necessary for catalysis (i.e., ribozymes), are poor templates in model prebiotic reactions for RNA synthesis. Second, once an RNA duplex is formed in a template-directed reaction the product strand must be separated from the original template strand for a full cycle of replication, a problem known as strand inhibition. We propose that viscous solvents on the prebiotic Earth could have facilitated the replication of RNA duplexes, including those containing ribozyme sequences. Solvent viscosity allows the trapping of single stranded templates by promoting the formation of intramolecular structures, and by slowing the diffusion of long, complementary strands. Oligonucleotides that are able to assemble on kinetically-trapped single stranded templates can be ligated to form full-length copies, thereby overcoming the strand inhibition problem. Solvent viscosity can also promote the trapping of ribozyme sequences in their active, folded forms. Our results suggest that such viscous solvents, which could have been ubiquitous on the surface of the early Earth, represent a plausible prebiotic environment that would have facilitated the replication and activity of functional nucleic acid sequences.

SERMACS 1095

Transcription factor discovery in the extreme thermophile *Thermus thermophilus* HB8

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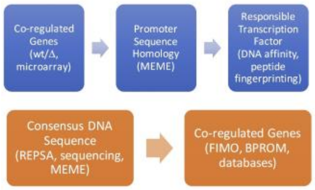
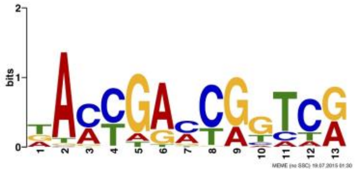
Our laboratory is investigating transcriptional regulation in the model extreme thermophilic organism, *Thermus thermophilus* HB8. Unlike the conventional genetic approach, using deletion mutants to identify co-regulated genes and searching for DNA sequence homology in proximal control regions, we instead use a biochemistry-centric approach, determining the binding specificity of a putative transcription factor, mapping its consensus sequence to an organism's genome, and identifying those genes/operons potentially regulated by this transcription factor. This allows us to go from transcription factor to biological function in relatively short order and at a minimal cost. Instrumental in our success has been the combinatorial selection method Restriction Endonuclease Protection, Selection, and Amplification (REPSA), which has proven adventitious in obtaining biologically relevant consensus sequences for many transcription factors. Here we report on ongoing studies on two classes of transcriptional regulators in *T. thermophilus* HB8: the TetR-related transcriptional repressors TTHA0101, TTHA0163, TTHA0973, and TTHB023 and the CRP/FNR transcriptional activators TTHA1357, TTHA1437, TTHA1567, and TTHB099. For several of these transcription factors, we have found superior consensus binding sequences and additional target genes than previously described. These findings demonstrate that our biochemistry-centric approach for transcription factor discovery can be an effective means of obtaining information on transcription regulatory networks, especially in organisms lacking tools for identifying co-regulated genes.



Flow charts for (top) conventional and (bottom) biochemistry-centric approaches for transcription regulatory pathway discovery.



Sequence logo for REPSA-selected TTHB023-binding sequences.

SERMACS 1096

Elucidation of the dynamics of transcription-coupled DNA repair initiation by RNA polymerase II and CSB using kinetic network models

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Eukaryotic transcription-coupled repair (TCR) is a crucial and well-conserved sub-pathway of nucleotide excision repair. Cockayne syndrome group B (CSB, also known as ERCC6) protein in humans (or its yeast orthologues, Rad26 in Saccharomyces cerevisiae) is among the first proteins to be recruited to the lesion-arrested Pol II during the initiation of eukaryotic TCR. Cryo-EM advances have begun to uncover their structural organization. Here we integrated the cryo-EM data and molecular dynamics simulations to reveal the S. cerevisiae Pol II–Rad26 complex's global motions, define Pol II-Rad26 partitioning into dynamic communities and delineate how structural modules function together to elucidate key roles for Rad26 in TCR. We also mapped Xeroderma Pigmentosum disease mutations onto defined communities to reveals CSB functions and dynamics.

SERMACS 1097

Evaluation of the binding contribution and cooperativity of TIAR/TIA-1 RRM modules for RNA

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T-cell Intracellular Antigen-1 (TIA-1) and T-cell Intracellular Antigen-related protein (TIAR), are abundant cellular proteins that shuttle between the nucleus and cytoplasm, functioning as splicing regulators for pre-mRNA and as translational regulators of gene expression. Both proteins share significant sequence identity and have a structure consisting of three RNA Recognition Motifs (RRMs) and the glutamine-rich Prion-Related Domain (PRD) at the C-terminal. TIA-1 and TIAR share similar binding specificity, preferentially bind to U-rich sequences, but some affinity to As, Cs, and Ts has also been observed. The binding preferences for each RRM have been characterized, and RRM2 has been identified as the main binding contributor. Most studies have explored binding modes with 1:1 short RNA-protein complexes; however multimeric complexes have been observed with two biologically relevant substrates, the *Fas*-intron and the 3'(-) stem loop of West Nile Virus. In order to determine complex stoichiometry and binding mode in the context of longer RNA sequences, a model substrate, rU_{20}, was used. Isothermal titration calorimetry in conjunction with fluorescence anisotropy confirms the formation of multimeric complexes where RNA binding is accomplished by the middle RRM domain (RRM_2). The binding of the proteins is cooperative and complex stabilization occurs through protein-protein contacts. These results highlight the need to consider stoichiometry and protein-protein contacts in addition the accessibility and presentation of single stranded RNA binding sites when developing binding models.

SERMACS 1098

Nurturing a safety culture through student engagement

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Safety is inarguably the highest priority in any research endeavor but training often occurs when students first begin their graduate careers, many months before they begin their research projects. Once a student joins a lab, the culture around safety is ultimately dictated by the Principle Investigator and can vary greatly between labs within a department. To develop and support a department-wide safety culture, the Department of Chemistry at the University of North Carolina at Chapel Hill created a student safety committee in early 2019 that is led and run by students. With direction from the Departmental Associate Chair for Research, the committee is made up of primary and secondary safety officers from each research group and meets once a month. In their inaugural year, the students developed an alert system for communicating safety-related issues such as building power outages and suspicious individuals on research floors. In addition to the committee, department personnel have the opportunity to opt-in to the alert system. The impact on department-wide safety communications has been breathtaking and perhaps more importantly, has given students ownership on departmental safety procedures. Students are also actively working with University Environmental Health and Safety to develop department-wide Emergency Action Procedures. Recommendations by the students are currently being formalized to present to the faculty and will ultimately be adopted as departmental policy. The success of a department's safety culture can be gauged by the number of participants who buy-into and support it. Engaging students not only helps assure their ownership over safety policy and procedure, but helps ensure safety is a priority for the next generation of scientists.

SERMACS 1099

Supporting a culture of safety with teachable moments

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Capitalizing on Teachable Moments can be a neglected strategy in developing a Culture of Safety. What is often used instead to make change is enforcement, but this tends to shut communication down and with it the robust relations needed to create and maintain safe conditions. By contrast, responding with recognition of the vulnerability of those in non-compliance can open communication and support the inquiry necessary to develop and sustain transparency. Within these vulnerable moments lies intense interest in specific information that the inquirer is prepared to apply immediately - the inquirer is hungry to learn and thus is Teachable. In addition once one Teachable Moment is met with support, inquirers will tend to initiate others rather than wait for their safety shortcomings to be discovered. Therefore learning how to recognize and respond to Teachable Moments is essential to developing a self-regulating environment of safety norms. This presentation will cover three examples of Teachable Momentsto demonstrate what qualities they have, how to utilize the opportunities, and what benefits can be anticipated.

SERMACS 1100

Successful execution of top-down safety culture at UNC-Chapel Hill

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With over 1,300 chemical fume hoods in hundreds of laboratories on the University of North Carolina at Chapel Hill's campus, UNC has made strides in improving the safety culture of those using chemical fume hoods over the course of the past three years. In conjunction with multiple University departments, many aspects of UNC's fume hood and laboratory ventilation program were improved. In a top-down display of leadership, school and departmental management within the university have been the driving force behind these changes at UNC. These leaders identified funding for improvements to infrastructure; training was added or improved for facilities workers, laboratory workers, graduate students, and construction engineers/project managers; and routine maintenance was prioritized. Although other universities or private industry facilities may not have the same number of hoods on their campuses, UNC's case can be used to show how multiple entities in an organization can work together to achieve a common goal, creating and sustaining a culture of safety in a research environment.

SERMACS 1101

Collaborative safety training and integrative program development

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Often safety program components fail to effectively integrate all of the user input possible in a multiple use facility. A collaborative approach to bringing simultaneous input from all users of the facility space can combine training with safety program evaluation, refinement, and effectiveness.

SERMACS 1102

Cultivating a culture of safety in undergraduate chemistry labs at UNC Chapel Hill

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The University of North Carolina at Chapel Hill Department of Chemistry is committed to teaching and promoting a culture of safety. This begins with the first undergraduate lab course and continues throughout the entire educational process to a PhD. Each semester teaching assistants are trained by the Department of Environment, Health, and Safety to prepare them to instill a culture of safety in their students. In addition, students must attend a safety lecture at the beginning of each laboratory course and are held accountable for following safety rules and regulations throughout the semester. This presentation will focus on safety education and training that we have incorporated into our undergraduate chemistry curriculum.

SERMACS 1103

From rules to ramp: Embracing safety culture's expanding frontier as a recent graduate

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Throughout my time as an undergraduate student majoring in chemistry, I considered myself mindful in the laboratory: I knew emergency protocol, I could perform techniques as the procedure specified, and I always wore personal protective equipment. Since graduating a few months ago, however, my internship with the American Chemical Society has exposed me to the concept of safety culture and proven that far more goes into being a safe scientist than I had originally believed. Over the course of this presentation, I will share how the perceptions of safety I had during my undergraduate experience have evolved as a result of my immersion in the Scientific Advancement division of ACS. Furthermore, I will illustrate how this evolution mirrors the paradigm shift we are seeing in science education, research, and industry from a rule-based safety culture to a risk-based safety culture.

SERMACS 1104

SOPs, SOCs, and docs: Developing peer-to-peer safety to fight complacency in synthetic inorganic chemistry

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When the same or similar experiments are carried out on a regular basis, it is natural for researchers to become complacent in their approach to safe practices. Best counteracted by continuous active engagement, this presentation will focus on our approaches to fight complacency in our synthetic inorganic chemistry laboratory. Annual activities such as Standard Operating Procedures (SOPs) review and Annual Safety Day allow for demonstrations of proper laboratory techniques and foster discussion about best practices. Weekly discussions of safety scenarios further cement active approaches, as researchers engage in hazard assessment, accident prevention, and discuss handling accidents. Safe Operating Cards (SOCs) afford daily engagement, as researchers perform initial hazard assessments for all reactions and provide a visual notice of hazards and shutdown procedures. Most importantly, SOPs and SOCS provide the tools for peer-to-peer mentorship and foster discussions on safety. Through a combination of these standard lab practices, trainings, and peer-led activities, students actively engage in lab safety culture and assist each other in fighting complacency in our research group.

SERMACS 1105

Laboratory safety culture at UNC-CH

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This prseentation will present the journey of the Laboratory Safety Culture at UNC-CH from 2008 to present.

SERMACS 1106

Measuring protein structure at the protein-nanoparticle interface via 2D infrared spectroscopy

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We are developing new 2D IR and isotope-labeling methodologies to determine and localize structural changes in nanoparticle-bound proteins. We have designed a set of isotope-labeling schemes for monitoring α-helical structures. Using a model peptide with tunable helicity, the sensitivity of each labeling scheme was determined by measuring changes in peak frequencies and crosspeak intensities in the 2D IR spectra. The most successful labeling scheme, along with established schemes for monitoring β-sheet structures, is applied to peptides to resolve changes to native structure that result when peptides adsorb onto nanoparticle surfaces.

SERMACS 1107

Probing plasmon-mediated processes with ultrafast surface-enhanced Raman spectroscopy

***Renee R. Frontiera**, rrf@umn.edu. Renee Frontiera, Saint Paul, Minnesota, United States*

Plasmonic materials are highly promising as catalysts for driving energetically unfavorable chemical reactions with light, due to their unique optical focusing and hot carrier generation properties. However, a complete mechanistic understanding of plasmonic photocatalysis is lacking, in part due to the rapid timescales of plasmonic processes and chemical bond–making and –breaking processes, which occur on the femtosecond and picosecond timescales. Plasmons can concentrate electromagnetic fields, can generate highly energetic electrons and holes, and can heat up local environments. An understanding of the energy partitioning into each of these processes is crucial to the design of plasmonic photocatalysts which are optimized for chemical selectivity. Here I'll discuss our development of ultrafast surface-enhanced Raman spectroscopy (SERS) to probe the behavior of molecules in plasmonic hot spots. By probing on the relevant timescales, we are able to uncover how and when the plasmon energy is converted into hot carriers, molecular heating, or resonant energy transfer. We use a new form of ultrafast Raman thermometry to probe energy transferred into adsorbed molecules as heat, showing that the plasmon-induced heating contribution to catalysis is negligible. Additionally, we probe hot carrier transfer events and use SERS substrates with tunable electromagnetic field enhancements to examine the effects of local fields on chemical reactivity. These results quantitatively determine the energy partitioning of plasmon decay, and highlight the unique ability of these plasmonic materials to drive energetically unfavorable chemical reactions.

SERMACS 1108

Raman spectroscopy for *in vivo* and *in vitro* neurochemical sensing

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Many neurological diseases are difficult to diagnose in the early stages of disease progression where treatment would be most beneficial. For various neurological diseases changes in neurotransmitter concentrations could indicate the onset or progression of the disease. Neurotransmitters are detected in various biofluids using different sampling techniques, however these techniques often involve multi-step sample preparations coupled with long measurement times. There is a need for the development of sensors for the detection of neurotransmitters that are selective, rapid, and label-free with little to no sample processing. Our group focuses on the detection of biomarkers for neurological activity in non-invasively collected biofluids and through the skull. Our approach is to apply surface enhanced Raman spectroscopy (SERS), which provides greatly enhanced Raman signals from very low concentration analytes that have been adsorbed to metal nanoparticles, for the detection of neurotransmitters. SERS is surface selective, highly sensitive, rapid, label-free and requires little to no sample processing. SERS can be applied towards *in vitro*neurotransmitter sensing. For *in vivo* detection, we use spatially offset Raman spectroscopy (SORS), where Raman scattering spectra is obtained from subsurface layers of turbid media through collection of Raman scattered light at a location that is spatially offset from the incident illumination point. We combine SORS with SERS (termed SESORS) for low concentration detection of neurotransmitters in the micromolar (µM) to nanomolar (nM) concentration ranges.

SERMACS 1109

Using Raman spectroscopy to probe the vibrational and structural properties of quantum dots

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We use micro-Raman spectroscopy to investigate two distinct series of metal chalcogenide quantum dots. First, we measure the vibrational structure of the atomically precise cadmium selenide quantum dots $Cd_{35}Se_{20}X_{30}L_{30}$, $Cd_{56}Se_{35}X_{42}L_{42}$, and $Cd_{84}Se_{56}X_{56}L_{56}$. These quantum dots have benzoate (X) and *n*-butylamine (L) ligands and tetrahedral (T_d) shape with edges that range from 1.7 to 2.6 nm in length. Room-temperature Raman spectra have broad CdSe peaks at 175 and 200 cm^{-1}, which we assign to molecular surface and interior vibrational modes, respectively. The Raman spectra do not change with temperature for molecular $Cd_{35}Se_{20}X_{30}L_{30}$, while the interior peak narrows and shifts to higher energy as temperature decreases for $Cd_{84}Se_{56}X_{56}L_{56}$, a spectral evolution typical of a phonon. This result shows that the single bulk unit cell contained within $Cd_{84}Se_{56}X_{56}L_{56}$ is sufficient to apply a phonon confinement model, and that $Cd_{56}Se_{35}X_{42}L_{42}$, with its 2.1 nm edge length, marks the boundary between molecular vibrations and confined phonons. We also investigate the structure of CdSe/CdS alloyed quantum dots with the compositions CdSe, $CdSe_{0.75}S_{0.25}$, $CdSe_{0.50}S_{0.50}$, $CdSe_{0.25}S_{0.75}$, and CdS. We observe CdSe longitudinal optical phonon peaks at 206 cm^{-1} that decrease in frequency with greater sulfur content, and CdS longitudinal optical phonon peaks at 302 cm^{-1} that decrease in frequency with greater selenium content. These trends are consistent with "two mode" behavior observed for homogeneous alloys.

SERMACS 1110

Implications of ice sheet retreat for nutrient export from periglacial landscapes in Greenland

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Retreat of the Greenland Ice Sheet (GrIS) since the Last Glacial Maximum (LGM) ~20 ka drained meltwater to the ocean through proglacial rivers, and meltwater runoff has increased recently with accelerated melting due to global warming. As continental ice sheets retreat, deglaciated watersheds form on exposed terrains and drain additional water from a network of lakes and non-glacial streams fed by local precipitation, groundwater, and permafrost melt. Proglacial rivers have chemical compositions controlled by supraglacial and subglacial processing of organic matter and mineral weathering reactions, but compositions of non-glacial streams depend on the biogeochemical processes occurring within the landscape that depend on variations in exposure ages, hydro-climatic

conditions, and soil and vegetation characteristics. These differences suggest solute fluxes may differ depending on relative discharge from the two stream types. While individual proglacial rivers deliver orders of magnitude more water to the ocean than individual non-glacial streams, specific discharge normalized to watershed area is similar between proglacial rivers and non-glacial streams. To characterize biogeochemical fluxes across the changing periglacial landscape of Greenland, we compared proglacial rivers draining the GrIS to non-glacial streams during the melt seasons of 2017 and 2018. We combined stream discharge measurements with measured nutrient concentrations to calculate annual fluxes. Differing biogeochemical controls in the two types of watersheds impact nitrogen (N) and phosphorus (P) concentrations. Non-glacial streams deliver less P relative to N than proglacial rivers, likely due to increased uptake in vegetation as well as interactions between phosphorus and iron oxide minerals that form in the oxic waters of non-glacial streams. Because N:P ratios impact coastal primary productivity, changes in nutrient export due to deglaciation may impact net coastal metabolism and biogeochemical budgets. Our results suggest large-scale shifts in nutrient export following exposure of deglaciated landscapes after the LGM, and further shifts as the GrIS continues to retreat.

SERMACS 1111

Is dissolved organic carbon the key to understanding the fate of Arctic permafrost soil carbon?

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Recent trends of increased global temperatures are amplified in the Arctic, where the soil contains twice as much carbon than is currently in today's atmosphere. This enhanced Arctic warming is projected to thaw permafrost and to increase microbial activity and may release large quantities of soil carbon to the atmosphere. While many studies focus on the microbial consumption of soil carbon, few studies consider the form of the carbon microbes are consuming. Using radiocarbon as an informant, this talk will explore that the premise that Arctic soil microbes are primarily consuming the water soluble component of the soil organic carbon and not the bulk soil organic matter. We have studied the in situ microbial carbon usage in mineral and organic soils from a dozen locations in Svalbard, the Canadian high Arctic and various locations in Alaska. We measured the natural abundance radiocarbon in microbial biomarkers of the viable microbial community as phospholipid fatty acids (PLFA) and the radiocarbon content of the bulk soil organic carbon that the microbes riside in. The premise of using the radiocarbon content of the phospholipid fatty acids is that this technique measured the membranes of the viable microbial community, which take on the isotopic value of the carbon the microbes are eating. Our results indicate that at all sites, the soil microbes are only accessing the youngest soil organic carbon and that portion is only a small amount of the total soil organic carbon. Additionally, when we explored the radiocarbon composition of some of the old soils as a function of chemical politity, we found that the youngest carbon was in the most polar fraction. These soil based findings are consistent with Arctic rivers containing younger dissolved organic carbon than particulate organic carbon. Therefore, these results suggest that the largest fluxes of carbon from Arctic soil microbes will be from microbes consuming the water soluble organic carbon.

SERMACS 1112

In a sea of microbes and organic matter: Identifying the organisms and metabolisms that power the ocean's carbon cycle through genomics and transcriptomics

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Microbes are the largest consumers of ocean primary productivity, controlling carbon flux between the ocean's dissolved organic carbon (DOC) pool and oceanic-atmosphere CO_2 reservoirs. Knowledge of what controls microbial metabolism in the ocean is substantially limited, although it is often likely to be the amount and biolability of organic matter. Therefore, identifying the types, sources, and flux of organic carbon supporting heterotrophic metabolism is key to understating ocean biogeochemistry. Currently, the ability to characterize the DOC sources powering microbial metabolism is hampered by the fact that the ocean's network of organic substrates and microbes is extraordinarily complex. The DOC pool is a highly heterogeneous mixture of hundreds of thousands of compounds that span orders of magnitude in size and lability. Furthermore, a liter of seawater contains over a billion bacterial cells belonging to numerous different species, each of which has a unique genome encoding thousands of different genes. Thus, the diversity of potential molecular and microbial interactions is vast. To overcome these challenges, we are leveraging the genetic information and native responses of the bacterial cellular system to identify the DOC substrates and microbial metabolisms most important to ocean carbon flux. In this talk, I will discuss our use of metagenomics (the sequencing of microbial community DNA) and metatranscriptomics (sequencing community RNA) to identify DOC substrates driving carbon cycling at sites such as the Galapagos Islands, the Northern Pacific as part of NASA's EXPORTS project, and in coastal North Carolina. In particular, the use of quantitative 'omic techniques will be discussed, which aims to numerically characterize cell properties *in situ* from genomics data to better incorporate microbes into numerical models of carbon flux in marine ecosystems.

SERMACS 1113

What controls dissolved organic matter composition in marsh-dominated estuaries?

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Dissolved organic matter (DOM) is a large and complex mixture of compounds with source inputs that differ with location, season and environmental conditions. Here, we investigated drivers of DOM composition changes in a marsh-dominated estuary off the southeastern U.S. Monthly water samples were collected at a riverine and estuarine site from September 2015 to September 2016, and bulk, optical, and molecular analyses were conducted on samples before and after dark incubations. Results showed that river discharge was the primary driver changing the DOM composition at the mouth of the Altamaha River. For discharge higher than ~ 150 $m^3 s^{-1}$, DOC concentrations and the terrigenous character of the DOM increased approximately linearly with river flow. For low discharge conditions, a clear signature of salt marsh-derived compounds was observed in the river. Microbial consumption of DOC was larger during periods of high discharge at both sites, potentially due to the higher mobilization and influx of fresh material to the system. The Georgia coast was hit by Hurricane Matthew in October 2016, which resulted in a large input of carbon to the estuary. The DOC concentration was ~ 2 times higher and DOM composition was more aromatic with a stronger terrigenous signature compared to the seasonal maximum observed earlier in the year during peak river discharge conditions. This suggests that extreme events substantially impact DOM quantity and quality in estuarine regions. Since both high discharge events and longer drought periods are becoming more common in the area, the results of this study have implications for composition and processing of DOM exported to the Atlantic Ocean.

SERMACS 1114

Elucidating tidally-driven factors influencing dissolved inorganic carbon export to the coastal ocean

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It is understood that the export of dissolved inorganic carbon (DIC) from salt marsh estuaries to the coastal ocean is disproportionally high considering the relatively small area these estuaries occupy. Although the research quantifying these exports is limited to seasonal observations, the dynamics of these systems truly function on smaller time scales driven principally by tides. Early work in the Savannah River and Wassaw Sound estuary identified variable DIC export during the ebbing of spring-tide inundation, but this could not be isolated to high-marsh tidal flushing, export of respiratory products collected at minimally-mixed tidal nodes, or from the interconnected high-alkalinity fresh Savannah River directly mixing with the upper regions of the Wassaw Sound estuary. At the Georgia Coastal Ecosystem Long-Term Ecological Research and Sapelo Island National Estuarine Research Reserve, the expansive unimpacted salt marsh provides a natural laboratory to investigate the tidally-dominated sounds with different riverine influences, and coastal marsh rivers and creeks with a variety of upland riverine and estuarine interconnections. These different hypotheses are explored during spring and neap, slack high and low tide sampling in the previously-studied Sapelo and Doboy Sounds, the Duplin River, and Old and New Teakettle Creeks. This research was funded by the National Science Foundation supplement to the GCE-LTER.

SERMACS 1115

Cation exchange reactions between silver nanoparticles and metal sulfides

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Silver nanoparticles (Ag NPs) are among the most common forms of nanoparticles in consumer products and the environmental implications of their widespread remain unclear due to uncertainties about their fate. Sulfidation of Ag NPs results in the formation of silver sulfide (Ag_2S) and may be an important removal mechanism of bioavailable silver in natural waters, and dissolved metal sulfides are an important pool of reactive sulfide for such reactions in oxygenated systems. The reaction of Ag NPs with zinc sulfide (ZnS) was investigated using a voltammetric method, anodic stripping voltammetry (ASV). ASV provided sensitive, *in situ* measurements of the release of zinc (Zn^{2+}) cations resulting from the cation exchange reaction between Ag NPs and zinc sulfide. The effects of various reaction parameters like dissolved oxygen, pH and Ag NP size and surface coatings were examined. Sulfidation of smaller Ag NPs generally occurred faster and to a greater extent due to their larger relative surface areas. Sulfidation of Ag NPs capped by citrate occurred more rapidly relative to polymeric surface coatings like polyvinylpyrrolidone (PVP) but no coating investigated was able to fully inhibit Ag NP sulfidation by ZnS. This study provides insights into important water quality parameters and Ag NP characteristics that control Ag NP sulfidation. Furthermore, this work demonstrates the importance of cation exchange reactions between silver and metal sulfides for Ag NP sulfidation, and how the environmental release of Ag NPs could indirectly alter the speciation of other metals of environmental significance.

SERMACS 1116

Multi-mechanophore stress-relieving polymers synthesized via raft polymerization

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Over the past decade, synthetic methods have been harnessed to make new classes of stress-responsive polymers that translate macroscopic deformations into tailored, molecular-level, covalent chemical responses along the polymer main chain through the introduction of mechanically responsive functional groups (mechanophores). The most common technique to date for synthesizing mechanophore containing polymers has been controlled radical polymerization (CRP) from a difunctional initiator. Although synthetically useful, CRP has largely been limited to polymer systems where a single mechanophore resides at or near the center of the mainchain, thereby limiting the magnitude of the desired mechanochemical response. We were curious if CRP could be used to synthesize multi-mechanophore polymers, which would enable larger chemical responses and broaden the applicability of mechano-responsive polymers. Specifically, the addition polymerization of cyclic alkenes potentially allows a mechanophore to be introduced at every other carbon along the backbone, which would provide greater mechanophore content than is found in other multi-mechanophore strategies to date. Inspired by the recently demonstrated ability to polymerize cyclobutene carboxylates that are fused to larger macrocycles via conventional free radical polymerization, in this work we report the reversible addition-fragmentation chain transfer (RAFT)-based random copolymerization of these monomers, leading to high content of stored-length mechanophores along the polymer backbone that are mechanically active. The impact of (co)monomer composition on the kinetics and “controllability” of the polymerization is also reported.

SERMACS 1117

Antifogging/frost-resisting polymer coating

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Various coatings have been developed to mitigate fogging problems, most of which are hydrophilic or superhydrophilic. However, it generally requires complicated procedures to obtain superhydrophilic coatings, and many coatings of this type suffer from poor mechanical robustness and poor frost-resisting performance. We have developed smooth antifogging coatings on the basis of a semi-interpenetrating polymer network (SIPN) of a random binary copolymer or terpolymer containing 2-(dimethylamino)ethyl methacrylate (DMAEMA) units. The excellent antifogging/frost-resisting property originated from the delicate balance between the hydrophilicity and hydrophobicity of the copolymer, and between the water-swellability of the copolymer and the cross-linking network. The DMAEMA units were further partially quaternized to render the coating highly antimicrobial, as demonstrated by total kill against both Gram-positive and Gram-negative bacteria. The dual-functional coating may find unique applications where both antimicrobial and antifogging properties are desired, such as medical device lenses and transparent food-packaging materials.

SERMACS 1118

Precision synthesis of degradable acrylate and acrylamide copolymers with thionolactones

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A common feature of nearly all materials prepared using radical polymerization is an all carbon backbone that is resistant to degradation. Radical ring-opening polymerization represents an opportunity to impart new responsivity into radical polymers, but traditional systems such as cyclic ketene acetals display poor copolymerization behavior with many commonly used monomers. This presentation describes recent developments from our group in the design of thionolactones for radical ring-opening polymerization that installs degradable thioester functionalities into acrylamides and acrylate copolymers. Through the design of two thionolactone monomers with different rates of copolymerization, the distribution of the thioesters in the polymer backbone can be tuned from largely random to localized in blocky regions. This leads to copolymers will significant breakdown using minimal thionolactone additive and also multiblock polymers that can fragment into its homopolymer constituents. Degradation with a variety of stimuli will be highlighted to show the versatility of this platform for the design of new responsive materials.

SERMACS 1119

Rethinking single-chain nanoparticles

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The concept is simple: to build functional nanomaterials in the protein size regime (i.e. 2-5 nanometers in diameter), one must be able to manipulate matter on a similar length scale. Canonical synthetic organic chemistry operates on a length scale an order of magnitude too small (i.e. a few Angstroms rather than and few nanometers). Traditional polymer nanoparticle fabrication techniques (e.g. solution assembly of block copolymers or emulsion polymerization techniques) operate on a length scale that is an order of magnitude too large (i.e. a few tens of nanometers). In between the two is a vast chemical space that remains largely unexplored towards these ends, and yet sits firmly in the realm of synthetic polymer chemistry. Nature's strategies and abilities in this regard are, regrettably, far superior to anything we can do in the laboratory. Still, using modern techniques in polymer and supramolecular chemistry it is possible to imitate Nature's methods and in the process, fill a significant gap in technological understanding. Our group's efforts over the past several years have focused precisely on this topic *via* an emergent class of materials termed "single-chain nanoparticles" (SCNP). SCNP are formed through the intramolecular cross-linking and collapse of single polymer chains in dilute solution to yield an architecturally defined network with dimensions similar to the parent linear chain. This talk will discuss new insights and new directions in this area that our lab has discovered over the past year.

SERMACS 1120

Bulk ADMET polymerization of aliphatic polysulfones

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Due to recent advances in metathesis catalyst design, materials prepared by high temperature bulk ADMET polymerization are now accessible. The ability to conduct polymerizations above 100 deg C has led to the development of scaled up bulk polymerization procedures to prepare quantities of precision materials whose bulk properties can now be fully characterized. We have recently prepared aliphatic polysulfones on a multi-gram scale, and we are now investigating their mechanical and tensile properties. This talk will discuss these findings along with thermal and crystallographic data for context.

SERMACS 1121

Hierarchical molecular design of benzothiodiazole, diketopyrrolo-pyrrole and thienothiadiazole containing polymeric materials via electro-polymerization

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Chemical synthesis of polymers has been plagued by low efficiencies, by-product contamination, and high-cost catalyst. Electrochemical synthesis is an alternative strategy that can overcome these failures to obtain high efficient results. Recently, our group synthesized benzothiadiazole containing thiophenes and furan polymers as tailored donor-acceptor type semiconductors with significant optical absorbance and emission for applications as efficient near-infrared (NIR) probes. As an extension of the work, we present here the study of diketopyrrolo-pyrrole-bisthiophene and thienothiadiazole-bisthiophene for diblock copolymerization with terthiophene as a π-linker to form tunable narrow bandgap polymers. The cyclic voltammograms (CV) of the diblock copolymers are unique in that they show appreciable currents in the entire potential domain from +1.2 V to -1.5 V demonstrating electrical conductivity at all potentials. The polymers suspended on thin films have similar redox characteristics of the monomers with potential shifts that prove the identity of the respective polymers. Electrochemical impedance measurements were carried out at different potential biases. High electronic conductivities were obtained at each potential, thus confirming the polymers to be intrinsically electrical conducting. Atomic ratios of the synthesized materials were calculated experimentally using energy dispersive x-ray analysis, which confirms the theoretical composition of the polymers. These doped polymers exhibit absorption in the visible to NIR region (800 - 1800 nm) in both solid and solution state. Incorporation of solubilizing groups afforded the formation of nanoparticles with sizes ranging from 80 - 200 nm. Results support an efficient strategy towards the creation of complex materials with various possible applications in optoelectronics.

SERMACS 1122

Simplifying the design of anti-icing polymers

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Antifreeze (glycol)proteins (AF(G)P) which exhibit ice recrystallization inhibition (IRI) are found in certain species of insects, plants, and fish in colder regions of the world. Although several synthetic approaches for the exploitation of these proteins have been investigated, challenges remain in the synthetic design of biomimics. Here, we present a systematic study where we developed a series of polymer bioconjugates towards reducing the AF(G)P complexity to polymer design variables simple to leverage and scale. To this end, we contrast a full anti-freeze protein (present in the desert beetle *Anatolica polita* (*Ap*AFP752)) conjugated to a water-soluble polymeric backbone with the same polymer containing pendent synthetic peptide sequences, to the same yet with a simplified amino acid trimer, and finally to a short series of fully synthetic macromolecules with simple pendent functionality. In addition to the assessment of the degree of complexity needed for anti-icing behavior (i.e. pendent tertiary structured protein vs. pendent peptide vs. pendent small molecule functionality), we explore the same functionalities but with variation in degree of freedom (e.g. distance pendent from the polymer backbone). The findings in this study will help pave the path for rational design of synthetic IRI polymers, useful for applications such as anti-icing coatings through to cryo-preservation methods for organ transport.

SERMACS 1123

Non-conjugated polymers as memristors in neuromorphic applications

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The long-term goal of this line of research is to develop a disruptive polymer “memristor”. The central hypothesis is that non-conjugated polymers with pendant carbazoles can exhibit inherent path-dependent conductive (PDC) characteristics. Specifically, the effect of chemical structure on the conformationally induced switching properties of a range of non-conjugated polymers with pendant carbazoles was investigated with a specific goal to create a polymer that exhibits a tailorable multi-state conductance appropriate for being employed as a synaptic substitute. One of the fundamental characteristics of synaptic plasticity in biological neural networks is spike-timing-dependent-plasticity (STDP) and its replication in a synthetic model is critical for emulating biological systems. The STDP response of an ITO/poly(11-(9H-carbazol-9-yl)undecyl methacrylate) (PUMA)/aluminum memristor is presented in **Figure 1** where the ITO and aluminum electrodes were designated the presynaptic and postsynaptic neuron, respectively. The potentiation and depression of the synaptic weight could be modulated with a variation in the timing offset of the two pulses. In **Figure 1**, when the presynaptic spike arrives before the postsynaptic spike there is a potentiation of the synaptic weight while depression occurs when the presynaptic spike arrives after the postsynaptic spike. This response is similar to a Asymmetric Hebbian Learning Rule, where leads to long-term potentiation (LTP) of the synapse and leads to long-term depression (LTD) of the synapse. This change in conductivity with voltage pulses is a basic attribute for building a synaptic substitute.

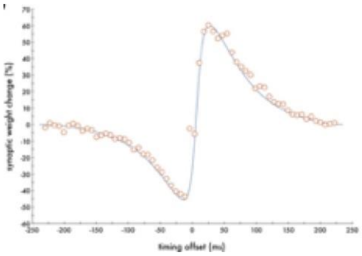

Figure 1: Spike-timing-dependent-plasticity of poly(11-(9H-carbazol-9-yl)undecyl methacrylate) (PUMA; n=11). Synaptic weight change with the variation in timing offset (δt) between the presynaptic and postsynaptic spike-pair. The presynaptic and postsynaptic spike was applied to the ITO and aluminum electrode, respectively.

SERMACS 1124

New insights into the chemical reactivity of dehaloperoxidase: Multifunctional catalytic hemoglobin

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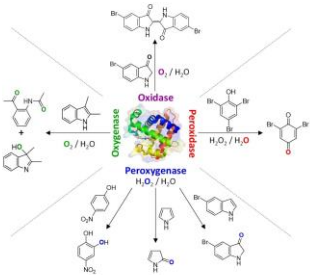
The enzyme known as dehaloperoxidase-hemoglobin (DHP) has provided us with a recent example of a multifunctional protein that challenges many of the assumptions behind the structure-function correlation. Of course structure is related to function, but the question is whether, or how, structure uniquely defines function. In a paradigm shift from the traditional protein structure-function correlation, we have found that the substrate itself, and not the protein structure, plays a pivotal role in determining which enzyme activity is performed by DHP. Termed the **S**ubstrate **D**irected **E**nzymati**C** **A**ctivity pa**R**adigm ("**SiDECAR**"), the choice of DHP activity "encoded" by the substrate enables us to interrogate in detail how Nature controls for activity differentiation across the heme protein superfamily: simply by changing the substrate, we can investigate the protein structure-function properties specific to the five known activities of DHP (oxygen-transport, peroxidase, peroxygenase, oxidase and oxygenase) using just a single enzyme, allowing us to pose questions related to how proteins control for electron and/or proton transfer, how specific amino-acid/substrate interactions influence oxidation mechanisms, and the role(s) of both conserved and non-conserved residues that enable specific discrete functions within the heme protein families. Thus, DHP provides an unprecedented platform for probing mechanistic questions relating protein structure to the tuning of an enzyme's activity without the bias inherent in studying a monofunctional protein.



The catalytic activites of the multifunctional globin Dehaloperoxidase.

SERMACS 1125

Neurodegenerative diseases and the mitochondrial unfolded protein response

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The mitochondrial matrix possesses a stringently regulated machinery to maintain proteostasis, the mitochondrial unfolded protein response (UPR^{MT}). The UPR^{MT} is highly conserved in eukaryotes and allows cells to manage stress that is imposed by unfolded proteins accumulating mitochondrial matrix. Because of that central position, the UPR^{MT} is involved in the onset of a multitude of diseases such as neurodegenerative diseases including Creutzfeldt-Jakob disease, Alzheimer's disease, Parkinson's disease, and Huntington's disease, inflammatory diseases, as well as cancer. Unlike other cellular compartments, however, the mitochondrial matrix is particularly unique in the way that it integrates folding and assembly of proteins that are derived from nuclear as well as mitochondrial genomes. The UPR^{MT} senses the accumulation of unfolded proteins in the mitochondrial matrix and induces changes in nuclear gene expression (e.g. mitochondrial chaperonins). Additionally, the UPR^{MT} also affects the matrix localized protein synthesis through translational inhibition by downregulating the mitochondrial RNase P, a protein that is involved in tRNA maturation. Human mitochondrial RNase P is the first of its kind in the sense that it does not require any RNA component unlike all previously discovered RNAses P. In humans, it only works as a trimeric complex consisting of mitochondrial RNase P proteins 1, 2, and 3 (MRPP1-3). Whereas all three mitochondrial RNase P proteins appear to bind RNA to some extent, their exact stoichiometry and modes of interaction, their individual contribution to substrate recognition and specificity, and their precise role in hydrolysis/catalysis remain elusive.

SERMACS 1126

Characterization of the genomically encoded fosfomycin resistance enzyme from *Mycobacterium abscessus*

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Mycobacterium abscessus belongs to a group of rapidly growing mycobacteria (RGM) and accounts for approximately 65-80% of lung disease caused by RGM. It is highly pathogenic and is considered the prominent *Mycobacterium* involved in pulmonary infection in patients with cystic fibrosis and chronic pulmonary disease (CPD). FosM is a putative 134 amino acid fosfomycin resistance enzyme from *M. abscessus* subsp. *bolletii* that shares approximately 30-55% sequence identity with other Vicinal Oxygen Chelate (VOC) fosfomycin resistance enzymes and represents the first of its type found in any *Mycobacterium* species. Genes encoding VOC fosfomycin resistance enzymes have been found in both Gram-positive and Gram-negative pathogens. Given that FosA enzymes from Gram-negative bacteria have evolved optimum activity towards glutathione (GSH) and FosB enzymes from Gram-positive bacteria have evolved optimum activity towards bacillithiol (BSH), it was originally suggested that FosM might represent a fourth class of enzyme that has evolved to utilize mycothiol (MSH). However, a sequence similarity network analysis identifies FosM as a member of the FosX subfamily and as a single unique member of a network cluster consisting entirely of enzymes from Gram-negative pathogens. In addition, we have synthesized MSH and characterized FosM with respect to divalent metal ion activation and nucleophile selectivity. Our results indicate that FosM is a Mn^{2+}-dependent FosX-type hydrase with no selectivity toward MSH or other thiols as analyzed by NMR and mass spectroscopy.

SERMACS 1127

Redox-modulator or metal buffer? Exploring the role of glutathione in cellular copper homeostasis

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Glutathione (GSH) is ubiquitous in most organisms where it plays critical roles in cellular redox homeostasis, detoxification pathways, and cell signaling. The cysteine-containing tripeptide has also been implicated as a potential metal buffer in cellular copper homeostasis. To study the speciation and thermodynamics of the copper-glutathione system, we performed combined spectrophotometric and potentiometric competition titrations at physiologically relevant glutathione/Cu(I) ratios using a suite of recently developed Cu(I) affinity standards. Corroborated by low-temperature phosphorescence studies, the titration data revealed spontaneous assembly of a tetranuclear cluster $[(GS)_6Cu_4]$ as the predominant species at physiological pH. Based on the derived thermodynamic model, glutathione thus limits free aqua-Cu(I) to the sub-femtomolar concentration regime, three orders of magnitude lower than previously estimated. To explore to what extent cytosolic glutathione might be involved in cellular Cu(I) buffering, we developed an emission-ratiometric Cu(I)-selective fluorescent probe, crisp-17, which offers a dissociation constant slightly below the Cu(I) buffer window of glutathione. Employed in live mouse NIH 3T3 fibroblasts, the probe revealed a low fractional saturation, both under basal conditions and when cells were grown in copper-supplemented medium, thus indicating buffering at low attomolar levels even under conditions of copper overload. In light of the thermodynamic model for the glutathione-Cu(I) equilibrium system, the ratiometric imaging data thus indicate that glutathione does not serve as an immediate Cu(I) ligand. As glutathione-bound Cu(I) can also catalyze the production of reactive oxygen species, low attomolar buffering might in fact be a necessity for normal cell physiology to avoid copper-induced oxidative stress.

SERMACS 1128

Exploring the heterogeneity of insect arylalkylamine *N*-acyltransferase

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Arylalkylamine *N*-acyltransferases (AANATs) have in recent years been suggested as potential new insecticide targets. These promiscuous enzymes are involved in the *N*-acylation of biogenic amines to form *N*-acylamides. In insects, this process is a key step in melanism (a role also performed by the lone mammalian AANAT: serotonin *N*-acetyltransferase), as well as hardening of the cuticle, removal of biogenic amines, and in the biosynthesis of fatty acid amides. The unique nature of each AANAT isoform characterized indicates that while catalyzing similar reactions, each insect accommodates an assembly of AANATs relatively exclusive to that organism. This implies a high potential for selectivity in insecticide design, while also maintaining polypharmacology. Presented here is a thorough kinetic and structural analysis of AANATs found in one of the most common secondary pests of all plant commodities in the world; *Tribolium castaneum*. *T. castaneum* AANAT (*Tc*AANAT), of which there are two, was determined to catalyze the formation via ordered sequential mechanism of short chain *N*-acylarylalkylamines, with short-chain acyl-CoAs (C2-C10) functioning in the role of acyl-donor. pH-rate profiles indicate key catalytic residues which were used to solve the chemical mechanism of *Tc*AANAT. The first crystal structure was also obtained for *Tc*AANAT bound to acetyl-CoA, revealing valuable information about its active site. This combination of kinetic analysis, and crystallography, alongside mutagenesis, and sequence analysis shines light on the heterogeniety of insect AANATs and garners further discussion into their core differences and some approaches possible to utilize these enzymes in insecticide design.

SERMACS 1129

On the mechanism of ANGPTL3 and ANGPTL4 inhibition of LPL

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Elevated plasma triglycerides are an independent risk factor for cardiovascular disease. The key enzyme responsible for clearing triglycerides from the circulation, lipoprotein lipase (LPL), has several macromolecular inhibitors including ANGPTL3 and ANGPTL4. Individuals with loss-of- function mutations in either ANGPTL3 or ANGPTL4 have lower plasma triglycerides, on average, and a reduced risk of cardiovascular disease. The precise mechanisms by which ANGPTL3 and ANGPTL4 inhibit LPL are not well-defined. Therefore, we measured the kinetics of LPL inhibition by both proteins, and used a variety of biophysical techniques to determine how LPL and its inhibitors interact. We found that ANGPTL3 and ANGPTL4 use different mechanisms to inhibit LPL. Whereas ANGPTL3 is an uncompetitive inhibitor, ANGPTL4 is a noncompetitive inhibitor. We found that ANGPTL4 binds LPL near the active site at the lid domain and a nearby alpha-helix. By contrast, ANGPTL3 interacts with LPL's lid domain but does not require the lid-proximal alpha-helix for binding. The mechanistic details of LPL-inhibitor interactions uncovered here may inform the development of therapeutics targeted to disrupt this interaction for the management of hypertriglyceridemia.

SERMACS 1130

Strategies and tactics inspired by biologically active alkaloids

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Since the landmark synthesis of tropinone by Robinson over one century ago, the synthesis of biologically relevant alkaloids has been of utmost importance not just to victories in world wars, but to the overall benefit of human health. The structural complexity of many biologically active alkaloids has inspired both concise strategic approaches and the generation of new tactics towards their synthesis. Results on this front will be discussed en route to various important alkaloid natural products.

SERMACS 1131

Marine natural products synthesis: Platform for chemical and biological discovery

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Marine natural products often have complex structures and potent biological activities; however, little is understood regarding how their molecular structure correlates with function or what biological targets or pathways are involved. Through rapid and efficient chemical syntheses of bioactive marine natural products we are able prepare ample quantities of material to explore both structure-activity relationships as well as target identification studies. In all our efforts, a key focus is the development of short, scalable and selective synthetic approaches, accomplished by new reaction development and strategic synthetic planning. This talk will focus on our efforts to develop novel approaches to nitrogen heterocycles in the context of alkaloid synthesis, specifically the batzelladines and melokhanines. Although historically significant structures in the chemical literature, little is understood regarding the biological function of these potent natural products and there remains a need for a robust, stereoselective and scalable approach for their synthesis.

SERMACS 1132

Umpolung approaches to the synthesis and application of heterocycles enabled by hypervalent iodine reagents

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Hypervalent iodine reagents in the I(III) oxidation state have emerged as a versatile, environmentally benign toolkit for the functionalization of organic molecules. Amongst their diverse reactivity is the ability to facilitate reversed-polarity, or "umpolung", transformations of typically nucleophilic functionalities, enabling novel bond disconnections. Our laboratory has leveraged an underexplored class of I(III)-reagents, (bis)cationic nitrogen ligated lambda-3 iodanes (*N*-HVIs), as a platform to develop umpolung transformations of heteroatoms and alkenes. The presence of datively bound heterocyclic ligands leads to enhanced, highly tunable, and novel reactivity relative to well-established oxygen or halogen ligated I(III) reagents. In this talk, application to electrophilic oxygen activation, enone C–H arylation, and pyridinium group transfer reactions will be discussed.

SERMACS 1133

Synthesis and study of polyfunctional and fused-ring heterocycles: Research progress at Georgia Gwinnett College

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The utility of heterocyclic compounds is well documented in the scientific literature. Exploration of synthetic strategies to construct and/or further functionalize single-ring and fused-ring heteroaromatic species have continued to dominate the agrochemical, industrial and pharmaceutical sectors. Investigation of the molecular properties of these important molecules has also received wide attention. Nevertheless, the elucidation of more efficient, milder and environmentally responsible processes requires continued study. In this work, we report the progress made in several areas of synthetic heterocyclic chemistry. See Figure 1. The efficacy of Baker-Venkatamaran rearrangements enroute to functionalized *4-H* chromones is examined. Efficacy studies of microwave and green processes in fluorinated heterocycle preparation are reported. Preparations of heterocycles using acridine and ninhydrin scaffolds with gelation properties are discussed.

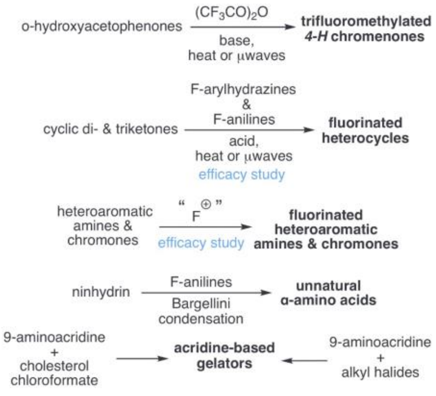

Figure 1. Heterocycle Research Projects

SERMACS 1134

Synthesis and characterization of high-performing explosive and propellant heterocyclic materials

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The synthesis, characterization and properties of several heterocyclic energetic materials will be discussed. Energetic materials disclosed will contain the 1,2,4-oxadiazole, 1,2,5-oxadiazole (furazan) and furoxan moieties, as these rings are known to possess high densities and high heats of formation. Such features maximize the energetic nature of a material. Discussed will be the key differences that distinguish a molecule from being used as an explosive or as a propellant. Where applicable, video will be shown of successful molecules that have been scaled and tested in an effort to convey the effectiveness of a given energetic material.

SERMACS 1135

Catalytic, enantioselective synthesis of indole derivatives by epoxide opening

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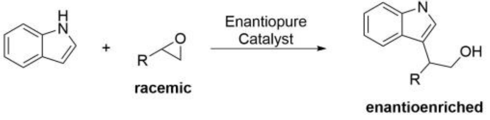
The nucleophilic ring-opening of epoxides is a crucial step to access important intermediates in organic synthesis. A practical strategy to synthesize enantioenriched novel indole-containing products is the enantioselective ring opening of epoxides. Our laboratory utilizes a chiral Lewis acid catalyst, indole nucleophiles, and racemic epoxides to generate functionalized indole derivatives. High enantiomeric excess and moderate to high yields are observed with various epoxides and nucleophiles. Synthetic utility of the products and mechanistic insight will also be discussed.



SERMACS 1136

Synthesis of azepinoindoles via ring expansion of 1-methyl-tetrahydro-β-carbolines

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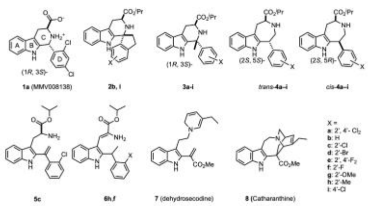
MMV008138 (**1a**) is an antimalarial lead that acts as the *Plasmodium falciparum* MEP pathway inhibitor. The tetrahydro-β-carboline ring could be constructed via the Pictet-Spengler (PS) reaction of tryptophan methyl ester and 2,4-dichlorobenzaldehyde; and the ester hydrolyzed to give the product. The (1*R*, 3*S*)-configuration was found to be the active isomer. To further explore the antimalarial activity of **1a**, spiral (**2**) and C1-methyl (**3**) analogs of **1a** were synthesized via the ketone PS reaction from methyl aryl ketones and indanones, promoted with the use of $Ti(O^iPr)_4$. Unexpectedly, reactions of methyl aryl ketones bearing ortho substituents did not yield the tetrahydro-β-carboline structure **3** but the azepane ring analogs **4**. While studying this expansion reaction intermediates **5** and **6** were isolated. Interestingly, alkene dehydrosecodine **7** was proposed to be the intermediate for the biosynthesis of catharanthine **8**, a natural product in the *iboga* family containing an azepane ring. Based on these intermediates, an expansion mechanism was proposed and validated by experiments. DFT calculations also support the experimentally observed results that analogs bearing ortho substituents cause steric strain in the tetrahydro-β-carboline ring and are thermodynamically unstable, resulting in the ring expansion; while the analogs without the ortho substituents lack this driving force for the ring expansion.



SERMACS 1137

Chemoselective aerobic 5-hydroxylation of a 2-aminopyrrole derivative

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2-Aminopyrroles lacking electron withdrawing substituents on the ring tend to be rather unstable due to their highly electron rich nature. There are thus relatively few examples of the chemoselective oxidation of these type heterocycles. Recently when attempting an intramolecular Heck annulation on the 2-bromobenzamide derivative of a 2-amino-1-benzyl-4,5-dimethylpyrrole, we found that the 3-unsubstituted compound was quite prone to air oxidation when in solution, as anticipated, although the oxidation was quite selective. Following up on this observation, we found that this pyrrole could be readily converted to a 5-hydroxy derivative in excellent yield simply by stirring in the presence of air, or better, molecular oxygen. Further examination of this novel reaction also showed that use of toluene as reaction solvent allowed for a near “spot to spot” conversion. On the other hand, attempted use of other oxidants typically gave multiple reaction products. These results build upon other chemistry from our lab which has shown that molecular oxygen can be useful for the chemoselective oxidation of 2-aminopyrrole derivatives.

SERMACS 1138

Millimeter/submillimeter spectroscopic detection of desorbed ices: New technique in laboratory astrochemistry

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A new laboratory technique has been developed that utilizes gas-phase, direct-absorption millimeter and submillimeter spectroscopy to detect and identify desorbed species from interstellar and cometary ice analogs. Rotational spectroscopy is a powerful structure-specific technique for detecting isomers and other species possessing the same mass that are indistinguishable with mass spectrometry. Furthermore, the resultant laboratory spectra are directly comparable to observational data from far-infrared telescopes. We will present the proof-of-concept measurements of the detection of thermally desorbed H_2O, D_2O, and CH_3OH originating in a solid film created at low temperature (∼12 K). The thermal desorption kinetics of H_2O will be discussed and compared to results from traditional techniques, including mass spectrometry and quartz-crystal microbalance measurements of mass loss. Future applications to thermal desorption of mixed ices, as well as photolysis studies of pure and mixed ices, will be discussed.

SERMACS 1139

Fragment species in the comae of comets: Observations and challenges

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The optical spectrum of the gas in a cometary coma is dominated by emissions of fragment species that arise through one or more processes from larger native species released from the nucleus. Optical spectral transitions of these species are frequently observed using various spectrographs, as well as photometry using narrowband filters. However, the full nature of the production of many of these species is poorly understood. Complete understanding of the presence and spatial distribution of these species in a comet coma is complicated by several factors, including uncertainties in the photodissociation and photoionization lifetimes of larger species, the nature of the reaction of the solar wind with coma gas, the processes that could release species from dust grains, a lack of robust chemical reaction rates that are applicable to cometary conditions, and an incomplete understanding of outgassing from the nucleus itself. In this discussion, we will review important observations of the gas coma, the ways that fragment species are connected to the larger species released from a comet nucleus, and the immediate challenges that multiple observed species present for understanding the full chemistry of comets.

SERMACS 1140

Molecular water ice formation and processing in solar systems

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Ice covered grains are present on the surfaces of the Moon, on satellites of the Jovian and Saturnian systems, in comets and are important with respect to the interplanetary and interstellar grain population. Despite the ubiquitous presence and general importance of water (ice), the chemical reactions leading to the formation of water in solar systems are not well understood. Experimental data on the formation and release of water from lunar mare and highland samples is modeled and related to the presence and absence of water on certain regions of the Moon, Mercury and interstellar grains. Generally, temperatures above 350 K are required for the formation of water by a process known as recombinative desorption. This involves thermally activated reactions of nearest neighbor terminal hydroxyls present in H-implanted mineral and interstellar grain surfaces. In contrast, low temperatures lead to the uptake and "condensation" of molecular water. When molecular water strikes surfaces with temperature below 100 - 110 K, it is assumed that amorphous ice will form with the porosity increasing as the temperature is lowered. Preliminary work shows that cryogenically quenched/deposited ice-dust mixtures actually lead to the formation of crystalline ice. This is likely due to the interfacial ordering inherent with the hydroxyl termination and varies with the chemical composition of the dust. Once formed, the crystalline ice is more stable with respect to sublimation.

SERMACS 1141

Laboratory studies of thermally processed ice mixtures relevant to outer-planetary surfaces

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Infrared absorption spectroscopy is a key tool for exploring the properties of ice mixtures found on planetary surfaces in the outer Solar System. As such, laboratory simulations of astrophysical ice mixtures have become an integral part of astrochemistry. It is of particular interest for the USC Aiken Dept. of Chemistry & Physics to focus on research opportunities for undergraduates but building a laboratory from the ground up can be difficult and challenging. This study outlines the successes and failures of starting a laboratory from scratch. Next, different ratios of thermally processed ice mixtures containing H_2O, CH_3OH, CO_2, N_2, CH_4, C_2H_6, and NH_3 are investigated based on observed and expected mixtures on outer-planetary surfaces. Mid-infrared (MIR) absorption spectroscopy (in the range $\lambda = 2.5 - 25$ μm) are used to analyze and document the different spectra.

SERMACS 1142

High impact chemistry: Design and testing an icy moon penetrator organic analyzer

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Highly sensitive organic analysis is key to understanding the processes that shape an extraterrestrial location, its potential habitability, and whether it could host life presently or in the past. However, some extraterrestrial locations, like those of the surface of icy moons, are challenging to access with a soft lander, making high-impact (from 5 km/s impact, or 50,000 g) kinetic penetrators an attractive mission platform. Laser-induced fluorescence (LIF) detection systems provide highly sensitive (sub parts-per-trillion) organic analysis, and programmable microfluidic architectures can enable complex fluidic mixing in a monolithic microfabricated device. In this work, we have developed an impact-robust instrument system with a hydraulically-actuated microfluidic processor at the core. Supporting hardware includes a miniaturized optical stack for laser-induced fluorescence detection and linear actuators for microvalve actuation. A majority of components have been tested and demonstrated to survive impacts at 12,000 g, 25,000 g, and 50,000 g. This work proves that microfluidic total analysis systems can be made robust to the high accelerations of a kinetic penetrator platform, enabling "smart" impactor mission formats and access to significantly more challenging, and interesting, terrains on icy moons.

SERMACS 1143

Potential pathway to O_2 observed in comets 67P/Churyumov–Gerasimenko and 9P/Tempel: Dissociation of radiolytically produced parent carbon oxide species

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The Rosetta Orbiter Spectrometer for Ion and Neutral Analysis Double Focusing Mass Spectrometer (ROSINA/DFMS) was recently able to detect molecular oxygen (O_2) for the first time within the comae of comet 67P/Churyumov–Gerasimenko. Not only was O_2 detected, but it was one of the most abundant species in the comae along with water, carbon monoxide, and carbon dioxide (H_2O, CO, and CO_2, respectively) where its averaged abundance was found to be ~3.8% (relative to water). Based on observations over a 6-month period, the sublimation pattern of O_2 seems to be correlated with that of H_2O rather than with CO or CO_2. Subsequent re-evaluation of the Giotto spacecraft measurements of the coma of comet 9P/Tempel also found evidence for O_2 at similar levels (~3.7% relative to water). These observations are surprising, given the fact that molecular oxygen is not abundant within the interstellar medium, it is not efficiently produced within water-dominated ices, and its high reactivity prohibit many proposed explanations as to how it could be present at such abundances within the comae of comets. We review some of the measurements, and proposed explanations thus far presented. We then provide an overview of a novel mechanism that could contribute to the observations of O_2, CO, and other volatile daughter molecules within cometary comae. Specifically, we examine the notion that less volatile carbon oxide species may be effectively produced during radiolysis of CO and CO_2 precursor ices, and may remain within cometary surfaces while other volatiles are lost. Subsequently, when these carbon oxides are released, they are broken down within the cometary comae. We overview whether this process fits the available measurements and constraints in comparison with alternatives, and present theoretical approaches that could help verify the contributions from these species from telescopic measurements, or laboratory approaches.

SERMACS 1144

Discovering complex microscopic interactions with broadband coherent Raman microscopy

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Spectroscopic coherent Raman imaging (CRI) methods allow label-free, chemically specific imaging of materials and biological systems, and are opening up many exciting possibilities for understanding complex phenomena in these systems. When we first introduced spectroscopic coherent Raman imaging in 2004, we could acquire spectra only from bulk polymers and liquids. After many years of development, we now easily acquire label-free micrographs of synthetic and biological materials at 3.5 ms for each spectral image pixel, with promise of significant speed increase still to come. Initially it was not clear that acquiring such spectra would be possible, but a recognition that an intrinsic and strong nonresonant signal could be used to enhance weak resonant signals made it possible to obtain these signals above detector noise. Further improvements in signal generation and spectral retrieval algorithms, now provide for highly robust and rapid spectral imaging. I will briefly introduce broadband spectroscopic coherent anti-Stokes Raman scattering (BCARS) microscopy, discussing some of the key concepts that make this method practical. I will also present selected application examples from studies on pharmaceutical and structural materials, as well as biological systems that highlight the utility of BCARS for discovering material and biological interactoins through in-depth characterization of spatially and chemically complex systems.

SERMACS 1145

Characterization of extracellular vesicles derived from red blood cells using Raman spectroscopy and machine learning

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Degradative changes that occur during storage of red blood cells (RBCs) include hemolysis, followed by formation of microvesicles and exosomes, collectively referred to as the “storage lesion”. Hemolysis is a critical component of the storage lesion, but there are no direct methods for determining the extent of in-bag hemolysis, or its degradation products. Our laboratories have used Raman spectroscopy to assess hemolysis in RBCs. Raman spectra indicated increased concentrations of oxyhemoglobin (oxyHb) and methemoglobin (metHb), and decreased membrane fluidity with storage age. Changes in oxyHb and metHb were associated with the intraerythrocytic and extracellular fractions, respectively. Hemolysis increased in a storage age-dependent manner. Changes in Raman bands reflective of oxyHb, metHb, and RBC membranes correlated with hemolysis; the most statistically significant change was an increased intensity of metHb and decreased membrane fluidity. We have studied extracellular vesicles (EVs) released from RBCs. EVs, both microparticles (MPs) and exosomes (Exos), are produced by a variety of cell types in response to diverse stimuli and are potential diagnostic indicators of disease. RBC’s release MPs and Exos due to aging and disease conditions. We have used Raman and infrared (IR) to differentiate MPs and Exos produced from RBCs. The EV’s produced from RBCs differ only slightly in size and protein expression, and exhibit highly overlapped spectra. However, we have been able to identify differences in oxyHb and metHb profiles in MPs and Exos from their Raman spectra. Multivariate statistical methods, including partial least square discriminative analysis (PLS-DA), random forest (RF) and support vector machines (SVM), have been used to characterize and classify MP and Exo spectra with 100% accuracy. These methods also provide a means for variable selection to identify the spectral markers most responsible for the differentiation of MP and Exo spectra. Vibrational imaging using Raman and IR identified the differential effects of MPs and Exos on pulmonary epithelial cells. These studies identify Raman and IR microscopy as a valuable noninvasive diagnostic modality for the study EV’s in relation to overall age-induced hemolysis and toxicity in RBCs.

SERMACS 1146

High-resolution label-free biochemical imaging of histology tissue sections can improve cancer detection and staging

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Label-free optical imaging methods with molecular sensitivity and high spatial resolution have emerged as powerful tools for identifying disease as they can probe many important endogenous biochemical species without destroying the samples or disrupting the biological environment. First, I will describe pump-probe microscopy, an emerging nonlinear optical technique based on femtosecond transient spectroscopy, and its application to image the biochemical composition of melanin in melanocytic lesions using thin, unstained tissue sections. The biochemical information provided by this method is used as an indicator of melanocyte activity, which in turn reflects the status of melanocytic lesions. The combination of the biochemical and subcellular structural information has shown significant promise in (1) differentiating melanomas from benign melanocytic lesions, and (2) assessing the metastatic potential of invasive melanomas. I will also present more recent work using multispectral deep-UV microscopy which enables detailed, high-resolution quantitative imaging with sensitivity to many other molecules known to play an important role in cancer, including FAD, NADH, DNA, RNA, cytochromes, tryptophan, elastin, and collagen. Its application to prostate cancer staging will be discussed. We will outline the advantages and disadvantages of these and other emerging technologies and discuss their applications to other types of cancers.

SERMACS 1147

Imaging mass spectrometry of lipid isomers using gas phase ion/ion reactions

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Imaging mass spectrometry (IMS) is a powerful technology that enables the visualization of biochemical processes directly in tissue specimens by combining the molecular specificity of mass spectrometry with the spatial fidelity of microscopic imaging capabilities. Especially when studying lipids and metabolites, there are many isobaric and isomeric species that complicate spectral analysis, with each isoform having a potentially unique cellular function. While traditional tandem mass spectrometry (MS/MS) approaches can distinguish amongst these species in some instances, oftentimes this is not the case. Additionally, the ion type most readily generated from tissue is rarely the ion type that affords the most chemical structural information upon MS/MS. Our lab is developing gas phase ion/ion reactions to enable unique molecular differentiation and structural identification. These chemistries afford the ability to rapidly transform the ion type without manipulating the sample, making these reactions ideally suited for implementation into IMS workflows. Gas phase charge inversion ion/ion reactions are performed on a 7T solariX FT-ICR mass spectrometer (Bruker Daltonics). Phosphatidylcholine cations generated from tissue using matrix-assisted laser desorption/ionization (MALDI) and doubly deprotonated 1,4-phenylenedipropionic acid (PDPA) reagent anions generated via electrospray ionization (ESI) are sequentially injected into the hexapole reaction cell. Following a defined mutual storage ion/ion reaction period (~500-1000 ms), the product ions are transferred to the ICR cell where they are subjected to sustained off-resonance collision induced dissociation (SORI CID) and then mass analyzed. This technology has enabled the identification of multiple sn-positional isomers directly from mouse brain tissue [e.g., PC(36:1) is comprised of a mixture of PC(20:1_16:0) and PC(18:0_18:1)]. The relative contribution of these lipid isomers varies depending on the region of the brain (e.g., cerebellum versus corpus callosum). Our group is also exploring other gas phase chemistries to enable lipid double bond localization and lipid class differentiation.

SERMACS 1148

Metabolomics approaches to decipher response of pathogens in disease

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The language with which microorganisms communicate with each other, and with us is chemistry, with small molecule secondary metabolites being the alphabets of this language. The secondary metabolites modulate the dynamics of our microbial make-up and have been correlated to a number of diseases including infections, inflammation, cancer, and neurological disorders, yet it remains a challenge to identify small molecular effectors of human diseases in the clinically relevant conditions and their associated biological functions. We employ mass spectrometry-based approaches to identify metabolomic profiles of pathogens correlating with capacity to cause disease, for use in assessing disease status and for developing new treatment strategies. Herein, a combination approach based on molecular networking, MS2LDA and in silico annotation tools will be highlighted that enables visualization and dereplication of key phenotypically relevant molecules underlying a human disease.

SERMACS 1149

Spatial mapping with portable X-ray fluorescence spectroscopy to identify corrosion on ferrous metal alloy substrates on U.S. Air Force assets

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The Department of Defense (DOD) reports spending over $20B annually to prevent and control corrosion. With the vast array of corrosion-related issues the United States Air Force (USAF) is facing in highly corrosive environments like those found in humid tropical environments, it is critical that DOD personnel understand the process and mechanics of corrosion. While laboratory, accelerated weathering, and even outdoor exposure tests provide information on what may be expected with certain coating stack-ups, these tests cannot replace real-time and real-world data on the performance of the units in the field. The electrochemical reactions associated with corrosion alter the chemical composition of a surface, with differences often being very subtle. Portable X-ray Fluorescence (pXRF) spectroscopy is a hand-held and field operable technique to quickly probe the elemental composition of a substrate or stack-up (paint and coating combination) in a nondestructive manner. We have deployed pXRF on sample coupons and directly on USAF equipment in high-corrosion environments to detect corrosion and premature coating failure on ferrous metal alloy-based assets. Spectroscopic identifiers of corrosion were determined and it was found that differences in chemical composition for compromised surfaces are dependent on stack-up and metal alloy substrate combinations. Additionally, even though the primary focus of pXRF is on the surface of a substrate, we have demonstrated that it can also probe through typical coating stack-ups to investigate the composition of the underlying metal substrate. Furthermore, spatial mapping with pXRF identifies corrosion and premature coating failure beyond the boundaries of visual confirmation. These results demonstrate proof of principle that pXRF can be utilized to investigate corrosion and corrosion-related issues directly on equipment at its operating location.

SERMACS 1150

Small molecule modulators of chaperone Hsp70 for amyloid remodeling

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Chaperone proteins play key roles in protein homeostasis, assisting in the proper folding and refolding of proteins. Neurodegenerative diseases, such as Parkinson’s Disease (PD) or Alzheimer’s Disease (AD) are neurodegenerative disorders that are caused by protein aggregate formation in the brain. Currently, there are no effective preventative or curative approaches for these diseases. One possible strategy to combat these diseases is through the generation of small-molecule agonists of chaperone proteins. Using Rosetta-based exemplar screening, we are exploring chemical structures which have the possibility of interacting with the chaperone Hsp70 and allosterically modulating its activity. Compounds are then tested for their ability to modulate Hsp70 ATPase activity and engagement with a model substrate peptide.

SERMACS 1151

Allergenicity of different fractions of protein extract from enzymatically hydrolyzed peanut flour

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Consuming peanuts has associated with many health benefits including weight control, heart disease prevention and the reduction of gallstones risk. Peanut flour, a by-product from peanut oil processing, has higher protein and dietary fiber and lower fat content than peanut kernels, but the use of peanut flour in food products presents a hidden risk to individuals who are allergic to peanuts because nearly 2.5 children and 1.8 adults are allergic to peanuts in the US. This study evaluated the effects of protease hydrolysis on the allergenicity of peanut flour. Both light and dark roasted peanut flours (12% fat) were hydrolyzed by a protease for 1-4 hours. After inactivating the enzyme, samples were centrifuged and supernatants were collected and fractionated into four fractions of different molecular weight ranges. Protein concentration of each fraction was determined. Precipitates were extracted using electrophoresis treatment buffer to dissolve insoluble proteins. SDS-PAGE and Western blot of supernatant and its fractions, and the precipitate extract were conducted. Results show that enzyme treatment increased protein solubility 2-4 times, and increased the protein/peptide concentrations and quantity more than 3 times; Western blot shows that enzymatic hydrolysis eliminated or remarkably reduced IgE-binding of protein molecules larger than 15kDa in both soluble and insoluble portions of peanut flour, but some residual allergenicity of proteins/peptides 5-15 kDa remained. The fraction smaller than 5 kDa did not show IgE-binding. This study shows that proteolytic hydrolysis greatly improved the allergic safety of peanut flour.

SERMACS 1152

Enzymatic biodegradation of polymers: Undergraduate study using poly(aspartic) acid

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Biodegradable and biocompatible polymers are ubiquitous in both medical and industrial applications. One such polymer with applications ranging from waste water treatment to gene therapy is poly(aspartic acid) (PAA). This polymer is partially degraded by the enzyme poly(aspartic) acid hydrolase-1 (PAAH-1) which is expressed by the soil bacteria Sphingomonas sp. KT-1. Knowing PAA is easily synthesized and enzymatically broken down, this green polymer is attractive for interrelating polymer concepts in multiple undergraduate courses. In response to ACS Guidelines and Evaluation Procedures for Bachelor's Degree Programs mandating inclusion of polymers in the undergraduate curriculum, we are threading this common theme of PAA throughout our laboratory exercises. PAA synthesized in the Organic Chemistry laboratory results in the formation of a branched polymer with both alpha and beta linkages between aspartic acid subunits. This student synthesized PAA is passed to the Biochemistry I Laboratory course to be used as a substrate for the enzyme PAAH-1, which has specificity for only the beta linkages. Through the use of a novel agarose gel assay, biochemistry students are able to visualize degradation of polymer and ultimately determine a value for unit activity using freely-available densitometry software. Our images have been captured on a gel-imaging instrument; however, we understand that not all universities have access to this equipment. Therefore, we have also developed a cheaper alternative method that only requires a smart-phone camera. Curricular flow of interweaving this polymer concept and the biochemistry assay will be discussed.

SERMACS 1153

Predicted functions of FtrA and FtrB protein from the four-component uptake system, FtrABCD, in *Brucella spp*

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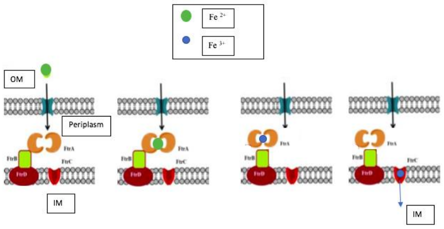
Brucella spp. is a zoonotic Gram-negative pathogen that causes the febrile disease, Brucellosis. Like most other living organisms this bacteria also require iron as a micronutrient for survival and growth. On the other hand, the host immune system reacts to incoming *Brucella spp.* like it does to most foreign bacteria, by lowering the concentration levels of accessible iron within the body, restricting *Brucella spp.'s* access to iron. In response to this iron starvation, Brucella expresses several dedicated and high-affinity iron uptake systems, of which the newly discovered FtrABCD is the putative Fe^{2+} uptake pathway. In our previous work we have biochemically characterized the periplasmic FtrA, showing like its homologs, P19-type proteins, it also requires Cu^{2+} for sequestering its cognate ligand. In addition, our past study also shed light on the importance of the Cu^{2+} binding residues in the proper folding of this protein. In this current work we have cloned the second periplasmic protein, FtrB, the putative ferroxidase with conserved Cu^{2+} binding sites in E. coli DH5α. Cu^{2+} binding abilities and the native folding stability of this proposed ferroxidase has been investigated using calorimetric techniques in this work. To our knowledge, this is the first report of biochemical characterization of this new class of proposed ferroxidase type of proteins' Cu^{2+} binding abilities.



SERMACS 1154

Trojan horse approach: Novel drug delivery mechanism

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Antibiotic resistance has become a prevailing problem in the world today as bacterial pathogens have recognized these molecules as toxins and pump these out by expressing efflux pumps. On the other hand, iron being an essential micronutrient for most pathogens and hosts alike, is actively taken up using high affinity uptake systems expressed by these organisms. One such bacterial iron uptake systems relies on siderophores, the bacterial Fe^{3+}chelator, which steals $Fe^{3+}$from the host system and is transported by cognate out membrane receptors of Gram-negative bacteria. Utilizing these Fe^{3+}-siderophore uptake systems to deliver drug molecules into the bacterial cell using a Trojan horse approach has gained much research interest recently. Strategically, in this approach, a drug molecule is chemically tethered to the siderophore molecule with the expectation that this Fe^{3+}-siderophore-drug conjugate will be actively taken up by the outer membrane receptors and transported into the periplasm avoiding the efflux pumps (Scheme 1). In this work we report the synthesis of a drug conjugate between dihydroxybenzoic acid (DHBA), a siderophore by-product used by several bacteria, including *Brucella spp.*, and sulfapyridine. As sulfapyridine's activity requires its translocation into the cytosol, we have also cloned and overexpressed the periplasmic Fe^{3+}-DHBA binding protein, FatB, from *Brucella spp.*and characterized its binding affinity with the drug conjugate.

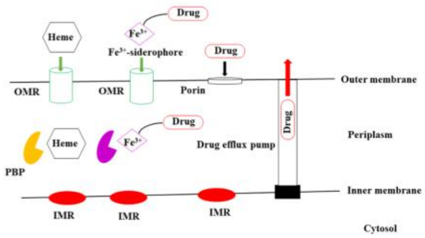

Figure 1.A schematic representation of heme and Fe^{3+}-siderophore uptake systems from Gram negative bacteria using OMR. Drug influx through porins and efflux through efflux pumps are also indicated. This scheme also shows the proposed research where drug molecules will be conjugated with siderophores with the hypothesis that these drug conjugates will be actively transported into the cell avoiding the efflux system.

SERMACS 1155

Characterization of a pH-responsive nanocage based on the ferritin iron storage protein

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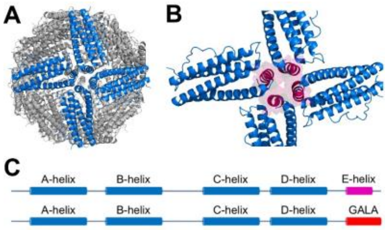
The iron-storage protein ferritin (Ftn) assembles into a protein cage structure with 24 subunits and octahedral (4-fold, 3-fold, 2-fold) symmetry. Each monomeric subunit contains a robust four helix bundle fold. The fully assembled Ftn structure has a high degree of thermal stability (up to 100°C), a small and monodispersed size (12 nm in diameter), and a large central cavity (7-8 nm in diameter). The central cavity is used for iron mineral storage in a phylogenetically diverse group of organisms, including humans. The central cavity has also been used for encapsulation of cargoes such as other metals, contrast agents for imaging, small molecule drugs for therapy, as well as smaller nanoparticles. Due to its attractive properties ferritin has been widely used for a number of biomaterials, ranging from nanostructured composite materials to semiconductors to imaging reagents. Here we describe our efforts to design, generate, and test a series of pH-responsive derivatives of ferritin (Ftn) protein nanocages that are competent for drug delivery through the endocytic pathway and may be useful as responsive scaffolds for biomaterials construction. We have used a combination of analytical, biochemical, and biophysical techniques to characterize the Ftn derivates thereby providing new insight into the principles for engineering bio-macromolecular assemblies for stimuli responsiveness.



SERMACS 1156

Bactericidal activity of copper-ascorbic acid mixture against *Staphylococcus aureus* spp.

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The purpose of this study was to investigate the bactericidal activity of copper (Cu, 10 ppm) and ascorbic acid (AA, 0.3% v/v) mixture against *S. aureus* ATCC 25923 (methicillin-susceptible) and ATCC 700698 (methicillin-resistant) strains. Approximately 5.5 $\log_{10}$ CFU/ml of each strain was individually inoculated into brain heart infusion (BHI) broth containing Cu, AA, and a Cu-AA mixture, and a time-kill assay was conducted to assess the bactericidal activity. In order to determine the efficacy of Cu-AA mixture as a surface decontaminating solution, the cells were first attached to glass slides (~ 6.5-7.5 $\log_{10}$ CFU per slide) and treated with a Cu-AA mixture for 1 min. The inner membrane permeability of the *S. aureus* strains was determined by measuring β-Galactosidase activity. Similarly, changes in the protein profile of treated bacterial cells were analysed by sodium dodecyl sulfate-polyacrylamide gel electrophoresis (SDS-PAGE). The time-kill study revealed > 3.0 $\log_{10}$ CFU/ml reduction in both strains within 24 h of incubation at 37°C. Attached cells on glass slides were also reduced by > 3.0 $\log_{10}$ CFU per slide after 1 min of exposure to the Cu-AA mixture. The results indicate that the Cu-AA mixture was bactericidal against *S. aureus* strains and the damage to the inner cell membrane could be attributed to this effect.

SERMACS 1157

QM/MM simulations of flavin electronic spectra in different electrostatic environments

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Flavin is one of the most ubiquitous cofactors in enzymatic functions, an may exist in protein either as flavin mononucleotide (FMN) or flavin adenine dinucleotide (FAD). At physiological conditions, flavin is usually encountered in one of five different redox/protonation states. Because of flavin's chemical versatility, flavoproteins are involved in wide array of biological activities including photosynthesis, apoptosis, redox reactions, DNA repair, and blue-light photoreception. In addition, flavin can undergo several types of photophysical processes upon absorption of blue light, depending on the surrounding environment. The first step towards the understanding how different protein environments influence the chemical and photophysical properties of flavin, computationally, is the construction of suitable hybrid quantum mechanical/molecular mechanical (QM/MM) models for flavoproteins and testing their ability to reproduce experimentally observable quantities. We also want to derive general relationships between protein structure and the flavin's absorption spectrum. Therefore, we not only model the spectra in different environments, we also computed spectral properties of each of the five redox/protonation states of flavin in different environments and discuss "electrostatic spectral tuning maps" (ESTMs) for prominent peaks in each of the five states. These ESTMs qualitatively describe how the flavin electronic spectra will be shifted by an anisotropic electrostatic environment such as a protein.

SERMACS 1158

Pharmacophore benchmarking: Role of ligand function in model development

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Integral membrane cell signaling receptors known as GPCR are attractive targets for drug development. Due to the high cost associated with targeted drug development, computational ligand identification methods have become increasingly popular. Pharmacophore modeling is an in silico method that uses comparisons of known ligand structures to build models relating positions of common functional groups in 3-dimensions. Pharmacophore database mining is frequently used to identify candidate ligands for in vitro and in vivovalidation. This in silico benchmark study aims to establish a pharmacophore construction protocol for the identification of novel GPCR ligands, examines the potential to develop functionally-biased pharmacophores using current datasets and methods, and whether or notsuccessful pharmacophores can be constructed using ligands of mixed (or the same) function. Pharmacophores for 8 GPCR have been developed with both ligand-based and structural-and-ligand-based methods and evaluated with Güner-Henry metrics such as Enrichment and Goodness of Hit score.

SERMACS 1159

Hemagglutinin mediated membrane fusion: Dynamics of fusion peptide insertion and interaction with transmembrane domain

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The influenza virus has a severe global impact on human health. The aim of this study is to provide information about how the virus achieves membrane fusion, which is critical for viral infection. In order for influenza to infect a cell, it must be taken up into the cell via the endosome and undergo fusion of the viral and endosomal membranes to transfer viral RNA inside the cell for protein synthesis and viral budding. Spontaneous membrane fusion does not happen on the biological timescale due to the high activation barriers, thus influenza utilizes a protein located on the viral surface known as hemagglutinin (HA) to facilitate this process. The temporal and spatial evolution of the HA-mediated membrane fusion process has yet to be elucidated. The final step of the HA-mediated fusion process has been hypothesized to involve two domains of the protein, the fusion peptide (FP) and transmembrane domain (TMD). We postulate that the TMD trimer serves as a "guiding rail" to assist the insertion of the N-terminus of FP, then together in the same membrane the two domains stabilize a fusion pore. Although it was previously thought that the TMD of influenza HA was a passive anchor, it is now proposed to have a dynamic interaction with the FP to induce fusion pore formation. We use a laser induced temperature-jump or pH-jump to initiate the process and time-resolved infrared and fluorescence spectroscopy to follow the dynamics in model phospholipid membranes. These experiments are in progress to test whether the TMD and FP form an oligomeric complex

that opens and stabilizes the fusion pore, by correlating the dynamics of FP insertion and oligomerization with the dynamics of pore formation. In addition, lipid and content mixing will aid in determining the extent of membrane fusion, whether the FP and TMD can induce full or hemi-fusion in a model membrane system. MD simulations of FP insertion and TMD interactions are essential to guide interpretation of the experimental results. This close integration of simulation and experiment should provide a detailed molecular understanding of the dynamics and mechanism of the FP-TMD interaction that is thought to drive fusion pore formation. In summary, through both experiment and simulation we will provide information about the dynamics of FP insertion and FP-TMD interaction to form an oligomeric complex that opens and stabilizes the fusion pore, an important first step in understanding the mechanism of viral infection.

SERMACS 1160

Characterization of CdSe based nanoparticles for integration into photocatalytic systems

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Harvesting the sun's energy for direct conversion to a fuel source has been the goal of researchers for decades. This light energy can be harnessed and converted into high-energy chemical bonds with photocatalytic systems composed of a photosensitizer and catalyst. Success with this approach has been observed with the use of hybrid systems composed of nanoparticles, a redox mediator, and hydrogenase as the catalytic hydrogen producer. With systems of this class, dot-in-rod (DIR) type materials are often used; however, optimization of photosensitizer properties, such as elongating the "dot" core into a more rod-like structure allow for a broader range for light excitation. The wider range of excitation sources which can be utilized make this nanoparticle-mediator system allow us to study and drive catalysis in a variety of biological systems, such as [FeFe] hydrogenase or electron bifurcating proteins. Steady-state photo-reduction experiments have allowed us to quantify the efficiency of both redox partner and enzyme reduction, utilizing 532 nm light with this other class of particles. Also important to broadening and adapting this methodology is an understanding of the principles influencing electron transfer efficiency, such as pH, photosensitizer physical characteristics, and band gap energies. Improvements to the photocatalytic system components described above, and others, will lead to more effective methods for harvesting light energy, and will yield a powerful tool for studying biological systems.

SERMACS 1161

Bioinformatic and *in vitro* characterization of primase-polymerase enzymes from viruses that infect Actinobacterial hosts

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Primase-polymerases (prim-pols) are enzymes that exhibit primase, polymerase, and helicase activities by way of a bifunctional N-terminal prim-pol domain and a C-terminal SF3-like helicase domain. We present a multifaceted analysis of prim-pols encoded by actinobacteriophages, which are viruses that infect Actinobacterial hosts. Bioinformatics analyses of sequenced actinobacteriophage genomes reveal nearly 600 phages that encode for prim-pols, with no apparent pattern of overall genome conservation. Phylogenic processing organizes these enzymes into three main groupings, with a number of outliers bearing little resemblance to known proteins. These phages span a variety of bacterial host types, genome sizes, and encoded genetic metabolism proteins. While the majority of phage prim-pols range in size from 700-1000 amino acids, 52 truncated primpols of 200-440 amino acids have been identified that contain an intact primpol domain but lack any helicase domain. Most, but not all, phages encoding for truncated prim-pols contain a separate gene that codes for a helicase resembling the helicase domain of full-size prim-pol proteins. Two of the three acidic active-site residues found in the prim-pol domain of previously characterized archaeal plasmid prim-pols, such as pRN1 ORF904 from *Sulfolobus islandicus*, are conserved across phage prim-pols. To begin to understand the importance of prim-pols in actinobacteriophage DNA replication, we have performed a detailed characterization of a prim-pol from bacteriophage Larva, which is the virus' only encoded DNA polymerase. Larva's prim-pol exhibits robust Mg^{2+}-dependent primase/polymerase and strand displacement activity on a circular, unprimed ssDNA substrate in the presence of dNTPs that is inhibited by the presence of ATP. It also exhibits Mn^{2+}-dependent 3' to 5' helicase activity in the presence of dNTP or NTP on an unprimed dsDNA substrate with a 3' tail, and binds ssDNA in the presence of ATP. Bacterial two-hybrid analysis reveals protein-protein interactions between Larva's prim-pol and at least five *Mycobacterium smegmatis* proteins, including transcription-related proteins. CRISPRi silencing of prim-pol is lethal to Larva, indicating prim-pol is essential for viral survival. We hypothesize that despite similarities in protein sequence, actinobacteriophage-encoded prim-pols fulfill a variety of different functions in the replication of phage DNA depending on the phage's genome architecture.

SERMACS 1162

Altering zinc oxide metal-based nanoparticles and the potential changes in the antimicrobial properties

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Zinc oxide metal – base nanoparticles have a proven antimicrobial property when fully synthesized at 12 hours. This synthesis has potential for alterains, and this focuses on the optimization of time the synthesis takes. In this process there is a focus on manipulating time, but also adding lanthanides to increase the antimicrobial properties. In finding the best alterations to produce the highest microbial resistance this is where the findings is applied to connectivity methods for practical applications.

SERMACS 1163

Interaction of Grx4 with the SUF machinery for iron-sulfur cluster biogenesis in *E. coli*

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Iron-sulfur (Fe-S) clusters are ubiquitous in biology and function in electron transfer and catalysis. Biochemical studies show that monothiol glutaredoxins, including *Escherichia coli* (*E. coli*) Grx4, can bind and transfer its cluster to apoproteins such as ferredoxin. Despite its ability to transfer clusters to apoproteins, the novel role the glutaredoxin Grx4 in Fe-S cluster metabolism is unclear. Using EPR and circular dichroism spectroscopies, we biochemically characterized *E. coli* Grx4 interactions with Fe-S cluster biogenesis and trafficking pathways with an emphasis on components within the stress-responsive Suf pathway. Our results shed new light on novel roles for Grx4 in Fe-S cluster metabolism.

SERMACS 1164

Heterogeneous oxidation of phenolic aldehydes

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Biomass burning emission releases reactive methoxyphenols to the atmosphere, where they are oxidized generating precursors to secondary organic aerosol (SOA) formation. Understanding the mechanisms of oxidation of methoxyphenols on surfaces can contribute to constrain the large uncertainty associated to SOA in climate models. This work explores the heterogenous oxidative processing of three model methoxyphenols: 1) 4-hydroxybenzaldehyde, 2) vanillin, and 3) syringaldehyde by ozone, $O_3(g)$, and hydroxyl radical, $HO^\bullet$. Aerosolized 50 µM solutions of each phenol by online electrospray ionization mass spectrometry (OESI-MS) generate microdroplets impinged by $O_3(g)$ molecules at mixing ratios between 48 and 5000 ppbv. OESI-MS spectra of methoxyphenols exposed to $O_3(g)$ display polyhydroxymethoxyphenol as main products, which implies the participation of in situ generated $HO^\bullet$. As O_3 levels increase, the production of polyhydroxymethoxyphenols is favored but new ring fragmentation products are also observed. Fragmentation products include conjugated aldehyde, double bonds, and carboxylic acid functional groups. The interfacial oxidation of the phenols studied is enhanced with an increasing number of methoxy ($-OCH_3$) group: 4-hydroxybenzaldehdye < vanillin < syringaldehyde. The experimental results are explained by two reaction pathways: (1) functionalization of the aromatic ring by $HO^\bullet$, (2) fragmentation of the aromatic ring. Mechanistic schemes explaining the highly oxygenated and low volatility products generated are proposed.

SERMACS 1165

Mesoporous adsorbents for perfluorinated compounds

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Most of the existing technologies used for clean-up of water contaminated by perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) are expensive and insufficiently efficient. The objective of this work was to synthesize materials with high adsorption capacity for their successful removal from water. Porous hybrid materials containing amino groups were synthesized by sol-gel method. Two bridged amines: bis[3-(trimethoxysilyl)propyl]amine (TMPA) and bis[3-(methylamino)propyl]trimethoxysilane (MAPS) were used as precursors. The synthesis proceeded for 24 h at 80°C in acidic media in the presence of various surfactants as pore-forming agents. Synthesized solid products with particle sizes up to 300 nm had high porosity and BET surface area that provided easy access of PFOA and PFOS molecules to the adsorption sites. The adsorption was conducted by mixing each adsorbent with 0.5% solutions of PFOA and PFOS. Obtained materials demonstrated superior effectiveness in their absorption. In some experiments, their adsorption capacity reached almost 90% of the weight of the adsorbent. Adsorbents obtained with MAPS and dodecylamine or sodium dodecyl sulfate proved to be the most effective. FT-IR spectra of the materials after adsorption contained a band at 1200 cm^{-1} characteristic for polyfluorinated compounds. Thermoanalysis demonstrated the stability of the materials with adsorbed perfluorinated compounds up to 180°C. After adsorption, the materials agglomerated and became hydrophobic that made their separation from the water easy.

SERMACS 1166

Computational predictions of polarizabilities and refractive indices of guanine complexes

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Guanine, a nucleobase found in DNA, is often present in crystalline form in organic systems such as fish scales and chameleon skin. In these organisms, guanine plays a role in the impressive optical properties (e.g. iridescence and color switching) of these biological materials. Guanine may exist as several tautomers that are close in energy and has also been shown to form tetramers and tetraplexes. In this study, we systematically explore various guanine structures in order to elucidate connections between the properties of the tautomeric forms and the complexes. In particular we explore the frequency-dependent polarizability of guanine structures. In some guanine clusters, such as the tetraplex, water molecules may be present and form hydrogen bonds in the gaps between molecules and stacks. Thus, the effect of explicit water on the structure and polarizability will also be examined. Applying density functional theory, we predict the frequency-dependent polarizabilities of guanine and guanine complexes at several wavelengths, and we then extrapolate to the bulk property of refractive index. This quantum chemical study aims to explore the single molecule/cluster influences on the varied optical response of larger guanine structures and develop a greater understanding of guanine-based biological materials.

SERMACS 1167

Potassium doped iron oxide catalyst on photocatalytic CO_2 reduction

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Photocatalysis by metal doped semiconductor is attracting major attention to enable the reduction of $CO_2(g)$ in the presence of water vapor as a hole scavenger. Such technology has the potential to produce chemical feedstock and simultaneously minimize environmental pollution. Potassium doped iron oxide (α-Fe_2O_3) of varying potassium compositions (100 Fe:x K, $0 \leq x \leq 5$) are synthesized using incipient wetness impregnation method. The structure, composition, and properties of the catalysts are investigated by X-ray diffraction, nitrogen adsorption-desorption experiments, DSC, TGA, and multiple spectroscopies, including: DRUV-vis, FTIR, Raman, ICP-AES, XPS and UPS, TEM with EDS and SAED. UV-visible light ($\lambda \geq 295$ nm) excited the catalysts uniformly deposited in a cylindrical photoreactor in presence of pure CO_2 or air (400 ppm CO_2), both under a saturated water vapor atmosphere. The maximum production of $CO(g)$ ($R_{CO} = 0.5836$ μmol g_{cat}^{-1} h^{-1} in pure CO_2 and $R_{CO} = 0.4267$ μmol g_{cat}^{-1} h^{-1} in air) quantified by GC- TCD-FID corresponds to 100Fe:1K photocatalyst. The surface doped potassium photocatalyst enhances the photocatalytic efficiency by creating a more negative conduction band than the CO_2/CO reduction potential as supported by UPS and DRUV-vis spectroscopies. The photoreduction mechanism and also the effects of other hole scavengers will be reported.

SERMACS 1168

Photochemical study on terrestrial dissolved organic matter using fluorescence spectroscopy

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Terrestrial dissolved organic matter (DOM) is an important component of the global carbon cycle being exported to the ocean, and constantly circulated in closed aquatic environments such as swamps and lakes. Photo-irradiation by sunlight is highly impactful to DOM's composition altering its physico-chemical properties significantly. Aquatic photochemistry is a relatively young sub-field of environmental science, and little is known of the exact photochemical mechanisms, and how they are kinetically controlled in the environment. To address some of these gaps in the literature, we have gathered a suite of nine river and swamp samples, and have evaluated their photo-transformability. The samples are of variable salinity, and have different content of metals (e.g., Fe), anionic nutrients (e.g., NO_3^-), and organic matter constituents (e.g., black carbon). Here we present the photochemical changes as evident by fluorescence spectroscopy, a common spectroscopic technique used by aquatic photo-chemists. The technique is structure-selective to aromatic structures, which are generally highly photo-reactive. The acquired three-dimensional excitation-emission matrixes (EEMs) allow for elucidating the photochemical transformation of fluorophoric components of DOM. The data and findings presented here are a part of a major project that evaluates multiple compositional aspects of the sample matrixes in attempt to determine the main factors regulating DOM's photochemical processes across different aquatic environments.

SERMACS 1169

Polymer fiber-based visible colorimetric sensor for selective and sensitive on-site determination of polycyclic aromatics hydrocarbons in aquatic ecosystems

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Water is an essential part of sustaining society, yet often faces pollution from human-made sources. Polycyclic aromatic hydrocarbons (PAHs) are carcinogenic compounds that result from oil spills and industrial pollution, thus capable of causing long-term health damage and cancer. These chemicals, a large class of uncharged non-polar organic compounds comprised of two or more condensed benzene rings arranged in various configurations, are also particularly harmful to aquatic ecosystems. Here, a nanofibrous polymer-based colorimetric sensor is used for the detection of PAHs at environmentally-relevant levels. An built-in two-step preconcentration method is used, where a hydrophobic polystyrene (PS) mat limits water in the above concentrated reaction chemistry, while a silica mat is employed on top of the PS mat for the colorimetric chemistry. Electrospinning is employed to produce both the silica and PS sheets. The highly hydrophobic PS fiber mat (contact angle of ~144°) aids in containing the water in the liquid phase. The non-polar PAHs will be concentrated in the vapor phase, allowing for detection. Formaldehyde, under acidic conditions, is used to colorimetrically detect the PAHs—reacting to brown quinoid compounds on top of the white sensor mat. Image analysis is used to quantify the PAH concentration. This robust and portable sensor provides a simpler alternative to the traditional, expensive analytical equipment (HPLC, GC-MS), and allows for on-site and simplified water monitoring.

SERMACS 1170

Molecular dynamics simulations of the interactions between triose phosphate isomerase and sulfonamides

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Malaria continues to be a widespread disease with debilitating health and negative economic impact in regions at high risk of infection. Parasitic resistance and side effects of current antimalarial drugs are major setbacks to the successful campaigns that have reduced malaria incidence by 40 % in the last decade. The parasite's dependence on glycolysis for energy requirements makes pathway enzymes suitable targets for drug development. Specifically, triose phosphate isomerase (TPI) from *Plasmodium*falciparum (pTPI) and human (hTPI) cells show striking structure features that can be used in development of new antimalarial agents. In this study MD simulations were used map and characterize binding sites on hTPI and pTPI interactions with sulfonamides. The molecular mechanics Poisson–Boltzmann surface area (MM-PBSA), method was used to estimate the interaction energies of four sulfonamide-TPI docked complexes. MD simulations explored the dynamics, binding energy and contribution of critical residues to the binding process. A unique combination of key residues at the dimer interface of pTPI is responsible for the observed selective affinity to pTPI compared to hTPI. For example, the representative sulfonamide (sulfaE) shows a strong affinity with pTPI (dimer interface, -64.79 kJ/mol and active site region, -100.48 kJ/mol). The interaction is considerably weaker with hTPI (dimer interface, 35.86 kJ/mol and active site region, -72.97 kJ/mol). The dimer interface and other pocket close to the active site are the main pockets observed. These results suggest triose phosphate isomerase (TPI) receptor as a vital candidate for development of sulfonamide based antimalarial drugs.

SERMACS 1171

Nanoscale infrared spectroscopy of beta amyloid fibrils and prefibrillar aggregates

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Aggregation of the amyloid beta (Aβ) protein into insoluble deposits or plaques is one of main pathological features of AD, but their exact role in AD pathogenesis and onset of dementia is unclear. It now believed that soluble Aβ oligomers and not mature fibrils are the primary neurotoxic species in AD, and that oligomers and prefibrillar aggregates are the key contributors to AD pathogenesis while mature fibrils possibly represent the end point of the disease. Mature Aβ fibrils have a parallel beta sheet structure, but Aβ oligomers have been shown to exhibit other secondary structures. It is also well known that all amyloid fibrils are not equivalent: Aβ fibrils are polymorphic, with variations in molecular structure associated with different morphologies of fibrils which not only exhibit different levels of neurotoxicity, but also have been shown to be associated with different stages of AD. Investigating different morphologies of amyloid fibrils necessitates nanoscale resolution. Optical implementations of infrared spectroscopic imaging are diffraction-limited to spatial resolutions of a few microns. This limitation can be circumvented by a novel technique that integrates infrared spectroscopy with an atomic force microscope (AFM-IR). AFM-IR bypasses resolution limits in conventional IR microscopy by using the tip of an AFM probe to measure infrared absorption and can examine nanoscale structural details by combining the spatial resolution of AFM and the chemical resolution of infrared. AFM-IR offers the unique capability of acquiring infrared spectra that are sensitive to protein structure with nanoscale resolution, so characteristic features of individual aggregates and fibrils can be measured. The main goal of this research is to observe the evolution of the beta amyloid structure at different stages of fibril formation and identify the spectral fingerprints of aggregates and fibrillar morphologies implicated in Alzheimer's disease. AFM-IR measurements on the beta amyloid 1-42 and 1-40 proteins that highlight the possibilities of this approach will be presented. Techniques to extend the infrared measurements to AD tissues will also be discussed.

SERMACS 1172

Decomposition of organophosphorus compounds on zirconium-based metal organic frameworks at the gas-MOF interface

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Metal Organic Frameworks (MOFs) are high surface area materials that have shown great promise for the capture and decomposition of toxic compounds. The development of effective materials and methods for the degradation of chemical warfare agents (CWAs), such as sarin and, soman is of particular national security importance. Zirconium (Zr)-based MOFs, due to their stability in harsh chemical and thermal environments and demonstrated ability to decompose CWAs in solution, have been investigated for their capacity to capture and destroy CWAs in the vapor phase. In this work, we determine breakthrough, adsorption capacities, and hydrolysis reaction products of nerve agent simulants on several commonly studied Zr-based MOFs. Experiments are conducted in an ambient pressure flow cell reactor in which reactants and products are monitored *in situ* by a differentially pumped quadrupole mass spectrometer. Both dry and low humidity atmospheres are studied to test the effect of water on organophosphorus decomposition as well as different practical exposure conditions. In addition, *ex situ* infrared spectroscopic analysis is used to characterize surface-bound species before and after simulant exposure. Understanding the hydrolysis reaction mechanism of these organophosphorus compounds and how catalysts preform under ambient conditions will hopefully lead to the development of new filtration and decomposition technologies, which will enhance safety for military personnel and the general public.

SERMACS 1173

Inverse temperature dependent conductivity of heme bacterial nanowires

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The electrically conductive structures of *G. sulfurreducens* (GS) are of both fundamental and practical interest. The pathway responsible for GS long-range extracellular electron transfer (EET) has been debated for many years. It was suggested that it is formed by a helical set of aromatic residues (phenylalanines and tyrosines) or, alternatively, redox-active cofactors (hemes). The mechanism has been proposed to involve metallic-like coherent transport or incoherent hopping. The inverse temperature dependence of GS pili conductivity suggests metallic-like coherent transport, but this is inconsistent with other theoretical findings, which support incoherent hopping. We studied the temperature dependent conductivity in the incoherent regime and found that in certain site energy and reorganization energy regimes, an inverse temperature dependence is possible for purely incoherent transport in GS Type IV pili[1]. We also analyzed the recently reported EET structure formed from hexa-heme proteins[2] and found that as the temperature increases, there

is a conformational change that alters the environment surrounding one heme, which may increase its reorganization energy and reduce its electronic coupling to nearby hemes. These findings indicate that single electron transfer rates may decrease with increasing temperature due to conformational changes of the protein structure, resulting in an inverse temperature dependent conductivity in the incoherent hopping regime. 1. Ru, Xuyan, Peng Zhang, and David N. Beratan. "Assessing Possible Mechanisms of Micrometer Scale Electron Transfer in Heme Free Geobacter Sulfurreducens Pili." The Journal of Physical Chemistry B (2019). 2. Wang, Fengbin, et al. "Structure of microbial nanowires reveals stacked hemes that transport electrons over micrometers." Cell 177.2 (2019): 361-369.

SERMACS 1174

Force constants and bond strength of functional groups in organic molecules: Fourier transform infrared spectroscopic analysis

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Quantum mechanical harmonic oscillator is a good representation of a vibrating diatomic molecule. It is reasonable to treat each bond in a large molecule as an individual quantum mechanical harmonic oscillator. A diatomic molecule can make a transition from one vibrational energy state to another by absorbing or emitting electromagnetic radiation whose observed frequency satisfies the Bohr frequency condition. A study of an absorption spectrum of such a molecule is capable of revealing the physical nature of the bond. In this investigation, force constants and the strength of the bonds of nine different functional groups in twenty-one organic molecules were studied by means of Infrared Fourier Transform spectroscopy. Among the studied functional groups, it was observed that the nitrile group has the largest force constant and alkyl halide group has the smallest force constant. The difference in force constant conclude that the triple bond in nitrile group is stronger than the single bond in the alkyl halide group even with the quantum mechanical point of view. Hence the force constants of different bonds can be used to predict the reactivity of different functional groups in organic molecules.

SERMACS 1175

Exploring the evaporative properties of acoustically levitated solvent droplets

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In the past decade, there has been increasing focus on chemical processes that occur in containers such as thin films, capillary tubes, microfluidic channels, and droplets which demonstrate unique properties including enhanced rates of reaction. These properties are most commonly attributed to increased rates of mixing and heat transfer due to the nature of a small volume. Specifically, droplets and micro-droplets exhibit very high surface area to volume ratios, making them ideal for processes dependent on high gas/liquid interfacial area, such as gas diffusion-limited reactions or physical changes such as evaporation. Droplets and micro-droplets are commonly generated using a number of methods including paper spray, electrospray, and aerosolization. Acoustic levitation is a less common generation method in which droplets are held in place within a localized node of a standing acoustic wave. In this manner, droplets are isolated within a given volume without the need of a solid container, such as a cuvette, leaving the droplet surface free for surface-dependent reactions and for monitoring processes occurring inside the droplet. We present here our group's work measuring the temperature of acoustically-levitated droplets to determine whether the resulting temperature profiles yield insight into the chemical nature of the droplet. To this end, a forward-looking infrared (FLIR) thermographic camera was used to monitor the droplet surface temperature of a variety of acoustically-levitated solvents including deionized water, methanol, n-propanol, and 2-propanol. Temperature data was collected during the evaporation process until droplet surface temperature reached ambient temperature, indicating cessation of evaporative cooling. By comparing the temperature profiles for each solvent to one another, certain trends seem to emerge based on both individual solvent molecule properties such as molecular weight and structure, and on intermolecular parameters such as hydrogen bonding and steric effects. These results suggest that combining acoustic levitation with thermographic imaging provides a viable technique for fundamental chemical analysis that is capable of monitoring physical and chemical changes within isolated droplets.

SERMACS 1176

Molecular structure of 1-isocyano-1-silacyclopent-2-ene: Combined microwave spectral and theoretical study

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The microwave spectrum of 1-isocyano-1-silacyclopent-2-ene has been obtained from broadband Chirped-Pulse Fourier Transform Microwave spectroscopy. The rotational constants (RC) for the standard abundant isotopic species are A = 4251.4918(23), B = 891.9066(53) and C = 839.5630(58) MHz. The symmetric quartic centrifugal distortion constants, using the I^r representation in C_S symmetry for D_J, D_{JK}, D_K and d_J have been evaluated; similarly, the ^{14}N nuclear quadrupole coupling has been determined. Several singly substituted isotopologues observed in natural abundance, enabled most of the heavy atom substructure to be determined. The 5-membered ring is close to planar, but the orientation of the isocyanate unit, derived from the $N^{13}CO$ spectrum, unexpectedly lies away from the ring. Our initial equilibrium structure searches led to a *trans* orientation of the $C_{2,5}$-Si-N=C unit, i.e. bending away from the ring. This enabled the full equilibrium structure to be determined with confidence. The principal bond lengths were 1.7157 (Si-N), 1.8696 (Si-C), 1.1998 (N=C) and 1.1737 (C=O) Å, with angles 163.3 (Si-N=C), 169.4 (N=C=O), 94.6 (C-Si-C), and 109.1° (Si-C=C). The extensive widening of the SiNC angle is particularly notable; the SiNCO unit has a *trans* dihedral angle. Systematic theoretical study of the Si-N=C angle potential energy surface (PES) relative to the ring, gave a very shallow double minimum with the barrier being less than 1 cm^{-1}; a polynomial fit to the surface shows major contributions of both harmonic and quartic components. Similar study of the XSiN angle, where X is at the ring centre, also gave a PES with considerable quartic character.

SERMACS 1177

Preparation, characterization, conformational stability and theoretical calculations of 4-methyl-1,1-dichloro-1-silacyclohexane

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The broadband chirped-pulse Fourier transform-microwave (CPFT-MW) spectrum (2-8 GHz) of 4-methyl-1,1-dichloro-1-silacyclohexane has been recorded. Isotopologues observed in natural abundance provided verified substitution structures of the lowest energy conformers. Infrared spectra (3100 to 400 cm^{-1}) of the sample have also been recorded. The enthalpy difference between the axial and equatorial conformers has been determined to be 400 ± 25 cm^{-1} (2.94 ± 0.32 kJ mol^{-1}), with the equatorial conformer as the more stable form. Approximately 54 ± 2% of the axial form is present at ambient temperature. By utilizing the microwave rotational constants of five isotopologues for equatorial and the structural parameters predicted from MP2(full)/6-311+G(d,p) calculations. The structural parameter values for the equatorial and axial forms are for the heavy atom distances (Å): Si−Cl = 2.074 (3); Si−C = 1.864 (3); and angles (deg): ∠ClSiC = 116.7 (5); $\angle C_lCSi$ = 110.4 (5). The results are discussed and compared to some related molecules.

SERMACS 1178

Computational study of the spin trapping behavior of melatonin and selected derivatives

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Free radicals, especially reactive oxygen species, have been implicated in numerous deleterious processes leading to cancer, degenerative diseases and aging. Spin traps may be used as a probe to examine radical reactions in cells. They react with radicals to produce a more stable radical adduct which may then be characterized by electron paramagnetic resonance spectroscopy. However, there is a need for less toxic and more lipid soluble examples. Antioxidants such as melatonin have the solubility and toxicity characteristics desired, and form a central part in protecting cells from radical damage. Melatonin is thought to undergo a multistep oxidation pathway in reacting with small oxyradicals such as the hydroxyl radical. This work looks at the possibility of using melatonin derivatives to obtain stable intermediates for use as spin traps. The optimized geometries for melatonin, selected derivatives and the radical adducts with $OH^{\bullet}$ were calculated at the DFT/B3LYP/6-31G(d) and HF/6-31G(d) levels of theory. Extrapolation to the complete basis set limit was also attempted using the cc-pVXZ (X = D, T, Q) Dunning basis sets.

SERMACS 1179

Effect of graphene oxidation rate and residue substitution on the adsorption of polyalanine peptides

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Graphene oxide (GO) surfaces possess strong physisorption properties, which opens up the possibility of using such surfaces in biosensors, drug delivery and enzyme immobilization applications. However, the oxidation rate of graphene can significantly affect the interactions between biomolecules and graphene-based surfaces. Here, we investigated the role of graphene oxidation between 0 % to 40 % on the secondary structure and physisorption of 20-mer polyalanine a-helix using all-atom molecular dynamics (MD) simulations. Graphene and graphene oxide surfaces with low oxygen coverage enhance the formation of 3-10 helices because of the strong van der Waals interactions between the polypeptide and the carbon atoms on the surface. The substitution of the central residue with a more hydrophobic residue enhances the formation of alpha-helices on graphene oxide with higher oxygen coverages because of the weak electrostatic interactions between the polypeptide and the hydroxyl and epoxy groups on the surface. By reducing the interactions between the polypeptide and the graphene oxide surface, the introduction of hydrophobic residues promotes the stabilization of alpha helices.

SERMACS 1180

Elucidation of prominent features in the spectra of N_4H^+ and N_4D^+ clusters: Driven molecular dynamics study

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Infrared (IR) spectra of N_4H^+ and N_4D^+ were calculated using driven molecular dynamics (DMD) and equilibrium molecular dynamics (MD) simulations with full-dimensional analytical potential and dipole surfaces. The prominent spectral features were analyzed and partially re-assessed based on new data obtained with DMD. Namely, MD calculations closely correlate the parallel proton stretch vibration in N_4H^+, at 750 cm^{-1}, with the one observed experimentally at 743 cm^{-1}. Secondly, the intense IR active feature originally reported, but ambiguously assigned, in the experimental spectrum measured by Duncan et al. (using Ar-tagging) at 1051 cm^{-1} has been properly recovered by DMD as strongly IR active and assigned as a combination band consisting of H^+ asymmetric stretch and $N_2…N_2$ intermolecular symmetric stretch modes. And finally, the effect of an Ar tag on the IR spectra is relatively small, with the most noticeable effect of argon on N_4H^+ observed for the perpendicular proton bend mode at 1225 cm^{-1} that splits to in-plane and out-of-plane components.

SERMACS 1181

Preparation and activity of palladium catalyst on fumed silica support

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A 5.0 wt% palladium catalyst on fumed silica support was prepared by a modified incipient wetness method followed by high-speed mixing using Voxtex method. A precursor solution of palladium nitrate hydrate in water was very slowly added at the rate of 20 uL/min through a syringe pump to the solid support (fumed, powdered silicon dioxide; surface area 395 m^2/g). The resulting “dough” was mixed in a Vortex mixer at a speed of 900 rpm for three hr. The sample was dried at 105 ^{0}C overnight and then calcined at 500 ^{0}C for 6 hr. The catalyst showed exceptional activity for complete combustion of methane to carbon dioxide and water. The conversion of methane was 70% at 250 ^{0}C and 100% at 275 ^{0}C. The activity and characterization data will be presented.

SERMACS 1182

Molecular dynamics of $O(^1D) + CCl_4 \rightarrow ClO + CCl_3$ probed by cavity enhanced sub-THz spectroscopy

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The UV photodissociation of ozone in the atmosphere is known to result in highly reactive oxygen atoms in their excited $O(^1D)$ electronic state. Subsequent collisions of these atomic radicals with other atmospheric constituents frequently occur without a barrier. Matsumi and Shamsuddin have previously studied the dynamics of these reactions with chlorinated compounds using vacuum-ultraviolet laser-induced fluorescence spectroscopy. In this poster, we discuss our recent efforts to revisit these experiments by probing the rovibronic distribution of ClO products in hyperfine detail using a recently developed millimeter wavelength cavity enhanced confocal Fabry-Perot molecular beam spectrometer. In the experiment, ozone is generated and passed over carbon tetrachloride and then the vapor is co-expanded through a pulsed nozzle. The resulting supersonic jet expansion is passes through the beam waste of the Fabry-Perot while a counter propagating 266 nm photolysis laser initiates the formation $O(^1D)$ atoms and their subsequent intra-beam collision and reaction with CCl_4. The resulting rovibronic state distribution of the ClO products in this PHOTOLOC-like experiment are then used to confirm whether the reaction occurs via a directed abstraction mechanism, as inferred in the earlier studies.

SERMACS 1183

Formation mechanisms of interstellar C_3H_2O isomers from quantum mechanical calculations

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Investigating the elusive relationship between our interstellar medium and its assortment of complex organic molecules provides a path to understanding the evolution of biological building blocks into life forms. Significant to this study are astronomical regions such as the giant molecular cloud some 26,000 light-years away from Earth called Sagittarius B2. This massive “liquor cabinet of space” is home to non-equilibrium reactions which may involve aldehydes, ketones, alcohols, and esters. Spectroscopic studies by Kaiser and coworkers investigated the formation of C_3H_2O isomers from carbon monoxide and acetylene in reaction conditions similar to those on interstellar ice grain surfaces found within Sagittarius. Through a collaboration of computational and experimental efforts, the excited state chemistry for the formation of C_3H_2O compounds are explored in more depth. In this contribution, we will present preliminary structural mechanisms for the formation of these isomers on the basis of ground and excited state quantum mechanical calculations.

SERMACS 1184

Photophysical modulation of a triazole molecule in a cationic micelle

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Due to their unique binding behavior, triazole- based molecules are currently being investigated as possible prodrugs for diseases. In our research, we are investigating the triazole molecule Phenanthrene based 1,2,3- triazole phenol derivative (PhTP), and it’s binding behavior In the cationic, cetyltrimethylammonium bromide (CTAB) ionic micellar medium. CTAB forms micelles in water when it reaches it’s critical micellar concentration, due to its amphipathic properties, which mimics a biological system. After investigating the PhTP alone in CTAB, we began additions of copper and fluoride ions in order to observe the effect on the binding behavior, and thus the location of the PhTP in the micelle. Fluorescence spectroscopy was used to determine the location of the PhTP in the CTAB micelles.

SERMACS 1185

Endocannabinoid entry into TRPV1, the ionotropic cannabinoid receptor

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Whether caused by inflammation or dysfunctional nerves, chronic pain affects nearly 10% of the world’s population. Since there are few treatments that are effective while being non- invasive and non-addictive, new targets are being explored. Found in the peripheral nervous system, the transient receptor potential subfamily vanilloid type 1 (TRPV1) ion channel can be activated by a plethora of exogenous and endogenous stimuli including capsaicin, temperatures above 43 o C and acidic conditions. In recent years, it has been discovered that TRP channels, including TRPV1, act as ionotropic cannabinoid receptors. The endocannabinoid anandamide has been shown to have a similar binding affinity to TRPV1 as capsaicin and can rapidly desensitize the channel giving an analgesic effect. Another endocannabinoid, 2- arachidonoylglycerol, has also been shown to activate and desensitize TRPV, though at a lower potency than anandamide. Models of the open and closed structures of TRPV1 were constructed from the published cryo-EM structures (PDB: 5IRX, 5IRZ). Prime (Schrodinger, Inc. Version 11.8.012) was used to complete unresolved regions of extracellular loops and ankyrin repeat domains were incorporated in the model using the available crystal structure (PDB: 2PNN). These models have been equilibrated (50 ns) in a fully hydrated POPC bilayer for use in molecular dynamics simulations (AMBER 16). Currently, simulations are focused on understanding the mechanism of anandamide entry and activation of the channel. Future work will include ligand docking and molecular dynamics simulations of other endogenous cannabinoids and acyl amides. The results of these simulations and dockings to date will be presented.

SERMACS 1186

Laboratory submillimeter spectroscopic detection of desorbed CO ices

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Interstellar ice chemistry has been investigated extensively through computational and laboratory studies, but after decades of research, we do not have fully-quantitative laboratory desorption data on species formed from processing of icy dust grain mantles. The primary means of analyzing desorption experiments is through mass spectrometry, and while mass spectrometry is an extremely sensitive technique, it is often not ideal for studies of structural isomers or varying conformers of a given species due to mass overlaps (e.g. glycolaldehyde, $HCOCH_2OH$, and methyl formate, $HCOOCH_3$). Many researchers use isotopic substitution to distinguish between isomers, but it has been shown that isotopologue desorption yields can differ significantly. An in-situ laboratory technique that is capable of probing desorbed ices is gas-phase molecular spectroscopy -- specifically rotational spectroscopy, which is structure-specific and highly sensitive. Therefore, we are developing a mm/submm spectroscopic method for detecting photo- and thermally desorbed ice analogues. Our laboratory spectra are also directly comparable to observational spectra from far-IR telescopes. Here we will present the development of this structure specific technique and the results of thermally and photo-processed CO ices formed at ~12 K.

SERMACS 1187

Spectral analysis of the reaction between O(^{1}D) and methylamine

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O(^{1}D) is well known to insert into stable hydrocarbons, preferentially via a barrierless insertion into C-H bonds. This method has proved to be an efficient way of forming unstable or otherwise reactive species under terrestrial conditions. Photolysis of ozone at 248 nm has been shown previously in our lab to be an efficient O(^{1}D) production route. We have studied the formation of methanol and vinyl alcohol via O(^{1}D) insertion into methane and ethylene respectively. The reactions are highly exothermic, and the products tend to undergo unimolecular decomposition. As such, stabilization of the products is achieved using a supersonic expansion. Using this technique, we aim to produce aminomethanol, an important glycine precursor, via insertion into methylamine for the purpose of collecting its rotational spectrum in the millimeter/sub-millimeter region. Here we will present the efforts made to understand the complex chemistry resulting from such a reaction and the efforts made towards producing and confirming the spectrum of aminomethanol.

SERMACS 1188

Effective determination of the theoretical infrared spectra of formic acid dimer $(HCOOH)_2$

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In this study, theoretical vibrational spectra of formic acid dimer were directly compared to experimental results from jet-cooling and cavity ring-down spectroscopy. Theoretical calculations at the B3LYP/aug-cc-pVDZ and B3LYP/aug-cc-pVTZ levels of theory agreed with experimental data. Consistent with expectations, the barrier height for the transition state of the double proton transfer in formic acid dimer was found to be a low 6.34 kcal/mol, at the MP2/aug-cc-pVDZ level of theory. Electrostatic potential calculations are consistent with expectations, expressing decreased electron density around the non-acidic hydrogens, and higher electron density around the oxygen atoms.

SERMACS 1189

Solid phase extraction of heavy metal ions from aqueous solutions using amorphous melamine zirconium phosphate

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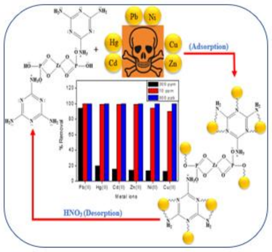
This work reveals a novel approach for the synthesis of Nitrogen-doped Carboxylated Activated Carbon (ND-CAC) from melamine-formaldehyde resin (MF-R) for the removal of the heavy metal ions Pb(II), Cu(II), Hg(II), Cd(II), As(V) and Cr(VI) from contaminated wastewater. The ND-CAC was synthesized by carbonization of MF-R at 1073 K under nitrogen atmosphere followed by chemical oxidation. FT-IR and XPS confirm the insertion of the carboxylic and nitrogen functional groups into the activated carbon structure. N_2 adsorption surface area measurement shows a very high surface area of 1135 m^2/g for the prepared ND-CAC adsorbent.

The results indicate that the ND-CAC adsorbent has a high adsorption capacity of 738 mg/g for the removal of Pb(II) ions from water. The maximum sorption capacities for Hg(II), Cr(VI), Cd(II),Cu(II) and As(V) are 257, 104, 28, 20 and 15 mg/g, respectively. The ND-CAC adsorbent shows 100% and 95.6% uptake of Pb(II) at concentrations of 50 ppb and 50 ppm within 30 seconds and 20 minutes, respectively. The ND-CAC shows a removal of 12.5% Ni(II), 25.0% Cd(II), 81.7% Zn(II), 91.3% Cu, 96.3% Hg(II) and 100.0% Pb(II) from a mixture containing different metal ions. The sorption kinetics can be fitted well to a pseudo-second-order kinetic model which suggests a chemisorption mechanism via pyridinic nitrogen, carboxylic acid, and pyridine oxide active sites on the ND-CAC adsorbent. Regeneration of the ND-CAC adsorbent shows excellent desorption capacities of 98.9% and 95.3% for Pb(II) and Cr(VI) ions, respectively.



SERMACS 1190

Nanoscale infrared spectroscopic imaging of chemical heterogeneities in hybrid organic-inorganic perovskites

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The last decade has witnessed a remarkable rise in the efficiency of solar cells constructed using hybrid organic-inorganic halide perovskites, namely $CH_3NH_3MX_3$ (M=Pb/Sn, X=Cl, Br, I). A significant amount of research effort has been dedicated to further the potential of perovskites as photovoltaic materials, but one important aspect that needs attention is the characterization of defects and heterogeneities in perovskite films. The method of fabrication of perovskite films can lead to different density and nature of defects and heterogeneities, which in turn affect photovoltaic efficiencies. The crucial parameters in the fabrication process are the stoichiometry, choice of solvent, additives and conditions of annealing. Previous research has studied the chemical composition of perovskites using vibrational spectroscopies and X-Ray Diffraction (XRD) while film morphologies are investigated using electron and atomic force microscopy. Though these techniques provide valuable information about average chemical and morphological variations, there is no straightforward way to understand the relationship between them and probe the chemical heterogeneity of films. Atomic Force Microscopy coupled with Infrared Spectroscopy (AFM-IR) is a technique which can resolve the question of understanding the inhomogeneity of the material. In AFM-IR, the thermal expansion due to absorbed infrared radiation at a specific wavenumber in a region of few nanometers is sensed by the AFM probe to create a chemical map, thus allowing for nanoscale measurements of film chemistry. This study presents AFM-IR investigations of nanoscale heterogeneities in methylammonium lead iodide ($CH_3NH_3PbI_3$). The results of our experiments present a comparison between $CH_3NH_3PbI_3$ made using different stoichiometries (1:1 and 3:1) of methylammonium iodide (MAI) and lead iodide (PbI_2). The spectral pattern of the intermediates and the final product in the formation of perovskites allow for mapping of unreacted methylammonium iodide (MAI) in nanoscale spatial domains, even when such spectral features are absent in the average FTIR spectrum. These localized densities of MAI represent nanoscale defects that could potentially affect the efficiency of the final device. The focus of this research is to relate the stoichiometric ratios of MAI and PbI_2 and other fabrication conditions to the morphological and chemical heterogeneities in perovskites using nanoscale infrared imaging.

SERMACS 1191

Excited state dynamics of photo-ODIBO using transient absorption and stimulated Raman spectroscopies

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Photo-click chemistry utilizes photoreactive molecules, inert molecules in which reactivity can be induced by specific wavelengths of light. Photo-ODIBO contains a cyclopropenone functional group which undergoes photodecarbonylation upon irradiation of 350 nm light. The resulting cyclooctyne is highly reactive and subsequent cycloaddition of an azide provides for ample applications such as labeling of biomolecules for imaging. The details of the photodecarbonylation mechanism are not yet understood and are the subject of the present study. As the dynamics of photoactivation take place on a femtosecond time scale, ultrafast transient absorption and stimulated Raman spectroscopies are ideally suited to investigate the underlying photochemical processes. Transient absorption spectroscopy is based on a pump-probe technique that employs an ultrashort pump pulse for photoexcitation of the sample and a time-delayed white-light probe pulse to observe the electronic relaxation dynamics. Femtosecond stimulated Raman spectroscopy additionally monitors the excited state structural evolution using a two-pulse probe scheme composed of a narrowband, picosecond Raman pump and white-light probe. The use of both electronic and vibrational spectroscopy is essential to fully understand the mechanism of the photoactivation dynamics. The transient absorbance decay is of multi-exponential nature suggesting a stepwise procession of the photo-ODIBO relaxation dynamics. The vibrational structural information from FSRS is a sensitive probe of the photodecarbonylation reaction to distinguish excited versus ground state dissociation. Preliminary results show decaying of the vibrational features associated with the C=O group (~ 1760 cm^{-1}) with similar time constants compared to global analysis results for the transient absorption data.

SERMACS 1192

Examining biomarker survivability in Enceladus plume capture conditions using laser-induced projectile impact testing

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One of Saturn's moons, Enceladus, has become a highly attractive target for astrobiology studies due to compelling evidence for ongoing geophysical activity and a subsurface liquid saltwater ocean beneath its icy crust, as well as new evidence for the possibility of large organic compounds from the sub-surface ocean of Enceladus. Cryovolcanism occurring at the southern region of Enceladus results in plumes of water ice grains being ejected into space at high velocities, which makes a flyby mission to analyze plume ejecta a viable approach. However, these sampling strategies assume that any molecular biosignatures present would survive both plume conditions and hyper-velocity impact capture onto the sampling plate, which could result in degradation of organics or partial racemization of any chiral molecules present. An understanding of the survivability of biosignatures in captured material at spacecraft velocities from the Enceladus plume is required for future mission design. However, biomarker survivability through these conditions is presently unknown, so the study of how molecular biomarkers are affected by low-temperature high-impact conditions is crucial to the development of effective sampling and analysis approaches for future missions to Enceladus. In this work, we aim to identify capture conditions under which potential biosignatures may be preserved using various capture media, which is relevant to any astrobiology mission, including sample return.

SERMACS 1193

Treatment of the free electron wave function in photoelectron spectroscopy: Systematic benchmark study

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Photoelectron spectroscopy (PES) probes photoabsorption processes involving individual, isolated molecules in the photon energy range above the ionization thresholds of the molecules. PES utilizes photoionization or photodetachment to analyze the energetics and movement of electrons and nuclei in molecules. However, the interpretation of experimental results is not straightforward, and often requires theory and computer modeling. The calculation of absolute total cross sections requires accurate wave functions of the initial and final states of the systems, most of which is can be represented in a one-electron function called the Dyson orbital. Dyson orbitals can currently be computed accurately using correlated electronic structure methods. However, the final state of the system also requires the description of the free electron wave function. At this moment, no black box method exists that can be applied in a fast and systematic way to obtain accurate photoelectron spectra of polyatomic molecular systems. We will present a series of benchmarks using approximate treatments of the photoelectron wave functions, where we will compare computed and experimental photoionization and photodetachment spectra.

SERMACS 1194

Investigation of the low-energy isomers of $SO4^{2-}(H_2O)_N$ (n=1-5) clusters

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Atmospheric particulate matter is known to have deleterious effects due to its toxicity and oxidative potential. Particulate matter is composed of liquid droplets of many different sizes, ranging from fine (2.5 µm or less in diameter) to ultrafine (1 µm or less in diameter), and it is a result of reactions and emissions from natural and artificial sources such as oceans and volcanoes as well as from vehicles and industry. Because mass spectra are unable to distinguish between thermally accessible isomers of weakly bound clusters, computational analysis is being used increasingly to study the structure and reactivity of small clusters. Sulfate, derived from oxidation of sulfur dioxide in the air, is a ubiquitous component of particulate matter and therefore an interesting system of study. Using CLUSTER, a genetic algorithm developed by Kanters and Donald, we perform randomized matings of one sulfate with *n* number of waters and optimized our structures with the M06-2X density functional augmented by Grimme's D3 empirical dispersion function and the aug-cc-pVTZ basis sets. Preliminary results show that the algorithm produces low-energy isomers largely consistent with literature as well as new structures not previously reported.

SERMACS 1195

Structure based drug design and synthesis of novel GPR6 modulator

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G protein-coupled receptor 6 (GPR6) is a cannabinoid-related Class A GPCR. It is highly expressed in the central nervous system and exhibits quite high constitutive activation of adenylyl cyclase. Several research groups showed GPR6 application in treating Alzheimer's Disease, Parkinson's Disease, and Huntington's Disease. Multiple patents suggested the use of a wide range of pyrazine derivative analogs as GPR6 inverse agonist and claimed its ability in treating Parkinson's disease and other dyskinesias syndromes. In the current study, we aim to design novel potent GPR6 inverse agonists based on the pyrazine scaffold. Due to the absence of structural information about GPR6, a suite of computational techniques was used to build a homology model of GPR6 using the X-ray structure of the Sphingosine-1-Phosphate receptor 1 (S1P1) as a template. The developed model helped to understand the unique structural features of GPR6. As well it has been used to perform docking studies of different pyrazine derivatives extracted from the patents, to reveal the strategic residues in the binding crevice that play an essential role in receptor-ligand molecular interactions. Fragment-based scaffold hopping approach was pursued on the pyrazine moiety of a lead scaffold from the patent, to guide designing novel GPR6 chemotypes. With taking into account, their ability in retaining the crucial interactions suggested in the docking studies as well attain more for better receptor-ligand interactions. The candidate chemotypes were selected through visual inspection, ADME properties, the absence of PAINS, ranking docking scores, and synthesizability. The hit leads were synthesized through an efficient synthetic route that enables derivatization to generate a rational SAR with new scaffolds. The synthesized compounds will be evaluated in GTP-gamma-S, cAMP, and β-Arrestin-2 recruitment assays. These potential GPR6 modulators may guide further understanding of the biological role of this orphan receptor.

SERMACS 1196

Recent investigations of pure and Cu decorated ZNo nanoparticles

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Pure, doped and decorated metal oxides (MO) have many interesting optoelectronic and physicochemical properties making them ideal candidates for applications in energy storage, production and transformation. For example: ZnO is a well-known sun block, an antifungal/antibacterial agent, used as laser diodes and UV detectors, and is a catalyst for methanol synthesis when decorated with Cu. It is important to note that Cu decorated ZnO has been modified using other constituent co-catalyst metals to reduce poisoning and optimize the reaction conditions. Continued research and development efforts have improved the production rate of methanol but, the research effort described here is aimed at investigating the habitat and chemical status of Cu on the ZnO surface. The objective is to develop an atomic level understanding of the conditions necessary to produce an optimal catalyst for methanol production. Our research activities involve using a novel, patented MO synthesis method to produce significant quantities of ZnO powders with specific morphologies and prescribed chemical stoichiometry. In an effort to eliminate the potential negative effects of solvent-based metal deposition methods, we have designed and constructed a RF magnetron-based, physical vapor deposition system to deposit Cu atoms on the ZnO nanoparticles. Characterization of the pure and decorated ZnO nanomaterials using powder x-ray diffraction (PXRD), photoluminescence (PL), diffuse reflectance spectroscopy (DRS), inductively coupled plasma optical emission spectroscopy (ICP-OES), and electron microscopy techniques will be presented. These measurements will be used to illustrate the structural, optical, and compositional properties of these MO nanoparticle materials. Future investigations of the catalytic, electronic, and microscopic structure /dynamics of these nanomaterials using x-ray photoelectron spectroscopy, Z contrast electron microscopy and x-ray/neutron scattering techniques are planned.

SERMACS 1197

Investigating the effects of nα-acetylation on amphiphilic peptide self-assembly with 2DIR spectroscopy

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Over 80% of solube human proteins undergo Nα-acetylation, a post translational modification which adds an acetyl group to the free amino group at the N-terminus of a peptide or protein sequence. While this process creates a seemingly minor change in chemical composition, the effects on protein folding and therefore function are vast. Molecular dynamic simulations have shown significant structural differences between acetylated and unacetylated derivatives of two amphiphilic peptides, KFKE-8 and FKEF-8, however, traditional experimental techniques lack the ability to you monitor self-assembly with the requisite structural and temporal resolution to determine mechanistic differences. We use two-dimensional infrared spectroscopy (2DIR) coupled with site-specific isotope labeling to monitor self-assembly of the acetylated and unacetylated peptides. By using isotope labeling, we obtain residue specific aggregation kinetics which yield a clearer mechanistic picture of the self-assembly process. This insight will help to build a model for how acetylation alters the self-assembly pathway of peptides and proteins.

SERMACS 1198

Nondispersive infrared (NDIR) sensing of CO_2 using CdO films

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The potential for realizing portable, light-weight devices reliant on narrowband, mid-infrared light is hindered by the low wall-to-plug efficiencies and large footprints of gas-phase lasers and quantum cascade lasers. There exists a demand for efficient, cost-effective, narrowband sources that could improve mid-infrared spectroscopy and sensing. Recent work has shown that narrowband thermal emission is feasible by using subwavelength films of n-doped cadmium oxide. These films are highly efficient thermal emitters due to the fact that cadmium oxide is a plasmonic material which supports epsilon-near-zero (ENZ) modes. ENZ modes are excited at the zero crossing of the real part of the permittivity and can couple to free space without any nanostructuring to create ENZ polaritons. Along with supporting ENZ polaritons, cadmium oxide exhibits low optical losses and has a highly tunable plasma frequency throughout the mid-infrared. While these films are a significant step towards practical, tunable narrowband mid-infrared sources, their peak emission occurs at an angle highly off normal, limiting their applicability. To increase the viability of these novel emission sources, it is necessary to achieve high narrowband emission at normal incidence. Here, we have shown that by growing n-doped cadmium oxide films on a patterned sapphire substrate, high emission is achievable at normal incidence. We conducted thermal emission measurements to confirm that our films were accurately tuned to emit at 2500 cm^{-1}. Angle dependent thermal emission measurements were also performed and have shown that the n-doped cadmium oxide films on a patterned substrate emit omnidirectionally. It was also observed that at high angles Fano interference occurred between the ENZ mode and a propagating surface mode. This caused the bandwidth of the thermal emission to become extremely narrowed, reaching Q factors of 14. These results are promising and can guide further optimization of n-doped cadmium oxide films on patterned substrates for narrowband thermal emission. With the tunability and high emissivity at normal incidence, these films could be used for applications such as nondispersive infrared sensing of gas molecules.

SERMACS 1199

Enhancing chemical sensing through SEIRA and silicon carbide gratings

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Chemical sensing is an advancing area with critical applications in medical, environmental, and military fields. Fourier transform infrared spectroscopy (FTIR) is a practical tool for chemical sensing as it provides a 'molecular fingerprint' of the substance being analyzed. Although IR spectroscopy is key for chemical sensing, traditional methods are not sensitive enough for many applications dealing with highly dilute samples We used refractive index liquids to detect strong specific absorbance peaks. Refractive index liquid 1.65 was chosen to be detected and to be diluted with large quantities of toluene. It has a strong absorption peak at 950 cm^{-1} while toluene does not absorb in this area. Recent publications have shown surface-enhanced infrared absorption can be utilized with polaritons to achieve this high sensitivity. Surface-enhanced infrared absorption (SEIRA) utilizes a rough surface that couples with modes to enhance absorption peaks. Surface phonon polaritons (SPhPs), which form from light coupled with optical phonons, require a grating or prism to slow down the incident light to be excited. A grating used to excite these SPhP's can also be used as the roughened surface needed for SEIRA. The silicon carbide grating used had their Reststrahlen band from 1000 cm^{-1} to 800 cm^{-1}. Reflectance measurements were done on grating structures with a height of 2μm and 10μm and period widths of 2μm, 2.5μm, 3μm, 3.5μm, and 4μm at varying dilutions. These were compared to scans of refractive index liquid 1.65 without being diluted and toluene. Several gratings were shown to have enhancements to the characteristic peak of 1.65 compared to the substrate in a part per thousandths dilution. In the future we are going to investigate grating with a larger height and using different refractive index liquids. The use of such SPhP structures could lead to easier chemical sensing and saving of resources in many different fields.

SERMACS 1200

Mapping polarity and hydrogen-bonding environments in live cells by hyperspectral stimulated Raman scattering microscopy

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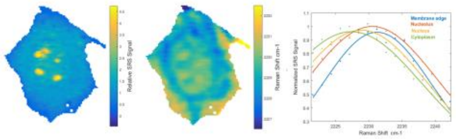
Direct visualization of the subcellular liquid-liquid phase separation and the distribution of water and ions is essential for understanding cellular functions. Although techniques such as NMR and Cryo-EM have been successfully utilized to map water and ion content in cells, it remains a challenge to measure these properties at high spatiotemporal resolution. Vibrational imaging methods have long been utilized for environmental sensing. For example, nitriles have proven to be effective to sense the local electric field due to the vibrational Stark effect (VSE) and capable to quantitatively assess the hydrogen bonding interactions. Compared to conventional IR techniques, stimulated Raman scattering (SRS) microscopy has emerged as a superior technique for elucidating the complex structure and dynamics of biological systems with unprecedented acquisition speed, high detection sensitivity, and high spatial resolution. Here, we present our work on vibrational-shift hyperspectral electronic pre-resonance SRS imaging using a near-infrared dye molecule with a conjugated cyano bond. This approach allows us, for the first time, to quantitatively measure the environmental heterogeneities in the degree of water exposure and hydrogen bonding environment at the subcellular level. This advance constitutes a stepping-stone towards a more complete picture of the distribution of water and ions in live cells using coherent Raman microscopy.



Left: SRS imaging of the HeLa cell at CN mode (2230 cm-1) Middle: Raman frequency mapping based on hsSRS peak positions of probe molecules (Rhodmaine800) Right: Extracted hsSRS spectra of probe molecules at different cell regions

SERMACS 1201

Investigation into the effect of aging and aluminum-substitution in ferrihydrite under aerobic conditions using flow microcalorimetry, XRD, and XAS

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The purpose of this study is to systematically investigate the effect of aging and aluminum (Al)-substitution in ferrihydrite (Fh) as it relates to changes in crystallinity and surface reactivity under aerobic conditions. Fh is environmentally pervasive and plays a significant role in numerous geochemical processes, most notably the fate and transport of anthropogenic and natural contaminants. In natural environments, Fh often co-precipitate in the presence of impurities, particularly Al and forms aluminum-bearing phases with various moles % substitution (%-Alfh) For this study, two sets of approx. 28 and 16-month old samples of 0%-AlFh, 12%-AlFh, and 24%-AlFh were used. Changes in crystallinity will be identified using structural information derived from quantitative X-ray diffraction (QXRD), specific surface areas measurements using the Brunauer–Emmett–Teller (BET) analysis, as changes in the specific surface area correlate to changing crystallinity, and Fe L-edge X-ray absorption spectroscopy (XAS) that will yield information on the local structural information of the samples. Surface reactivity will be assessed by probing the positive surface charge of the samples by measuring the energies associated with the exchange on the surface of two anionic probes, chloride (Cl^-) and nitrate (NO_3^-), using flow microcalorimetry. The two anions are reported to undergo reversible outer-sphere reactions on the surface of Fh and AlFh samples and are thus excellent proxies of changes in surface reactivity (Harvey and Rhue, 2008). For the 28-month old set of samples, crystallinity and surface reactivity were also characterized after initial synthesis; the results of the comparison between the original post-synthesis data and the current post-aging data will be discussed. Preliminary QXRD analysis of the 0%-AlFh samples showed an increase in crystallinity as well as an increase in the ratio of goethite to hematite transformation from Fh with aging. For the 12%-AlFh, QXRD also showed an increase in crystallinity with aging, and for the 24%-AlFh, QXRD analysis showed little to no change in the amount of crystalline iron oxide phases present. An examination of the results should provide insight into the role of impurities on Fh and provide a more realistic framework for the incorporation of Fh into predictive models of fate and transport of contaminants.

SERMACS 1202

Development, characterization and reactivity of phosphate mineral thin films

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Surface chemistry plays an integral role in processes such as soil formation, biomineralization, and heterogeneous catalysis. However, most surface sensitive analytic techniques require a conductive substrate. Charge build up and problems with sample temperature control can make the surface analysis of insulators and other poor thermal/electrical conductors difficult. One way to overcome these problems is to deposit thin films of target minerals onto metal supports. We have electrodeposited hydroxyapatite (HA) or $Ca_{10}(PO)_6(OH)_2$ onto several metal substrates (e.g., copper, iron, and stainless steel) to make thin films that are conducive to surface-sensitive reflection-absorption infrared spectroscopic measurements. HA is prevalent in the rock record dating back to the Hadean and Archean eons, and this mineral may have been an important source of phosphorus for the origin of life. After growth by electrodeposition and characterization by scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDX), and x-ray powder diffraction (XRD), the films were reacted with prebiotic solution containing urea, ammonium formate, and water (UAFW) to study the mineral dissolution and liquid solid reactivity. These experiments reveal that the UAFW solution reacts with an exposed metal oxide layer that forms between the metal supports and the HA film.

SERMACS 1203

Developing a hybrid surface complexation model for aluminum-substituted ferrihydrite

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Ferrihydrite (Fh) is a naturally occurring mineral with high specific surface area and surface reactivity. Due to these properties, Fh is one of the most important components controlling solubility and mobility of anthropogenic contaminants in the environment. It is unusual to find Fh in its pure form (Fe_5O_8H); instead, it often co-precipitates with other elements, particularly Aluminum (Al) due to its abundance in natural environments and its ability to fit into the Fh structure based on size similarity. Al has been reported to substitute for Iron (Fe) by up to ~24% into the structure of Fh, and hence affects its surface charge properties, and the numerous exchange and adsorption reactions that implicate Fh [1]. These surface chemical reactions have been rationalized by using surface complexation models (SCM) which combine chemical descriptions of surface protonation and ion adsorption reactions with an electrical double layer model of the interface. The goal of SCMs is to link the microscopic world of adsorption and the macroscopic level of solution chemistry [2]. The project aims to build an SCM model for Al-substituted Fh (AlFh). To our knowledge, this will be the first effort in that regard. Our approach will be to focus on identifying the most-likely sites to be replaced with Al. Based on experimental evidence, we hypothesize that the substitution occurs on singly coordinated Fe-sites. Consequently, an existing SCM based on an 11-site Fh model will be modified accordingly. Chemical equilibrium constants for both Fh and Al will be combined to represent the Al-Fh surface, and electrostatic parameters will be defined based on the Basic Stern Layer electrostatic model. The model will utilize specific surface area values and batch adsorption data obtained from the literature. Furthermore, Density Functional Theory (DFT) theory and calculations will be performed on a model Fh nanoparticle cluster to identify the Fe sites likely to be replaced by Al. The new SCM is expected to predict surface charging, and hence electrolyte adsorption and protonation on Al-Fh.

SERMACS 1204

Galantamine: History of an Alzheimer's drug

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The alkaloid galantamine is one of the three major drugs used to treat Alzheimer’s. Galantamine inhibits acetylcholinesterase, resulting in a longer half-life in vivo for the neurotransmitter acetyl choline. Commercially, galantamine is isolated from daffodils and snowdrops (both in the *Narcissus* genus), as well as synthesized in the laboratory. This presentation will trace the discovery of galantamine. A.W. Gerrard, a pharmacist working in London, was the first to isolate alkaloids from daffodils in his 1877 report, "The proximate principles of the *Narcissus pseudonarcissus."* The Russian chemists N.F. Proskurnina and L.Y. Areshkina reported the isolation of an alkaloid which they named galantamine from the snowdrop *Galanthus woronovi* in 1947. In 1957, S. Uyeo and S. Kobayashi, working at the Universities of Osaka and Kyoto, respectively, isolated an alkaloid they named lycoremine from the red spider lily; this would prove to have the same structure as galantamine. There are reports that a Bulgarian pharmacologist in the 1950s noticed people rubbing common snowdrop on their foreheads to ease nerve pain (apparently a folk treatment for poliomyelitis). This led to continued interest in *narcissus* alkaloids as pharmaceutical agents. In 1957, the English chemist D.H.R. Barton, considering likely biochemical pathways, proposed the correct structure of galantamine at the Festschrift for the Swiss biochemist Arthur Stoll. Barton went on in the early 1960s to establish the structure experimentally and detail some of the relevant biosynthetic pathways. Alkaloids continue to be a significant part of the chemical repository of drugs. Modern analytical tools have allowed continued discovery of new members of this class from a variety of species; these discoveries put a premium on retaining biodiversity for pharmaceutical development.

SERMACS 1205

Look back at two important chemurgy projects

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The term chemurgy has been used to describe the use of "farm" products in industrial applications and manufacturing. Two historically important projects from the field of chemurgy centered around goldenrod and soybeans. The first project explored the use of goldenrod as a domestic source of rubber in a project carried out by Thomas Edison, Harvey Firestone, Henry Ford and coworkers. This project was carried out in the late 1920's and early 1930's. The second project explored the production of soybean oil and other products from soybeans. This project was carried out by Henry Ford and coworkers and enjoyed multiple applications in the automobile manufacturing industry. This presentation will provide a look back at these two important projects from the early days of the field of chemurgy.

SERMACS 1206

Gallic acid-based bacterial DNA gyrase inhibitors

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Bacterial DNA gyrase is a type II DNA topoisomerase that can introduce (-) supercoils to DNA substrates with the hydrolysis of ATP. Since DNA gyrase only exists in bacteria and is an essential enzyme for bacterial survival, it is possible to identify inhibitors targeting DNA gyrase without affecting host human enzymes. Gallic acid is a natural product found in a variety of plants, such as tea leaves and oak bark, and does not inhibit DNA gyrase activities per se. However, several gallic acid derivatives, such as ellagic acid and epigallocatechin gallate (EGCG), are potent DNA gyrase inhibitors. In this study, we screened a group of natural polyphenolic products containing gallic acid moieties and discovered that digallic acid is a potent DNA gyrase inhibitor with an IC50 of 2 mM. Digallic acid does not inhibit other DNA topoisomerases including bacterial DNA topoisomerase I, human DNA topoisomerase I and topoisomerase IIa. Further we found several food additives based on gallic acid including octyl gallate and dodecyl gallate potently inhibit bacterial DNA gyrase activities. Interestingly, the inhibitory IC50 of DNA gyrase is correlated with the length of hydrocarbon chain. octyl gallate and dodecyl gallate have strong antimicrobial effects against *Staphylococcus aureus*and methicillin-resistant *Staphylococcus aureus* (MRSA). Our results provide a solid foundation for the design and synthesis of gallic acid-based DNA gyrase inhibitors that may be used to combat antibacterial resistance.

SERMACS 1207

New fluorescence-based method to identify DNA topoisomerase inhibitors

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DNA topoisomerases are essential enzymes for all living organisms and plays critical roles in transcription and DNA replication. Although they are targets of several important anticancer drugs and antibiotics, high throughput screens (HTS) have not been performed to identify potential initiators for drug development. Part of the reasons are the lack of an HTS assay to screen and identify inhibitors from compound libraries that contains hundreds of thousands of compounds. Previously, we reported the synthesis of a type of fluorescently-labeled plasmids that can be used as an HTS assay to screen compound libraries for drug discovery. However, the synthesis of these fluorescently-labeled plasmids is very costly due to the use of the expensive, purified enzymes, i.e., nicking endonuclease Nt.BbvCI, T4 DNA ligase, T5 exonuclease, and T4 DNA polymerase. In this study, we found a unique property of T5 exonuclease that can degrade supercoiled plasmid pAB1 that contain a hairpin structure at certain experimental conditions and does not digest relaxed pAB1. After the T5 exonuclease digestion, the DNA samples can be stained by a DNA-binding dye, either DNA intercalators or groove binders to differentiate relaxed and supercoiled DNA. We will present our efforts to develop this unique property of T5 exonuclease into an HTS assay to screen compound libraries to identify potential topoisomerase inhibitors.

SERMACS 1208

Electrostatics dominate the interactions between the tethered intrinsically disordered regions and the DNA-binding domain of PU.1, a model eukaryotic transcription factor

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Eukaryotic transcription factors are enriched in intrinsically disordered regions (IDRs) that serve many essential functions. The ETS-family protein PU.1 represents a model eukaryotic factor in which its structured DNA binding domain is flanked exclusively by IDRs. Cellular assays report that PU.1 exhibits a negatively cooperative 2:1 complex at a single specific binding site. Further characterization of PU.1/DNA binding reveals an additional dimeric species in the absence of DNA that opposes 2:1 complex formation. A combination of spectroscopic (CD, NMR, fluorescence), volumetric, and calorimetric experiments show that dimer formation without DNA is favored by low salt and both tethered IDRs. Unlike the 2:1 complex, which involves primarily surface residues, unbound dimer formation is accompanied by destabilizing structural changes to buried residues relative to the monomer. In addition, PU.1 dimerization is promoted by phosphomimetic substitutions of IDR residues that are phosphorylated *in vivo* and reproduced by the action of acidic crowding agents on truncated PU.1 lacking the IDRs. A synthesis of the functional, structural, and thermodynamic data leads us to postulate a model of PU.1 regulation, unknown in the ETS family, by two distinct dimers that are reciprocally controlled by its tethered IDR and by cognate DNA. In both the unbound dimer and 2:1 complex, the flanking IDRs remain disordered while they are engaged in distinct fuzzy complexes. To better understand how the acidic IDRs are perturbed by the structured basic DBD, we are investigating the conformational dynamics of the disordered regions of PU.1 by solution NMR. When DNA is not present, the acidic IDR is expected to interact with the tethered DBD. Inversely when the DBD is bound to DNA, the acidic IDR experiences repulsion from the DNA while it is moderated by the sandwiched basic DBD. Therefore, we postulate that the induced disorder of the acidic IDR by the DNA induces a positive entropic contribution to the complex stability. Considering the abundance of the acidic IDR/basic DBD tethered in eukaryotic transcription factors. Our findings provide new insights into the relationship between the oppositely charged domains of the transcription factor subproteome.

SERMACS 1209

Long-lived intermediates in oxidation of guanine by one-electron oxidants: Kinetics of formation and lifetime under biologically relevant conditions

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Oxidative damage to DNA nucleobases generally occurs at guanine (G) due to its low standard reduction potential. As a result, the majority of identified end products of oxidative DNA damage originate from G. These include, in particular, 2,5-diaminoimidazolone along with its hydrolysis product, oxazolone, and 2′-deoxy-8-oxo-7,8-dihydroguanosine (8-oxoG) along with products formed through its further oxidation. Kinetic studies, however, show the presence of at least two more fairly long-lived intermediates (further denoted as X1 and X2), which can accumulate in significant quantities in this system and which possess the UV-Vis characteristics that does not match those of any known end product of G oxidation. Identification of X1 and X2, quantitative characterization of the efficiency of their formation, and determination of their chemical fate is the purpose of the present study. The study was performed in a model system using guanosine as a substrate and a set of selectively generated one-electron oxidants including the sulfate, dibromide, and carbonate radical anions in phosphate (pH 6.4 –7.6) and acetate (pH 4.0 -5.2) buffers. It was found that: a) accumulation of both X1 and X2 occurs linearly at early times, indicating the absence of long-lived precursors to these products; b) the X1 to X2 ratio is independent of the type of oxidant, but X1, unlike X2 readily undergoes further oxidation; c) the X1 to X2 ratio changes in favor of X2 under acidic conditions, d) lifetime of these products is a few hours at pH 7, with X2 being less stable than X1, and e) neither of these products is formed by hydroxyl radical attack on guanosine. Identification of X1 and X2 and further investigation of their reactivity is currently underway.

SERMACS 1210

Recognition of single ribonucleotides in duplex DNA by RNase HII

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Ribonucleotide inclusion is by far the most prevalent damage to DNA. Single ribonucleotide damage impacts the local structure and dynamics of the affected double-stranded DNA. This damage is recognized and repaired by RNase HII which is specific for single ribonucleotide damage. Our previous work has shown that for an rG intrusion the perturbation is strongly dependent on the flanking sequences. This suggests that the recognition and repair of the damage are also modulated by the flanking sequence. To test this hypothesis we have prepared a series of DNA oligonucleotides with a single rG or rC inclusion in different flanking sequence contexts. The repair efficiency/recognition of the damaged DNA duplexes has been examined for RNase HII. Preliminary results reveal that RNase HII activity on these substrates strongly depends on the flanking sequence.

SERMACS 1211

Identification and characterization of preferred DNA-binding sites for the *Thermus thermophilus* HB8 transcriptional regulator TTHB099

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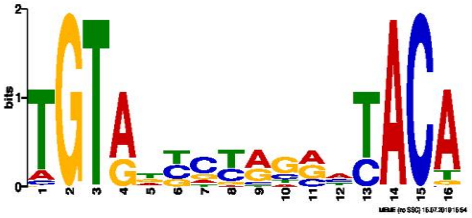
Genetic analysis of the extremophile model organism *Thermus thermophilus* has revolutionized applications in biotechnology, and our understanding of structural biology and ancient bacteria. To complement such advances, our laboratory uses the novel selection method Restriction Endonuclease Protection, Selection and Amplification (REPSA), which utilizes a ligand-dependent inhibition of enzymatic template inactivation, to identify consensus sequences for putative transcriptional regulators. Such an approach provides a more direct, empirically derived correlation to the potential biological functions of a transcriptional regulator than structural homology more commonly used. In the present study, REPSA followed by massively parallel sequencing and MEME analysis were used to identify the preferred DNA-binding sequence of the *T. thermophilus* transcription factor, TTHB099, a member of the CRP/FNR superfamily of transcriptional activator proteins. Specificity of the identified consensus sequence, a 16-base pair palindromic motif, was validated through electrophoretic mobility shift assays (EMSA) and Restriction Endonuclease Protection and Amplification assays (REPA). Kinetic binding parameters were determined using biolayer interferometry (BLI). Future bioinformatic studies will be performed in order to identify genes and operons regulated by TTHB099, leading to a better understanding of its biological roles.



Sequence logo for REPSA-selected TTHB099-binding sequences.

SERMACS 1212

Oxidative damage to guanine bases in DNA: Reaction pathways leading to the formation of 2,5-diaminoimidazolone lesion and their relative contribution

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Oxidative damage to DNA is a natural result of living in an aerobic environment. It may be caused by a variety of oxidants including reactive oxygen species, oxidizing free radicals, nitrogen oxides, transition metal ions in high oxidation states etc. Among all DNA bases, guanine is the most prone to oxidation due to the lowest one-electron oxidation potential (E^o = 1.29 V vs. NHE at pH 7). 2,5-Diaminoimidazolone (Iz) is one of the most abundant end products of guanine oxidation by a broad range of oxidants; its yield, however, varies significantly depending on the reaction conditions. At present, two sources of Iz have been considered, which are the recombination of guanine free radicals with superoxide radical anions and further oxidation of 8-oxoguanine. These and other options were explored using oxidation of guanosine as a model reaction, and a set of selectively generated one-electron oxidants with well-defined redox behavior. The latter included the hydroxyl radical along with the sulfate, dibromide, and carbonate radical anions under carefully controlled gassing conditions (air, vacuum, N_2O, and N_2O/O_2 mixtures). Our study found that: a) there are oxygen-dependent and oxygen-independent pathways leading to the formation of Iz; b) there is an oxygen-dependent pathway that does not require the presence of superoxide; and c) the oxygen-independent pathway leading to Iz likely proceeds through a long-lived intermediate which, however, is not 8-oxoguanine. This intermediate is yet to be identified.

SERMACS 1213

Tunable immunostimulation through chemically modified nucleic acid nanoparticles

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The chemical structure of natural biopolymers DNA and RNA present a unique opportunity for their use in several applications such as materials, pharmaceuticals, and sensors. Recent advances in understanding their structure and folding have enabled the generation of multi-strand nanoscale assembles, called nucleic acid nanoparticles (NANPs). Through careful design and intricate prediction software, these NANPs can be programmed to assume nearly unlimited shapes and structures and have the capacity to carry potent pharmaceuticals. Furthermore, the ability to modify the chemical structure of their intrinsic strands adds an additional layer of customizability, modulating the melting temperature and resistance to nuclease degradation. Although nucleic acid based therapeutics hold great potential, unpredictable and unwanted immunostimulation has become a major hindrance towards their transition to a clinical setting. Understanding the immunostimulation based on the structure and composition of NANPs is paramount towards their advancement into medicine. Here we explore the use of chemical modifications for tuning the immunostimulation elicited by NANPs. We employ both endogenous and artificial chemical modifications of nucleic acids for desired interactions with human Toll-like receptors, as well as tune their general cytotoxicity and biocompatibility. In addition to surveying the immunostimulation, we confirm their modified physicochemical properties. This method of chemically modifying NANPs presents a new approach for tuning the immunostimulation elicited by NANPs, furthering their progress towards clinical use.

SERMACS 1214

Immune stimulation by functionalized RNA nanorings

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Nucleic acids as programmable biomaterials have been designed to form a vast library of nucleic acid nanoparticles (NANPs) which have been demonstrated for broad applications as scaffolds, biosensors, and therapeutics. However, their transition into the clinical setting downstream of therapeutic development has been greatly impeded by their unknown immunostimulatory properties, resulting in adverse side effects. Here, we explore how the designs of hexameric RNA-based nanorings functionalized with therapeutic moieties in various orientations affect immune stimulation and processing in the cell. These therapeutic moieties embedded into the NANP design are Dicer Substrate RNAs which can then be processed for gene knockdown via RNA interference. As a proof of concept, these Dicer Substrate RNAs are designed against green fluorescent protein to explore the efficiency of uptake and silencing in cells. The immune stimulation of various design orientations has been extensively analyzed in human peripheral blood mononuclear cells as well as in reporter cell lines for investigating the link between design parameters of RNA nanoparticles and their immunomodulatory properties. By characterizing patterns in functionalization by immune recognition, NANPs can be optimized for either immunoquiescent delivery or therapeutic adjuvants.

SERMACS 1215

Exploring stability and steric effects of disulfide bonds incorporated into the backbone of peptide nucleic acid (PNA)

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Peptide nucleic acids (PNAs) are synthetic pseudopeptides with the potential to act as either anti-gene (DNA transcription blockers) or anti-sense (RNA translation blockers) chemical agents. PNA's utilize the same nucleobases as DNA and RNA, allowing for their participation in Watson-Crick base pairing in homogenous (PNA:PNA) and/or heterogeneous (PNA:DNA, PNA:RNA) duplexes. Unable to penetrate into the cytoplasm of the target cell alone, the antisense strand is duplexed with a "delivery" strand of PNA containing chemical markers, which will effectively hijack existing cellular transportation systems. This modified "delivery" PNA strand is designed to be temporary; once the PNA duplex enters the cell, a disulfide linkage synthesized within the delivery PNA strand's backbone will be cleaved in the cytoplasm. This leads to the dissociation of the duplex, freeing the antisense strand to seek its target. Our research initiative is the synthesis of a trio of sterically unique disulfide monomers, which will then be incorporated into different delivery strands. This shift in the steric environment around the disulfide linkage is hypothesized to induce some change in the kinetics and efficacy of disulfide cleavage and duplex formation/dissociation. These changes will be monitored via thermal denaturation assays and fluorescence analysis.

SERMACS 1216

Role of flanking amino acids in DNA binding by AT-Hook peptides

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The AT-hook motif is a conserved GRP sequence that binds the minor groove of B-form DNA. The binding interaction is stabilized by the electrostatic interactions between the positively-charged arginine residue and the negatively-charged DNA. While the binding affinity and DNA complex structure of the canonical RGRP consensus sequence are well-researched, the role of the amino acid residues flanking this sequence is not as well-understood. The present study assesses the DNA binding affinity and global structural changes of RGRP peptides comprising variant flanking sequences. Binding affinity is analyzed by filter binding, and peptide structure is monitored by circular dichroism. Analysis of the variant sequences reveals which amino acids and amino acid positions are critical to the AT-hook-DNA binding interactions.

SERMACS 1217

Dynamic RNA and DNA nanoassemblies with controlled immunological properties

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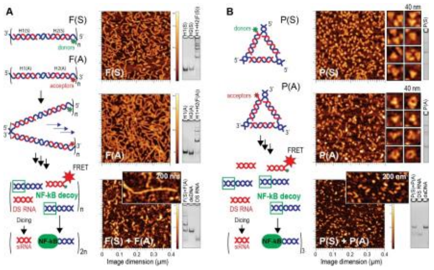
Nucleic acid–based assemblies that interact with each other and further communicate with the cellular machinery in a controlled manner represent a new class of reconfigurable materials that is able to overcome limitations of traditional approaches and improve the potential therapeutic utility of nucleic acids. This strategy enables the development of novel biocompatible 'smart' devices and biosensors with precisely controlled physicochemical and biological properties. We extend this novel concept by designing RNA–DNA fibers and polygons that are able to cooperate in different human cell lines and that have defined immune-stimulatory properties confirmed by ex vivo experiments. The mutual intracellular interactions of constructs result in the release of a large number of siRNAs while giving a fluorescent response through FRET and activating NF-kB decoy DNA oligonucleotides. Our system offers multiple advantages, including: (i) very simple design and assembly protocols that significantly lower the production costs and shorten the experimental time; (ii) released dsDNAs that are no longer nonfunctional byproducts, as well as embedded NF-kB decoys that restrain the immune stimulatory responses; (iii) the ability to change the shapes of the hybrids from long fibers to closed polygons by simply changing the orientation of DNA–DNA interacting parts, which in turn leads to distinguished physiochemical and immunological properties. In addition, such a novel strategy provides controlled rates of reassociation, stabilities in human blood serum, and immunorecognition.



SERMACS 1218

Design and synthesis of cyano-nilutamide conjugated DNA bis-methylating molecules that can target androgen receptor positive cancer cells

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Research in our laboratory is focused on developing novel anti-cancer molecules that can selectively target cancer cells and cause cytotoxic but non-mutagenic DNA damage. In this project, we have designed a molecule that can selectively target androgen receptor positive prostate cancer cells and can bis-methylate DNA within the minor groove at A/T-rich regions. This molecule contains a central bispyrrole triamide unit that can selectively bind to the minor groove at A/T-rich regions, which is flanked on either side by methyl sulfonate units that can methylate nucleophilic sites on DNA. The cell-targeting ligand, a cyano-nilutamide unit which can bind to the androgen receptor is attached to the nitrogen atom on one of the pyrrole units. The design of this molecule should allow it to selectively target androgen receptor overexpressing prostate cancer cells, and form two N3-methyladenine adducts in close proximity to each other. The formation of two such proximal adducts on opposite strands of DNA can lead to the formation of lethal DNA double strand breaks. The design and synthesis of this molecule and its stable methyl sulfone analog, and the results of preliminary biological studies with the molecules will be presented.

SERMACS 1219

Design and investigation of DNA bis-alkylating agents for increased toxicity towards cancer cells

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DNA alkylating molecules have been widely used in cancer chemotherapy, but the high doses needed to eliminate cancer cells completely often lead to harmful side effects such as hair loss, gastrointestinal problems, immune suppression, and in some cases, secondary cancer. In order to improve the potency of DNA-alkylating molecules, we have designed and synthesized a group of bis-methylating molecules that can bind to DNA in the minor groove at A/T-rich regions and methylate two different nucleophilic sites within this region. The three molecules that we have designed each consist of a central DNA-binding unit which is flanked on either side by methyl sulfonate units. The distance of the sulfonate units is varied by using different linker units in order to determine the composition that affords the highest methylation levels. In principle, these molecules can lead to the formation of DNA-double strand breaks if the two methylation events take place on opposite strands of DNA in close proximity to each other. Initial studies with these molecules indicate that they efficiently produce N3-methyladenine adducts, exhibit toxicity in U251 glioma cells, and appear to form DNA-double strand breaks. The design and synthesis of these molecules, the characterization of their DNA methylation abilities, and the results of toxicity studies on U251 glioma cells will be presented.

SERMACS 1220

Potent inhibition of the mammalian high mobility group protein AT-Hook 2 binding to DNA by natural polyphenols

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The mammalian high mobility group protein AT-hook 2 (HMGA2) is an intrinsically disordered protein (IDP) that specifically recognizes the minor-groove of AT-rich DNA sequences. It works as a multifunctional DNA-binding protein and plays important roles in tumorigenesis and adipogenesis. Previous studies showed that HMGA2 is a potential therapeutic target of anticancer and anti-obesity drugs by inhibiting its DNA-binding activities. In this study, we found that several natural polyphenols, such as aurintricarboxylic acid, gallic acid, ellagic acid, and (−)-epigallocatechin gallate (EGCG) tightly bind to HMGA2 and, as a result, strongly inhibit HMGA2 binding to AT-rich DNA sequences. Since these polyphenols can inhibit adipogenesis in vitro and in animal models, our results suggest that their anti-obesity activities may stem from their inhibition of HMGA2-DNA interactions. Because polyphenols are naturally occurring chemical compounds enriched in vegetables and fruits, our discovery strongly support that vegetables and fruits are natural remedies to treat obesity.

SERMACS 1221

Role of hydration in DNA recognition by structurally homologous transcription factors

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Transcription factors are proteins that initiate DNA transcription by binding DNA with divergent mechanisms and affinities. While protein and specific DNA sites are considered in the context of direct interactions, water-mediated contacts also enable specific DNA site selection. To improve understanding of the role of water in molecular recognition, we studied Ets-1 and PU.1 of the ETS family for their differing hydration in high-affinity binding. ETS members share a structurally conserved, sequence divergent DNA binding domain which recognizes a cognate sequence (5'-GGAA-'3). We designed structural chimeras to reduce the osmotic sensitivity of PU.1, where structural elements of the DNA binding domain that interact with DNA directly or through water-mediated contacts in PU.1 were swapped with those from Ets-1. Osmotic stress experiments demonstrated several constructs were osmotically insensitive while retaining wild type binding to high-affinity DNA. Taken together, the retention of high-affinity binding under osmotic pressure proves that hydration is not required for high-affinity interactions. To now assess the role that DNA has in hydration in high-affinity binding, we have modified the second guanosine of the cognate site. The selected guanosine directly contacts an evolutionarily conserved arginine in ETS family members. Substitution with inosine removed the exocyclic NH_2 and, despite a lack of interaction to the protein, returned osmotic sensitivity to the chimeras while retaining high-affinity binding. However, wild type PU.1 suffered decreased binding to inosine DNA while retaining osmotic sensitivity. Conversely, removal of a direct contact from the guanosine by 2-aminopurine reduced binding in all cases, and eliminated osmotic sensitivity in wild type PU.1. The results indicate that guanosine substitutions define the roles that individual hydrogen bond donors and acceptors have in hydration and facilitating high-affinity binding. Combining the chimeras with single-point comparisons of DNA enables us to parse the elements of PU.1 and DNA that govern protein/DNA interactions, particularly regarding the role of hydration. Pinpointing specific roles of individual elements in proteins and DNA provides the possibility of engineering de novo variants with desired patterns of hydration or affinities.

SERMACS 1222

Suboptimal binding drives DNA site recognition in the transcription factor ETS-1

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Transcription factors bind specific sequences with a spectrum of affinities as a mechanism to regulate gene expression. Low-affinity binding by transcription factor Ets-1 is crucial for development, as replacing low-affinity with high-affinity sites causes dysmorphic outcomes. How Ets-1 segregates cognate sites remains unclear, offering a useful model to examine the interplay of affinity and DNA recognition. Molecular dynamics simulations of the DNA binding domain of Ets-1 unbound, and bound to DNA of varying affinity indicated an allosteric mechanism coupled to low-affinity binding. Binding experiments with site-directed mutants showed a DNA-contacting residue that detects low-affinity DNA, which triggers the loss of a distal salt bridge to compromise the hydrophobicity of core helices. Loss of the salt bridge in only low-affinity binding relative to other observed states of Ets-1 suggests a mechanism for regulating affinity and activity. To expand upon how Ets-1 regulates binding, we examined autoinhibited unbound Ets-1 by simulated tempering. Simulated tempering is an ensemble method which increases the rate of exploration of the conformational landscape by combining multiple simulations at different temperatures. Structural studies have shown two helices distal to the DNA interface unfold in the μs-ms timescale upon Ets-1/DNA binding. This timescale corresponds to energetically expensive conformational motions, which are difficult to observe by conventional simulations without specialized resources or modified protocols such as simulated tempering. Secondary structure and principal component analysis of the tempering simulations of Ets-1 show the helices transitioning to multiple unfolded sub-states, indicating unfolding is not inclusive to DNA binding. The variation and number of folded/folded states suggests a potential mechanism to predispose the affinity of the unbound protein to DNA. This illustrates the first known molecular mechanism for how ETS proteins distinguish cognate sites. DNA recognition by transcription factors is not only a function of DNA sequence or shape but is driven by changes to the internal dynamics of the transcription factor itself. Furthermore, the simulations demonstrate the feasibility of simulated tempering as a robust method for enhancing conformational sampling in biological systems larger than peptides and mini-proteins in diverse compute environments.

SERMACS 1223

Identification of a DNA-binding consensus sequence for TTHA1359, a *Thermus thermophilus* HB8 transcriptional regulator

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Transcription factors are sequence-specific DNA-binding proteins that perform essential functions in gene expression regulation occurring at the level of gene transcription, the primary level governing gene expression in most organisms. Despite the central role of these proteins in gene regulation, DNA-binding sites and biological roles have yet to be determined for many transcription factors, including those in model organisms such as *Thermus thermophilus* HB8. Here, we employ Restriction Endonuclease Protection, Selection, and Amplification (REPSA), a combinatorial selection method for probing a ligand's double-stranded DNA-binding specificity, as well as electrophoretic mobility shift assays (EMSAs) and biolayer interferometry (BLI) to identify and validate a DNA-binding consensus sequence for the *T. thermophilus* HB8 transcription factor TTHA1359. Future research will be focused on using the TTHA1359 DNA-binding consensus sequence to identify potential TTHA1359 genomic binding sites within the *T. thermophilus* HB8 genome to obtain insight into the biological role of this transcriptional regulator.

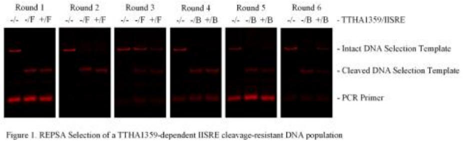

Figure 1. REPSA Selection of a TTHA1359-dependent IISRE cleavage-resistant DNA Population

SERMACS 1224

Magnetic characterization of chromium intermediates in the reduction of chromium(VI) by glutathione in acidic solutions

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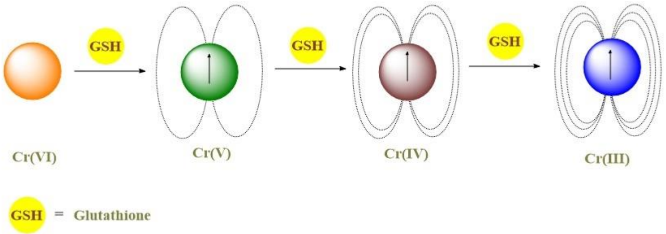
Chromium (VI) is carcinogenic through intermediates formed in the cellular milieu by reduction with small reductants like glutathione (GSH), ascorbate, cysteine, and NADPH. Although the reduction of chromate by thiols has been investigated, the participation of Cr(IV) intermediates has been inferred only indirectly due to the Cr(IV) refractive behavior towards EPR spectroscopy. Biological data from numerous reports indicate that Cr(IV) is the species most likely responsible for the carcinogenicity of Cr(VI). Our kinetic studies suggested that in acidic solutions, glycine buffer at pH 2.8, the reduction of chromate with GSH involves mostly a chromium(IV) intermediate. As a step towards the full characterization of the paramagnetic species involved in the reduction of chromate by thiols at neutral pH, we embarked on an investigation of the reduction of chromate with GSH in glycine buffer at pH 2.8 using a Superconducting QUantum Interference Device (SQUID) magnetometer. Our results indicate a strong influence of temperature and confirm the presence of Cr(IV). At 2 K, the saturation magnetization method was applied to the frozen reaction when it reached the peak of formation of intermediates and the contributions were calculated to be 30% of Cr(IV) and 69% of Cr(V). When the Curie–Weiss method was applied to determine the effective magnetic moment, the use of the linear portion of the curve, 100–200 K, yielded 58% Cr(IV) and 42% Cr(V); when data from the region below the temperature of liquid N_2 (77 K) is employed, the intermediate is exclusively Cr(IV).



Reduction of chromate by glutathione.

SERMACS 1225

Infrared spectroscopic studies of the CO oxidation reaction mechanism on Cu/TiO_2 and the role of strong metal-support interactions

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The effectiveness of Au/TiO_2 catalysts for numerous reactions is well documented, but high material costs limit practical applications. TiO_2 aerogel-supported Cu materials have recently been explored as a economical alternative for supported nanoparticle catalysts. While early work showed that Cu/TiO_2 is active for CO oxidation, available surface sites and reaction mechanisms are not well understood. In the current study, fundamental interactions of CO with Cu/TiO_2 materials are investigated. CO is used as an infrared probe molecule to elucidate available surface sites on the material and reveal numerous distinct binding sites. The infrared spectroscopic measurements, conducted in a high vacuum cell, have revealed the mechanism for CO oxidation to be a Mars-van Krevelen extraction of lattice O in TiO_2 directly surrounding the Cu particles. Studies also identify product adsorption modes that contribute towards catalyst deactivation. Variable temperature infrared spectroscopy was employed to evaluate adsorption enthalpies of CO on TiO_2 regions within the Cu/TiO_2 catalyst and on TiO_2 sites within pure titantia. A significant change in CO adsorption enthalpy when Cu is present on the support indicates strong metal-support interactions that increase the reducibility of the TiO_2 support. These discoveries present a deeper understanding of fundamental reaction mechanisms and electronic structure effects on Cu/TiO_2, and offer insight into the important role of metal-support interactions on support reducibility.

SERMACS 1226

Hydrogen atom abstractions from carboxylic acids: Experimental mechanistic interpretation

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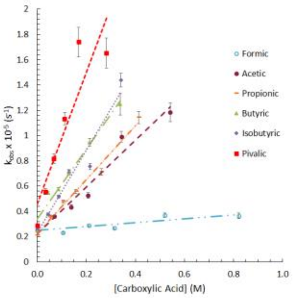
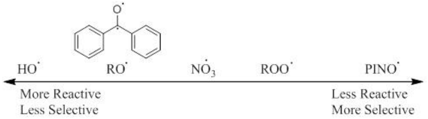
Carboxylic acids are a vitally important class of compounds involved in synthesis, biochemistry, and the environment. Since these compounds are well studied, the pathway in which oxidative degradation of these compounds is known to be stepwise: $RCO_2H \rightarrow RCO_2 + H^{\cdot} \rightarrow R^{\cdot} + CO_2$. However, Denisov and Shestakov have provided a theoretical framework for the existence of a concerted abstraction and fragmentation reaction. Herein, experimental evidence will be provided that support the notion that hydrogen atom abstraction can be coupled to bond breaking elsewhere in the molecule, such as in decarboxylation. Further, investigations into some factors affecting the transition state will also examined. Laser flash photolysis was utilized to monitor the transient spectra of the abstracting nitrate radical generated by the photolytic dissociation of ceric ammonium nitrate. Investigations of other oxygen-centered radicals with varying reactivity are ongoing.



A plot of rate constants versus concentration for a series of carboxylic acids from which the nitrate radical is the abstracting species.



A general scheme for the relative reactivity and selectivity of different oxygen centered radical species.

SERMACS 1227

Transient absorption microscopy in the total internal reflection geometry

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Transient absorption microscopy (TAM) has the capability to image nonfluorescent chromophores and capture excited-state dynamics with a temporal resolution in the femtosecond regime. However, all samples are either required to be optically transparent or reflective because of the instrumental restriction of imaging in a through geometry. The through geometry requires two high numerical aperture (NA) objectives for optimal focusing of the multi-photon process in transient absorption. By utilizing a single high NA objective and a lens, we have constructed a transient absorption instrument that can excite a sample and collect signal using a single objective. The total internal reflection (TIR) geometry allows, for the first time, transient absorption to be performed on samples with only one optically accessible side. This technique is also versatile because it was applied using an established microscope base, so TIRTAM could be extended to many different microscope designs. Two different solutions of IR-144 in methanol and in dimethyl sulfoxide (DMSO) were flowed through the microfluidic device and excited-state dynamics were used as a contrast in the imaging. These images prove that our TIRTAM instrument can be used to monitor excited-state dynamics on a microfluidic platform and provides a pathway for TAM to be used as on-line detection for microfluidic reactors.

SERMACS 1228

Acoustic levitation and infrared thermography: Sound approach for studying processes occurring in isolated droplets

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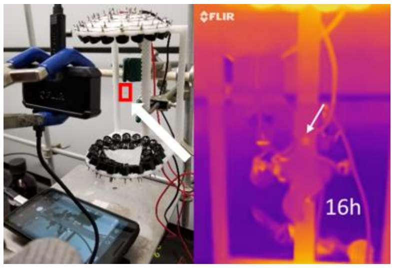
Containers such as thin films, compartments within microfluidic systems, and droplets require small amounts of solvent and therefore provide an inherently environmentally friendly alternative to reactions that take place in typical laboratory glassware and cuvettes. Additionally, reactions that take place in small volumes seem to exhibit improved rates for processes ranging from simple organic syntheses to complex protein folding. These rate increases are attributed to increased surface area availability, rapid reagent mixing times, and increased heat transport properties as compared to the bulk. Acoustic levitation is a common technique for the suspension of small volumes, most commonly droplets, in a “contact-free” container that preserves the large droplet surface area, a leading contributor to increased chemical activity. Our research group, along with our collaborators, is currently developing a technique that combines the unique properties of small volumes isolated via acoustic levitation with the in situ temperature sensing capability of infrared thermographic imaging. Using a FLIR thermal camera, our group is able to directly monitor the surface temperature of a levitating droplet. As a result of the inherently large surface area of a droplet, our technique allows for observation of the extent of a reaction or physical change and uses this data to calculate thermodynamic parameters for the chemical process. This presentation outlines preliminary results including example processes such as droplet evaporation rates of conformational isomers, in-situ measurement of acid/base neutralization enthalpies, as well as the monitoring of photo-initiated polymerization in levitated methyl methacrylate-based droplets. Results presented here indicate that the combination of acoustic levitation and infrared thermographic imaging may prove to be a central component of a powerful new calorimetric technique.



(Left) FLIR camera monitoring a levitating room-temperature ionic liquid droplet boxed in red, (Right) FLIR image of droplet after 16 hours of levitation.

SERMACS 1229

Laser spectroscopy of OCS dimers in helium nanodroplets

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Quantum-cascade laser spectroscopy was used to characterize OCS dimers embedded in ^{4}He nanodroplets. Rovibrational bands corresponding to the polar parallel and nonpolar “sulfur-in” dimers, which have previously been characterized in the gas phase, were detected in addition to a third dimer which has been predicted by theory but heretofore undiscovered experimentally. This dimer has a nonpolar, “oxygen-in” configuration and was identified using Stark spectroscopy.

SERMACS 1230

Particle-by-particle *in situ* characterization of the protein corona via real-time 3D single particle tracking microscopy

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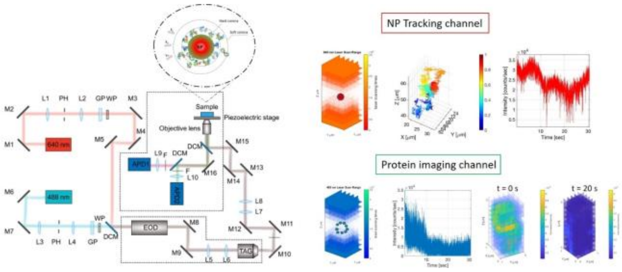
Engineered nanoparticles adsorb proteins when they are exposed to biological fluids, forming a dynamic protein corona that consists of tightly bound “hard” corona, and rapidly exchanged “soft” corona. This full protein corona alters the surface identity of nanoparticles, affecting their behavior in biological systems. However, a thorough understanding of the protein corona is lacking due to the insufficiency of current ensemble techniques. Here, we introduce real-time single 3D particle tracking microscopy to “lock-on” to single freely diffusing polystyrene nanoparticles (PSNPs) and probe their individual protein coronas in solution. Using this method, we study the protein corona content of individual PSNPs in solutions containing bovine serum albumin (BSA), immunoglobulins (Ig) and fetal bovine serum (FBS). Using mean squared displacement measurements combined with real-time protein fluorescence, we quantified “hard” corona growth particle-by-particle. Our results show the quantity of both BSA and Ig “hard” corona drop dramatically with the existence of FBS, compared to single component protein solution. It was also observed that the “hard” corona remains stable in H_2O for over 2 hours, independent on incubation time, protein identity, or concentration. Furthermore, we applied a lock-in type frequency filtering method to extract the full protein corona signal (i.e. both “soft” and “hard” corona) in high background environments. Our method enables the study of individual protein coronas without removing the particle or the protein from its native solution, opening up the possibility to study transient and dynamic protein-nanoparticle interactions which are destroyed by current bulk techniques.



Real-time single particle tracking microscopy to "lock on" freely diffusing nanoparticle-protein complex

SERMACS 1231

Covalently-linked rhodamine B dimers: Stereochemistry and photophysical interplay

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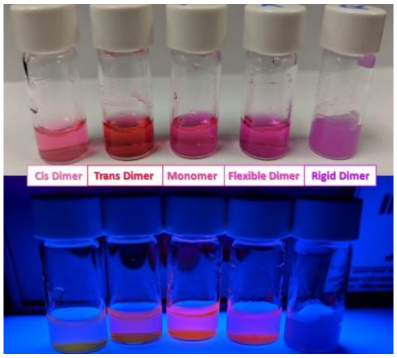
We synthesized covalently linked homo-dimers of the fluorescent xanthene dye, Rhodamine B, and subsequently explored the impact of linker stereochemistry on their photophysical properties. The dimers were linked at their carboxyl termini by 1,4-diamines with various conformational flexibilities so that the xanthene moieties are constrained to different geometries. The synthesized dimers were then characterized using absorption, emission, and fluorescence correlation spectroscopies to obtain a wealth of data, including absorption and emission maxima, hydrodynamic radii, quantum yield/molecular brightness, spectral profiles, and time-dependent photophysical processes. The variable linker stereochemistry of different Rhodamine B dimers resulted in appreciable differences in both solubility and photophysical characteristics. The data meshed well with existing theoretical models of intermolecular interaction between fluorescent dyes. The design and characterization of this model system highlights potential strategies for molecular-level control of aggregation in optically sensitive applications such as optoelectronics, laser media, and dye-sensitized solar cells.



SERMACS 1232

Thermodynamic, modeling, and neutron scattering investigation of acetylene adsorption of graphite

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While the structure and thermodynamics of many adsorbed systems of hydrocarbons have been largely studied in the literature for their applications in areas such as energy materials and the hydrogen economy, small, rigid, linear hydrocarbons such as acetylene and allene have not received as much attention. In keeping with our research group's interest in studying homologous series of adsorbed systems and the effect of molecular and surface symmetries, this study investigates the behavior of acetylene adsorbed on graphite's basal plane. This is the first in a planned series of such studies involving the simplest of the small linear hydrocarbons, acetylene and allene. Acetylene is a small, rigid, linear molecule with an anomalously high quadrupole moment. High resolution volumetric isotherms have been recorded over a range of 119 K to 140 K to obtain thermodynamic and phase information regarding these films, which indicate a potentially complex phase behavior within that range of temperatures. Additionally molecular dynamics simulations have been used to examine the molecular behavior of these films, in which we looked at the binding energies of single molecules, trajectories of films at a range of coverages and temperature, and pair correlation functions to look for ordering transitions within the trajectory files. Preliminary neutron diffraction data have also been used to investigate structure and phase transitions within this system.

SERMACS 1233

Design and development of a quartz microbalance based ethylene detector

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A recognized need for an inexpensive, portable, lightweight instrument that can be used to sensitively and selectively recognize airborne molecular gases has stimulated the design and development of a quartz crystal microbalance (QCM) based detector system. Although a variety of optical and mass spectroscopic instruments exist for such molecular detection, these methods are more expensive and not extremely portable. The QCM based detector relates changes in the resonant frequency of a quartz oscillator operating in the shear mode directlyto the mass added to the surface of the quartz crystal. The target molecule to demonstrate the performance of this QCM based instrument is ethylene. It is important to recognize that identifying the presence of ethylene gas is of interest because it serves as a hormone in plants at trace levels throughout the life of the plant by stimulating or regulating the ripening of fruit, the opening of flowers, and shedding of leaves. Hence, the ability to identify concentrated areas of ethylene "hot spots," in food storage warehouses or supermarkets could be used to effectively decrease the amount of fruit and vegetable spoilage. However, the QCM by itself is not sensitive to the presence of ethylene gas. Hence, the surface of the quartz crystal must be modified to enhance the sensitivity and selectively for ethylene adsorption on the QCM based apparatus. This heightened sensitivity was accomplished by decorating the silver electrodes on the surface of the microbalance with thin films of HKUST-1 metal-organic frameworks (MOF), made using a modification of the Eddaoudi procedure (ACS Appl. Mat. Inter., **2016,** 8, 20459-20464). The MOF coating was produced by spin casting alternating solutions of the ligand and metal ion in a series of cycles. The decorated QCM was air dried in a silica filled desiccator. The response of the HKUST-1 coated QCM when exposed to ethylene (i.e. the mass loading) is monitored by observing the changes in the oscillator frequency; an increase in mass results in a decrease in frequency. A presentation of the QCM design and operation will be given. Preliminary results show that the 8 MHz quartz crystal used in these experiments is stable to within 0.1 Hz and produces a sensor with sub-nanogram sensitivity of ethylene gas with reasonable selectivity.

SERMACS 1234

Speeding up 3D fluorescent laser scanning microscopy for live cell imaging

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Conventional point-scan 3D fluorescent imaging requires long acquisition times due to the large number of voxels that must be scanned when using a typical acquisition scheme which involves stepping a motorized stage between image planes to capture raster-scanned frames in sequence. Introduction of a continuous focal change during the raster frame scanning creates sparse 3D patterns which are repeatable and tile without multiply sampling voxels when appropriately timed. The sparsity of scanned voxels in this sampling regime enables incompletely scanned volumes to be interpolated to completion using an inpainting algorithm. This method, called 3D Fast Acquisition via Z-Translating Raster (3D-FAZTR) provides up to a 4x speed increase as compared to conventional stage-step acquisition. This theoretical framework was implemented into a modified commercial confocal microscope using an ultrafast laser and an electrically-tunable lens to image live cells and capture diffusive motion in 3D.

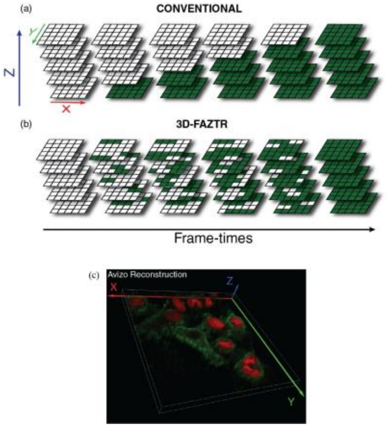

Figure 1: Demonstration of 3D-FAZTR principle and results. Fig. 1(a) demonstrates how a simple volume of size 5x5x5 voxels is filled sequentially over 5 frame-times using a conventional stage stack. Fig. 1(b) shows the same volume filled over time using the optimized sparse scanning of 3D-FAZTR. Fig 1(c) shows a volumetric reconstruction produced from a 3D image stack of live HeLa cells generated in 50% of the time required of the conventional stage stack .

SERMACS 1235

Analysis of the Calcination of Plutonium(IV) Oxalate to Plutonium(III) Oxalate

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Plutonium(IV) oxalate is known to calcine through a plutonium(III) oxalate intermediate, which necessitates a chemical and morphological change in the material. The precise mode that these microstructural modifications to the morphology would take is unknown as the precise intermediates have not yet been verified experimentally. To identify these intermediates, the potential structures for plutonium oxalate in both oxidation states were optimized using PBE-D3 with a Hubbard U correction and used to identify the specific crystal morphologies that occur during the reaction. The electronic energies will also be calculated and used to determine the preferred crystal structures for both oxidation states and the minimum energy pathway between the two intermediate compounds.

SERMACS 1236

Reactivity studies of dehaloperoxidase B with biphenol substrates: Spectroscopic and mechanistic studies

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Dehaloperoxidase (DHP) from the marine polychaete *Amphitrite ornata* is a multifunctional enzyme that possesses peroxidase, peroxygenase, oxidase and oxygenase activities. Previous research has reported that DHP catalyzes the oxidation of a diverse panel of substrates, including halo/nitrophenols, haloindoles, and pyrroles, by these activities. Herein, we investigated the reactivity of DHP isoenzyme B with a variety of biphenol substrates (2,2'-biphenol, 3,3'-biphenol, 4,4'-biphenol, and 3,3'-Br_2-4,4'-biphenol). As a previously unknown class of substrate for DHP B, the anthropogenic biphenols are both estrogenic and cytotoxic, used as lubricants and fuel additives, antioxidants, polymerization intermediates, and fungicides. Reactivity studies with these substrates were investigated using high performance liquid chromatography (HPLC), resulting in 2,2'-biphenol having the highest reactivity (89% conversion) and 3,3'-biphenol the lowest (26% conversion). The reaction products for each biphenol were determined to be oligomers (n = 2-4) by liquid chromatography mass spectrometry (LC-MS). The substrate-enzyme binding affinities were measured by UV-visible spectroscopy optical difference spectra; 2,2'-biphenol has a relatively strong binding affinity (K_d = 68 μM) for DHP B when compared to previously studied substrates. Stopped-flow UV-visible spectroscopy methodologies were utilized to investigate the mechanic details and enzyme oxidation states during the reactions. Preliminary evidence suggests a mechanism where activation of DHP B by H_2O_2 leads to the ferryl-containing Compound ES reactive intermediate, followed by reduction back to the ferric state concomitant with biphenol oxidation. The data presented here strongly suggest that DHP B could be used in bioremediation efforts of biphenol pollutants.

SERMACS 1237

Investigation into the catalytic cycle of cytochrome P-450 involving imidazolium-based ionic liquid cations as substrate in a QM-based framework

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Ionic liquids (IL) have environmentally benign characteristics like inherent low vapor pressure and flammability that have deemed them to be potentially ‘green’ solvents. They have negligible role in air emissions and their physical properties can be tuned owing to their design flexibility. Out of the several ionic liquid classes, imidazolium-based ionic liquids have been one of the most widely utilized in diverse applications such as catalysis, liquid-liquid extraction, reactive distillation among many others. Though being instrumental in driving complex industrial processes, experimental investigations have highlighted their resistance to environmental degradability. Thus, their synthesis must include rational design among other aspects. Considerable experimental efforts have been put in this direction but detailed computational investigations into the degradation mechanism have not been carried out. The concerned work aims to address thermodynamic aspects into the phenomena of ionic liquid biodegradability to aid in their future design. The superfamily of cytochrome P-450 is widely for its role in oxidation of a wide variety of biologically relevant molecules in aerobic and anaerobic environments. Thus, to develop a computational framework for IL biodegradability, it was deemed necessary to capture the effects of the cytochrome’s active site molecule on imidazolium-based ($[\mathrm{C_n mim}]^+$) cations. The enzymatic center of the P-450 molecule (heme) was modeled as an iron porphyrin molecule with an Fe-based center attached to amino acid residue cysteine (FePCys) at its proximal side to mimic its active site model. Density functional theory (DFT) calculations were performed on the active side model at the M06 level of theory. Two distinct conformations of the ionic liquid cation, namely, tail up and tail down conformations, were considered in this work varying the 1-n-alkyl chain on the cation progressively along the homologous series (n=2,4,6,8,10). Different steps of the catalytic cycle were modeled using a synchronous approach to provide insight into the molecular level properties of the complex. Result and discussion would describe the energetics and properties evaluated for the model from the binding, reduction and subsequent dioxygen insertion processes in the cycle. Also, key analysis of the interaction strength and thermodynamics of the system derived from each step would be included to provide further insight into the protein-ligand model.

SERMACS 1238

Enzymatic degradation of 4-cyanophenol pesticides with the multifunctional hemoglobin dehaloperoxidase

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For several decades, substituted 4-cyanophenols, also known as benzonitriles, have been used as pesticides in the agricultural industry and were found to contaminate surrounding water sources. Studies have shown high toxicity to freshwater fish when exposed to 3,5-dibromo-4-hydroxybenzonitrile: one case reported 2,6-dichlorobenzonitrile concentration of 100 ng/L in the Shinano River of Japan. This concentration is over the LD50 of most freshwater fish, creating a need for a detoxification system. One such system, the hemoglobin dehaloperoxidase (DHP) from the marine worm *Amphitrite ornata*, may prove to be a solution. As a hemoglobin, it provides native oxygen transport, but DHP also has four enzymatic activities: peroxygenase, peroxidase, oxygenase, and oxidase. This multifunctional globin has been found to oxidize a variety of different organic molecules, such as halophenols, haloindoles, nitrophenols, pyrroles, guaiacols, and cresols. The reactivity of benzonitriles with DHP was investigated using chromatographic (HPLC and LC-MS) and spectroscopic (UV-visible and stopped-flow UV-visible) methods. The scope of this study includes the following substituted benzonitriles: 4-hydroxybenzonitrile, 4-hydroxy-3-methoxybenzonitrile, 3,5-dibromo-4-hydroxybenzonitrile and 3,5-diiodo-4-hydroxybenzonitrile. Preliminary results show a binding affinity between DHP the substrates 4-hydroxybenzonitrile (K_d= 910 µM) and 4-hydroxy-3-methoxybenzonitrile (K_d= 1695 µM). Additionally, the enzyme has the ability to degrade two of the compounds studied, 4-hydroxybenzonitrile (17%) and 4-hydroxy-3-methoxybenzonitrile (97%). While additional studies are ongoing to identify the products of DHP-mediated benzonitrile oxidation, these results demonstrate that DHP has reactivity against these pesticides, which supports the hypothesis that DHP may have applications as a bioremediation agent to remove benzonitrile pollutants from the environment.

SERMACS 1239

Antimicrobial properties of cotton treated with altered zinc-metal based nanoparticles

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Minimizing microbial-based, hospital acquired infections (HAIs) continues to be challenging even with the most modern advances in technology and medicine. Altering Zinc metal-based nanoparticles to optimize their antimicrobial properties and incorporate them into fabrics and other materials can help minimize the presence of HAIs and help keep patients and employees in Emergency Medical Services and Military Field Operatives safe. This project takes several altered zinc metal-based nanoparticles and test them against the three most common bacterium and several present in clinical settings and determines which has the best potential to be applied with the new advances in Nanotechnology fabrics.

SERMACS 1240

Enhanced protonation of amino acids and dipeptides using Cr(III): Developing the basis for proteomics studies

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The addition of Cr(III) to peptide solutions increases the signal in electrospray mass spectrometry of some protonated species as well as multiply charged species, thus increasing the sensitivity and accuracy. Experimental work shows that both acidic or basic sites can be involved in the enhanced protonation of peptides. Computational electronic structure density functional theory calculations are being used to study the interactions of Cr(III) with neutral and anionic amino acids and acidic dipeptides to provide a detailed molecular level mechanism. Proton transfer from a water in the coordinated Cr(III)-water complex to the N-terminus or basic R-groups is predicted to occur in anionic species leading to the formation of zwitterion neutrals for amino acids and a OH^- group bonded to the Cr(III). Neutral arginine, histidine, lysine, glutamic acid, asparagine, and glutamine favor enhanced protonation. Cr(III) coordination to acidic dipeptides can occur between the carboxyl-terminus or the carboxylic acid of the R-group regardless of the position of the acidic residue in the dipeptide, but addition to the side chain is more common. When the location of the acidic residue is closest to the amine-terminus, Cr(III) addition can occur between the carboxyl-terminus and carboxylic acid side chain. This is consistent with experimental ESI-MS results, which show that heptapeptides undergo the greatest enhanced protonation caused by Cr(III) when the acidic residue is at the C-terminus.

SERMACS 1241

Corynebacterium diphtheriae heme uptake: Roles of HTaB, CHtA and ChtB

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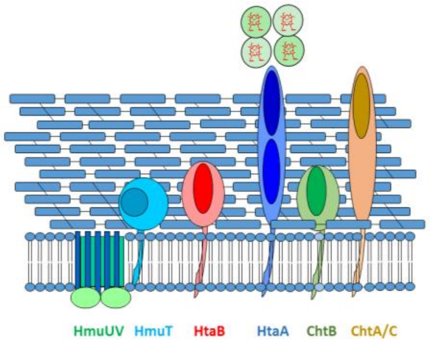
Iron is required for infection in essentially all bacterial pathogens. In vertebrate infections, the most abundant source of iron is heme, which comes primarily from hemoglobin. Bacteria have developed sophisticated approaches to transport heme into the cytoplasm. *Corynebacterium diphtheriae* uses multiple proteins to bind and transfer heme into the cell. The first pathway discovered involves HtaA, with two conserved heme-binding domains (CR1 and CR2), HtaB, HmuT, and an ABC transporter. The heme-binding protein HmuT delivers heme to the HmuUV ABC transporter. Hemoglobin, when bound to haptoglobin, serves as a heme source for ChtA, a homolog of HtaA and HtaB. Deletion of HtaB does not result in significant growth inhibition, indicating that another pathway must be present. ChtB can substitute for HtaB. Optical and Raman spectroscopies, as well as thermal and chemical denaturation, allow biophysical characterization of these proteins. Unfolding is quite slow, perhaps indicating a role for protein-protein docking in heme transfer. Axial ligation, heme pocket hydrogen-bonding interactions, and heme iron oxidation state all play a role in the mechanism of heme uptake and/or release.



SERMACS 1242

Copper-thiolate cluster selectivity and assembly in human metallothionein-3

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Metallothioneins (MTs) are cysteine- and metal-rich proteins that play central roles in Cu(I)/Zn(II) homeostasis and detoxification. In humans, four MT isoforms exist (MT-1/4) possessing 61-68 amino acids and a conserved array of 20 cysteines involved in coordination of d^{10} metal ions in two separated metal-thiolate clusters. Despite the coordination similarity, the MT-3 isoform shows a unique copper-thionein character which gives rise to its isoform-specific structural and biological functions. Zn_7MT-3 thiolates efficiently reduce Cu(II) to Cu(I) and bind it to form $Cu(I)_4Zn_4$MT-3 via cooperative formation of a redox-inert $Cu(I)_4$-thiolate cluster in its N-terminal β-domain. This reactivity underlies its protective effect in controlling biological aberrant copper-protein interactions. By using spectroscopic and spectrometric techniques we have addressed the structural features underlying the unique copper-thionein character in MT-3 over other MTs. We define the process of Cu(II) reduction and Cu(I)-thiolate cluster assembly, its Cu(I) redox-silencing properties, and compare them to other MT isoforms. We devise a novel sequential pathway for $Cu(I)_4$-thiolate cluster formation in which unique long-lived metal-stabilized disulphide radical anions are formed and metal-metal interactions exist. By conducting mutational studies, we revealed how non-coordinating residues are instrumental for outer-sphere control of Cu(I) selectivity bias in MT-3 metal cluster. We dissected their key roles in modulating cluster dynamic and metal exchange rates, in increasing the Cu(I)-affinity in MT-3 β-domain and/or modulating the higher stability of the Zn(II)-thiolate cluster in MT-2 β-domain, which shows instead a zinc-thionein character. We thus engineered variants in which the MT copper-thionein character is converted into a zinc-thionein. These studies provide new insights into the molecular determinants governing metal selectivity and assembly in metal-thiolate clusters.

SERMACS 1243

Investigation of the catalytic cycle of [FeFe] hydrogenase using time-resolved infrared spectroscopy

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Hydrogenases (H_2ase), and in particular [FeFe] $h_2$ases, provide a tantalizing model for a H_2 production catalyst. Despite considerable effort devoted to unraveling the mechanistic details of the [FeFe] $h_2$ase catalytic cycle, there remains several questions in the field. The lack of cohesion highlights the need for a fresh approach to studying this enzyme. We hypothesized that time-resolved IR kinetics of intermediates of an [FeFe] H_2ase would yield critical insight into the catalytic mechanism. The CO ligands bound to the active site are excellent reporters for the redox state of the active-site and so serve as convenient spectroscopic handles for time-resolved measurements. With this technique we measured the formation rates and respective decay rates of intermediate states and established the kinetic competency of some controversial intermediates. We have been able to discern the roles of several of the disputed intermediates and have a better understanding of the role of the [Fe_4S_4] clusters in the catalytic cycle. With the results of this study we tentatively present the first catalytic cycle modeled exclusively on kinetic measurements made under sub-turnover conditions.

SERMACS 1244

Development of a genetically-encoded methyltransferase biosensor

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Methyltransferases catalyze the transfer of a methyl group from S-adenosylmethionine to various carbon, oxygen, and nitrogen-containing substrates across all domains of life. Methyltransferases target a remarkable diversity of substrates including DNA, proteins, and secondary metabolites. For example, several classes of natural product pathways utilize methyltransferases as a tailoring enzyme and whereby methylation is required to achieve full bioactivity. Other critical functions of methyltransferases include cell signaling and epigenetic regulation. Manipulation of methyltransferase specificity would aid in efforts to redesign natural products for drug discovery and to control complex biological systems. However, our ability to engineer the activity and specificity of methyltransferases is limited by our insufficient understanding of methyltransferase structure and function. Directed enzyme evolution could address this but critically relies on a high-throughput screen for methyltransferases that does not currently exist. This research focuses on developing a biosensor that can be used to report the activity of methyltransferases in a general and high-throughput manner. Bacterial transcription factors are regulatory proteins that modulate gene expression in response to intracellular metabolites that offer the opportunity to develop a high-throughput methyltransferase screen. With the proper configuration, biosensors based on transcription factors couple small molecule binding to a reporter signal. Here, a transcriptional repressor protein that is known to naturally recognize S-adenosylhomocysteine (SAH), the common by-product of most methyltransferase reactions, is used to develop a biosensor for detection of methyltransferase activity inside living cells by coupling SAH binding to expression of a fluorescence reporter gene. It is expected that a transcription factor-based methyltransferase biosensor will enable directed evolution of any methyltransferase, setting the stage to develop engineered enzymes for natural product bioengineering and other applications.

SERMACS 1245

Observations, hypothesis, and consequence in the role of selenium and selenocysteine into HIV *Nef* protein expression and Zika viral RNA interactions with host cell mRNA and protein expression

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Selenium is an important micronutrient in terms of redox reactions in the body and the development of neuronal cells. Selenium is incorporated into mammalian selenoproteins with amino acid selenocysteine, where instead of a sulfur atom in the sidechain of the amino acid, there is a selenium atom. Selenocysteine is created by a ribosomal readthrough of a UGA stop codon. Our group has conducted extensive experiments that highlight an unlikely correlation around the addition of selenium to cells that have been transfected with plasmid constructs mimicking the HIV viral genomes specifically surrounding the expression of the HIV *nef* protein. Addition of selenium into the cell media allows for a readthrough of a highly conserved UGA stop codon in the HIV genome that supposedly terminates the transcription of the *nef* gene. This readthrough also leads to a frameshift, which we have documented. Our group is interested into what this means to HIV in terms of possible advantages the virus has in selenium rich environments. We have also identified and tested several favored interactions between Zika viral (ZIKV) RNA and host cell mRNA coding for the expression of selenoproteins selenoprotein P (SePP1) and thioredoxin reductase 1 (TR1). Our group believes these possible interactions between host cell mRNA's coding for selenoproteins and ZIKV RNA could shed light as to why microcephaly is reported in cases where the mother was pregnant at the time of viral infection; since SePP1 is expressed highly in placental cells and essential to the transport of selenium into the brain for neuronal development. The goal of this talk is to surmise our groups observations into the behavior of these viruses; primarily regarding how there seems to be some affinity/motivation/advantage for these viruses in the presence of environmental selenium or host cell selenocysteine and hypothesize as to why that may be.

SERMACS 1246

General chemistry lab practical exams at Augusta University

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In the course of evaluating our chemistry program learning outcomes, we recognized that although one of our goals for our students was for them to be proficient with standard laboratory equipment and techniques, we never assessed those skills. In order for us to evaluate whether general chemistry students were gaining proficiency with basic laboratory skills, we decided to institute a lab practical exam. Looking at the experiments students performed during our general chemistry courses, the skills imbedded in those experiments, and the skills that would translate to the most upper division courses (in all sciences), we decided to focus our assessment on making solutions. In the spring of 2018, the first lab practical exam was designed and implemented by the general chemistry faculty to assess our students' ability to prepare a solution safely and correctly. We designed a detailed rubric that was used during the examination period to monitor the students' proficiency in several areas of interest including calculation of appropriate amounts of reagent used to make the desired solution, choice of appropriate glassware to make the solution, accuracy of concentration of prepared solution, and (for second semester students only) appropriate use of the visible spectrophotometer. During the lab practical, only 3 to 5 students were present in lab at a time (in 30 minute time blocks) carrying out their individual assignment during which time several faculty and/or teaching assistants directly observed the student's work and filled in the rubric. After running lab practical exams for several semesters now, we have developed an effective method for assessment of basic laboratory skills and modified our course based on what we learned and have seen improvement in the performance of students on measured outcomes.

SERMACS 1247

Teaching organic chemistry concepts to non-science majors

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Georgia Gwinnett College designed its physical science courses to be theme based, lending to a variety of physical science themes for non-science majors. One of these themes is founded in organic chemistry and introduces students with little to no chemistry background to the field of carbon chemistry. In the first half of the semester, basic chemical instruction prepares students for application of chemical concepts to their chosen areas of focus for the second half of the semester. At the end of the term, each student researches and presents one side of a debate involving some issue related to Organic Chemistry. Additional insights from this course will be presented.

SERMACS 1248

CalLevIR: Modern alternative to coffee cup calorimetry

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Recent experimental evidence suggests that chemical processes that occur in small volume containers such as thin films and microdroplets exhibit increased rates of reaction in processes ranging from various syntheses to protein folding. This increase has been attributed to the increased surface area to volume ratio in a small volume which results in rapid mixing times and increased heat transport time properties as compared to the bulk. Acoustic levitation is one method of droplet generation which allows chemistry to take place within a "contact-free" volume via a standing acoustic wave. Acoustic levitation has proven a reliable method for use in various processes such as protein structure analysis, crystal nucleation and development, and Raman spectroscopy. The resulting liquid sample isolation increases the liquid-air interfacial area, thereby increasing the rate of reaction for mechanisms dependent on surface area, such as heat transfer. Furthermore, the increased surface area of droplets enables the use of surface temperature measurement techniques, such as infrared (IR) thermography, to monitor the extent of these processes. This work focuses on combining acoustic levitation and IR thermography to develop a calorimetric technique suitable for studying reaction enthalpies which provides an alternative to the popular "coffee cup" calorimeter used in thermochemistry instruction. "Coffee cup calorimetry" is a common undergraduate chemistry experiment in which the student determines the heat of neutralization for a strong acid and strong base using a Styrofoam coffee cup. We propose an alternative methodology to bulk measurement by which a small volume of strong acid is injected into an acoustically levitated droplet of strong base whereby the resulting heat released is monitored using an IR thermal imaging camera. We also demonstrate a technique used to create a calibration curve correcting for the increased heat transfer rate of the droplet. Correcting the measured enthalpies of neutralization yields values in agreement with the literature value for this reaction, approximately -57 kJ/mol. The results we present here suggest that a combination of acoustic levitation and IR thermography is a viable method for measuring reaction enthalpies within droplets and provides a "modern" update to a classic general chemistry laboratory that uses technology that is exciting for students, needs less preparation time, and consumes less resources.

SERMACS 1249

Culinary transformations: Translating chemistry for non-majors

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How do we engage students outside their major discipline to learn chemistry? This is a persistent challenge since student perceptions of a discipline often impact enrollment and motivation. Recent curriculum changes have led to increases in science course offerings for non-majors not only to bolster science literacy but also to demonstrate the relevance and impact of science on their everyday lives. This presentation will detail the design of a course (Culinary Transformations) connecting food and chemistry utilizing ACS anchoring concepts and experiential learning techniques. Preliminary assessment of student learning outcomes will be disclosed.

SERMACS 1250

Redesign of general chemistry with digital and adaptive learning courseware/technology supported high-touch student services

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We will describe the motivation for implementing course redesign in General Chemistry I & II, how Clark Atlanta University piloted and assessed course redesign with digital and adaptive learning courseware. We will describe our path to scale up and scale out course redesign with digital and adaptive learning courseware, student learning outcomes and student perceptions of the intervention, faculty development activities to support implementation of course redesign at scale, and how we developed resources to support this effort. We will describe challenges to course redesign with digital and adaptive learning courseware and how we are working to overcome them. We will also describe the development and implementation of holistic student services enabled by analytics to further improve student learning outcomes.

SERMACS 1251

Impact of group quizzes in undergraduate organic chemistry

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Previous studies have repeatedly shown that group work is beneficial to students in undergraduate chemistry courses. However, many undergraduate chemistry courses are of a large lecture format and the challenges of integrating collaborative work into large lecture sections are well known. While there have been several attempts to make collaborative learning suitable for a large classroom, to our knowledge, no work has been done on the impact of group quizzes in chemistry. We hypothesize that group quizzes will not only result in collaboration on the quizzes, but encourage collaboration outside of class on the associated homework assignments, ultimately resulting in higher student quiz and exam performance. In this study, first-semester organic chemistry students take nine quizzes, each covering one chapter of material. The first and last three quizzes are group quizzes, and the middle three quizzes are individual quizzes. On each quiz, student behavior is observed, and students are asked to indicate how much of the associated homework they worked on with other people. On each of three exams, students are asked how much the group (Exams 1 & 3) or individual (Exam 2) quizzes helped them prepare and improved their confidence. Finally, at the end of the semester, a survey is disbursed covering student perceptions of both types of quizzes, as well as help sessions in general. Student level of collaboration on homework is analyzed by type of quiz. Student performance on the quizzes and exams is analyzed by type of quiz and level of collaboration. Performance on group quiz and individual quiz topics on the ACS final exam are compared.

SERMACS 1252

Development of an instrument to comprehensively assess core concepts in general chemistry

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General chemistry has served as the gateway for approximately 500,000 entry level students per year choosing to study in the STEM program for several years and there is no evidence that it is instilling an understanding of chemical principles, due to a lack of reliable measures. Therefore, it is our long-term goal to develop an instrument that produces evidence by targeting general chemistry concepts, which measures students' comprehension of the core learning objectives. This instrument is designed to test general chemistry students' understanding of the fundamental principles of atomic and molecular behavior, using only the context of water. The instrument consists of four tiers: multiple-choice questions, explanation questions, and a confidence rating for both tiers. A pilot version of the instrument which included an open-response explanation tier, was administered to General Chemistry 2 students (N~600). The student responses have been collected and will be analyzed to generate a close-ended explanation tier for the pilot test. Generation of the close-ended explanation tier will take place by using a method of comparison to find a pattern in the students' explanations to ultimately reveal a positive or negative understanding of the fundamental principles of atomic and molecular behavior in the context of water. Using these responses to create a close ended explanation tier allows researchers to more accurately explore the ideas that students have about the content. A high measure in validity from the instrument will show that students' comprehension of general chemistry content is being accurately captured. Overall the outcome is to develop an instrument that provides reliable and valid evidence of students' knowledge of fundamental chemical principles.

SERMACS 1253

Increasing the yield in general chemistry: How students think about stoichiometry

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Stoichiometry is a threshold chemistry concept that is foundational across science, technology, engineering, and mathematics (STEM) areas. Previous studies indicate that although students are able to solve problems, they may feel limited and struggle with understanding the problem and putting it into context. Because students often have a difficult time conceptualizing stoichiometry, solving stoichiometric problems, and explaining their reasoning in a problem, both course performance in chemistry and persistence in STEM are reduced. In this study, I use a phenomenographic approach to qualitatively explore the different ways students conceptualize stoichiometry in general chemistry. My research findings will help bridge chemistry education research with instructional practices. The existing literature lacks a theoretical framework or model to describe the various ways students conceptualize and connect fundamental topics when solving stoichiometric problems. I will present a combination of two theories guiding the work: Action, Process, Object, and Schema (APOS) theory and Knowledge Space Theory (KST). A study combining APOS theory with KST has not previously been seen in chemistry education research literature. The combination of these two theories provides a strong foundation for exploring student conceptualization, allowing me to identify students' various knowledge states and further dissect how KST is embedded in APOS theory. I will present early results and a partial model of the different ways general chemistry students conceptualize stoichiometry. Once completed, the model will inform future studies in chemistry education and provide a foundation for instructors and curriculum developers to improve ways to help students understand stoichiometry. If students can understand stoichiometry, they are more likely to pass their general chemistry course, which can affect their decisions in pursuing a degree in a STEM field.

SERMACS 1254

Developing and maintaining a multi-year, multi-disciplinary faculty learning community focused on the implementation of a specifications grading assessment protocol in courses at Georgia Gwinnett College

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Starting in the fall semester of 2017, a Faculty Learning Community (FLC) initially formed to focus on adapting select sciences courses to a specifications grading approach at GGC. Specifications grading (SG) is an assessment protocol based on mastery learning, clear learning objectives, and frequent evaluations/feedback. Students control their grades through multiple attempts (with limitations) on assessments of course objectives. While SG was initially applied to chemistry courses, the FLC has now grown to include members teaching courses in biology, chemistry, math, physics, biochemistry, microbiology, exercise science and environmental science. In this FLC, practitioners share their common experiences, gain knowledge from the collective, share resources and advice on best practices, and assist with proctoring. The diversity of academic backgrounds within the FLC particularly provides an opportunity to share different teaching pedagogy. As the FLC has grown and matured, focused sub-groups have been developed based on individuals interests. Details on how the FLC formed, has operated, has developed an electronic sign-up retake system, has evolved and the roles of the sub-groups will be discussed.

SERMACS 1255

Only time will tell: Imagining the future of the scientific poster

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During my final semester as an undergraduate student, I assembled and presented my first scientific poster to complete my B.S. in Chemistry. While subsequently interning at the American Chemical Society, I came across an article proposing a new format for posters that could possibly improve the efficiency of poster sessions. With my research poster only a few months old, I decided to test how effectively I could translate my traditional poster into one incorporating this new design. Over the course of this presentation, I will walk through my initial thoughts of the article, the process for adapting my original poster, and my evaluation of how well the revised version of the scientific poster communicates the same results.

SERMACS 1256

Chemical Facility Anti-Terrorism Standards (CFATS)

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The Chemical Facility Anti-Terrorism Standards (CFATS) is a program that identifies and regulates high-risk chemical facilities to ensure they have security measures in place to reduce the risk of a terrorist attack associated with more than 300 chemicals of interest (COI). If held in specified quantities and concentrations, these chemicals trigger reporting requirements under CFATS. The program currently regulates approximately 3,000 high-risk facilities.

SERMACS 1257

Novel coordination and catalytic properties of Pd(II)-compounds of di-2-pyridyl ketone hydrazonic compounds

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Di-2-pyridyl ketone hydrazonic compounds (dpk-h) react $PdCl_2(CH_3CN)_2$in CH_3CN in air at room temperature to form $[PdCl(h^3\text{-}N_{py},N_{im},O\text{-dpk-h})]Cl$ (h = hydrazine moiety) and when dpk-tsc (tsc = thiosemicarbazone moiety) was used $Pd_2Cl_3(h^5\text{-}N_{py},N_{im},S,N_{py},N_{am}\text{-dpktsc})$ where py = pyridine, im = imine, and am = amide. Spectroscopic and X-ray crystallographic data confirmed the identities of the compounds. Electrochemical measurement in the presence and absence of a proton source revealed sequential electronic transfers and significant hydrogen evolution. The Pd-dpk-k and Pd-dpktsc compounds were tested toward Suzuki-Miyuara C-C cross coupling and showed good activity for the coupling of aryl bromides and phenyl boronic acid.

SERMACS 1258

Synthesis, characterization, and reactivity of bis(phosphino) pyrrole ligands and their complexes

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Aminophosphine ligands are used in a wide range of applications, including catalysis, and have proven to be effective in cross-coupling reactions. We have successfully prepared a library of N-phosphino-2-(phosphino)pyrrole ligands along with their corresponding nickel, palladium, and platinum complexes. The facile, two step-synthesis of these ligands demonstrates their modular nature. The reactivity of the metal complexes was tested in several C–C and C–N cross-coupling reactions and the impact of ligand identity on catalytic activity was evaluated.

SERMACS 1259

Synthesis, characterization, and reactivity of palladium proazaphosphatrane complexes

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Transition metal catalysts enable the synthesis of a wide array of compounds that otherwise might be completely inaccessible. The synthesis and reactivity of palladium proazaphosphatrane complexes that are believed to be intermediates in C–N cross-coupling reactions are described. The findings support the long-standing hypothesis that fluctuating transannulation in proazaphosphatranes enables conformational changes that stabilize catalytic intermediates. The catalytic ability of the proazaphosphatrane complexes as intermediates is verified through stoichiometric and cross-coupling reactions.

SERMACS 1260

Understanding the photophysics of Ln(III) doped nanoparticles

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Lanthanide ions are employed in luminescent materials due to their high quantum efficiencies and narrow linewidths. However, a sensitizing ligand is necessary to populate the excited states of the lanthanides due to *f-f* transitions having a low molar extinction coefficient caused by the Laporte forbidden transitions. The use of sensitizing ligands has been termed the molecular antenna effect and has been extensively study in lanthanide complexes. These studies have shown the distance of efficient energy is 10 – 20 Å, and highly dependent on the energy of the $^3\pi^*$ energy level of the ligand relative to the lanthanide f-f levels. Earlier studies on EuY_2O_3 and $Eu:ZnAlO_4$ in our group have shown that TTA is very effective sensitizing Eu^{3+} emission. This presentation will discuss the photophysical properties of Ln(III) doped nanoparticles by interpretation of quantum yields, lifetimes, photoluminesce, as well as structural characterization of these doped nanoparticles.

SERMACS 1261

Synthesis and reactivity of benzyl-silyl phosphines for transition metal complexation

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The synthesis of novel Ruthenium complexes bearing diphosphine-disilane was achieved from the reaction between $[Ru(Cl)_2(CO)_3]_2$ and $(C_6H_5)_2P(C_6H_4)CH_2Si(R)_2\text{-}X\text{-}Si(R)_2CH_2(C_6H_4)P(C_6H_5)_2$ (Where R= Me, Ph, ^{i}Pr and X= none, O, CH_2CH_2). Nuclear magnetic resonance spectroscopy (NMR), Infrared spectroscopy (IR) and single-crystal X-ray diffraction were used to characterize the new species. In particular, Ruthenium (II) and Ruthenium (III) complexes were found to firm macrocycles by axial coordination of the unmodified ligands. On the other hand, mixed valance and 14 electron complexes of Rhodium and Iridium were also accessed from the reactions of $PhP(o\text{-}C_6H_4CH_2Si^iPr_2H)_2$. The chemistry of the new species towards a variety of reagents was also investigated as was their catalytic activity in dehydrogenative silylation and hydrosilylation.

SERMACS 1262

Sterically encumbered dianionic dicarboranyl pincer ligand $(c_5h_3n)(C_2B_{10}H_{11})_2$ and its nickel(II) complex

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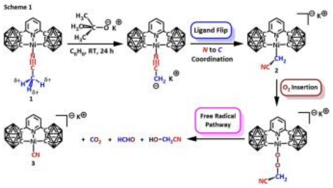
Carboranes are of topical interest due to their unique structures and applications in the fields of catalysis, polymers, material sciences and supramolecular chemistry. Icosahedral closo-dicarbadodecaboranes are remarkably robust three-dimensional boron-carbon clusters with two slightly acidic C-H bonds. Coordinatively unsaturated transition-metal complexes containing C-functionalized ortho-carborane are considered as potential catalysts for activation of small molecules. Recently, we reported the synthesis of a pyridine-backbone pincer complex $\{(C_5H_3N)(C_2B_{10}H_{10})_2\}Ni(CH_3CN)$ (1) in which two ortho-carboranes act as the arms of the pincer ligand. The complex 1 was found to be a competent catalyst for nucleophilic addition of piperidine to acetonitrile. Upon addition of KOtBu, we observed activation of a C-H bond of a labile acetonitrile ligand at the nickel center, and N-bound acetonitrile ($Ni\text{-}NCCH_3$) was converted to a C-bound cyanomethyl ligand ($Ni\text{-}CH_2CN$). Oxidation of $K\{(C_5H_3N)(C_2B_{10}H_{10})_2\}Ni(CH_2CN)$ (2) by oxygen yielded a cyano complex $K\{(C_5H_3N)(C_2B_{10}H_{10})_2\}Ni(CN)$ (3), along with HCHO, CO_2, $HO\text{-}CH_2CN$ and another unidentified compound. EPR and 1H NMR studies revealed that the reaction followed a free radical pathway (Scheme 1). Currently we are working to identify the active free radical species by using a spin trapping agent, 5,5-Dimethyl-1-pyrroline N-oxide (DMPO). Furthermore, we observed the formation of acrylonitrile and acrylamide by coupling of acetonitrile with aldehyde at the nickel center.



Activation mechanism of C-H and C-CN bonds of acetonitrile at Ni(II) center

SERMACS 1263

Nickel catalysts supported by redox active ligand scaffold for aziridination

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Transition metal mediated aziridination reactions have been shown to be effective synthetic strategies for complex molecules with potential biological applications. Recent efforts in this area have been focused on developing highly efficient aziridination reactions using earth abundant transition metal catalysts. This presentation will describe our group's efforts to develop Ni(II) catalysts for aziridination reactions. The synthesis and characterization of a series of distorted square planar Ni(II) complexes supported by redox-active ligand scaffolds that incorporate *N*-amidate donors will be reported. The ability of these complexes to catalyze aziridination reactions, including aziridination reactions using aryl azides and PhINTs as nitrogen sources will be described. Studies to elucidate the potential reaction mechanism will also be discussed.

SERMACS 1264

Development of modular bis(phosphino) pyrrole ligands for late metal-catalyzed cross-coupling

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Modular ligand architectures permit systematic modification of transition metal catalysts. Such ligand design also facilitates rational development of new ligands and establishment of structure-reactivity relationships. Bis(phosphine) compounds represent a particularly versatile class of ligands for cross-coupling; however, the synthesis of these ligands often require multiple purification steps and expensive starting materials. To address these obstacles, our lab has developed a class of bis(phosphino) pyrrole ligands that can be accessed in a single step from a common intermediate and can be purified by crystallization. Ligands of dramatically different steric and electronic properties are accessible in this concise synthesis. These ligands are easily metallated using late transition metals and the resulting complexes are competent precatalysts in cross-coupling. Furthermore, we have examined the electronic properties that our new ligands impart in comparison to their phenylene congeners.

SERMACS 1265

Thermodynamic characterization of Ca(II) and Cd(II) binding to wild type and mutant C35A, C84A, and C35A/C84A HcTnC using isothermal titration calorimetry and inductively coupled plasma optical emission spectroscopy

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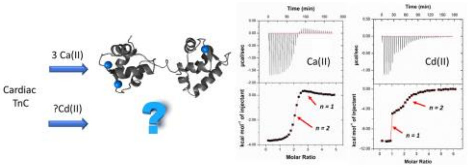
Metals play critical structural, signaling, and catalytic roles in biological systems. As such, biological systems have evolved to maintain an acute essential metal homeostasis. Divalent cadmium, Cd(II), is a toxic heavy metal that can disturb this delicate balance, leading to a disruption in biological pathways. Cd(II) can disrupt these pathways through its ability to mimic essential metals such as calcium, Ca(II). However, not much is known regarding the binding affinity and stoichiometry of Cd(II) to metal binding proteins. The model protein of interest in this study is Human Cardiac Troponin C (hcTnC), which is an EF-hand protein that natively binds Ca(II) to regulate heart muscle contraction. Previous studies in the Spuches Lab have shown that there are two Cd(II) binding events to wild type hcTnC, but the location and the stoichiometry of these binding events are still unknown. Therefore, the purpose of this study is to determine the binding characteristics of Ca(II) and Cd(II) to wild type and mutant C35A, C84A, and C35A/C84A hcTnC using isothermal titration calorimetry (ITC) and inductively-coupled plasma optical emission spectroscopy (ICP-OES). Ca(II) titrations reveal that the first two Ca(II) ions bind with similar thermodynamic parameters in all mutant constructs, but the third binding event has altered enthalpies and entropies, despite equal Gibbs free energy values. Cd(II) titrations reveal that the there are two exothermic heat events, with the first heat event binding much tighter than the second event and a total of approximately three Cd(II) ions binding. Our current Cd(II) binding model suggests that Cd(II) is binding to Loops III & IV of the C-Domain, as well as one of the loops in the N-Domain. These results have implications on Cd(II) routes of toxicity and EF-hand protein structure, as well as implications on Cd(II)-mediated heart disease.



SERMACS 1266

Modulation of proton movement at the active site of a [NiFe]-hydrogenase: Cooperativity between the first and second coordination spheres

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Metalloenzymes catalyze a variety of reactions with large turnover frequencies and minimal overpotentials. These properties have caused interest to utilize components of the enzymes as frameworks of catalysts for chemical feedstock and fuel production. A key component of these enzymes is facile proton movement; unfortunately, factors controlling proton moment in bioinorganic enzymology are largely elusive, but critical to understand for designing sustainable and economical catalysts feasible for widespread use. The simplest of these enzymatic processes is the deceptively elementary $H_2 \leftrightarrow 2H^+ + 2e^-$ interconversion carried out by hydrogenases, which are thus model enzymes to study the principles of bioinorganic proton transfer. The elementary proton-coupled electron transfer mechanism at the bimetallic $(CN)_2(CO)Fe^{II}(\mu\text{-Cys})_2Ni(Cys)_2$ catalytic core of the soluble hydrogenase-1 from the *Pyrococcus furiosus* is well understood, but role of the protein scaffold during proton transfer remains unclear. However, it is known the first and second coordination spheres orchestrate bridging hydride formation between the nickel and iron atoms, and also facilitate proton movement to and from the catalytic core. We utilized site-directed mutagenesis to study these processes. One variant had a conserved arginine above the active site bridging position mutated to a lysine. Standard activity assays, H/D exchange, and infrared spectroscopy demonstrated the arginine guanidinium functionality is essential for the catalytic bias and stabilizing bridging hydride formation when the nickel atom is in a critical +3 redox state, with lysine variant stabilizing a low valent tautomer with a protonated terminal cysteine, which we estimated to have a $pK_a > 8$. Another variant mutated a glutamic acid adjacent to this cysteine to a glutamine. Time-resolved infrared spectroscopy demonstrated the glutamic acid functions as a proton relay beyond this cysteine. Our results provide insight into the interplay of electrostatic and protonation events to aid designs of bioinspired redox catalysts.

SERMACS 1267

Selective imine and amine synthesis catalyzed by a well-defined cobalt complex and a base

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The first well-defined cobalt complex supported by a tripodal ligand has been employed for the selective synthesis of secondary amines and imines from primary alcohols and amines. Base amount (KO^tBu) played a crucial role to switch the resulting products (amines vs. imines) with high chemoselectivity. A variety of primary alcohols and amines including aromatic and aliphatic substrates, were selectively converted to secondary amines and imines in good to excellent yields. Additional experiments indicate that borrowing hydrogen (BH) mechanism, a commonly recognized mechanism for base transition metal-catalyzed N-alkylation of amines with alcohol to generate secondary amines, is not responsible for amine formation. Notably, it is further revealed that our selectivity control strategy is also viable for C-alkylation of secondary alcohols with primary alcohols to selectively afford ketones or alcohols, indicating the generality of this method.

SERMACS 1268

Early transition metal complexes for C–N bond formation: New insights towards DNA hybrid catalysis

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Finding alternates to increasingly expensive chiral ligands, especially by biological based methods, has been of interest in recent years. DNA has been shown to be a reasonable chiral source, which is able to impart enantioselectivity onto a series of copper complexes for Lewis acid-based reactions. However, little has been done in quantifying how the interactions between metal complexes and DNA foster this selectivity. To expand this, a series of different transition-metal dependent catalysts have been synthesized and their reactivity alongside their DNA binding affinity has been quantified. Connecting reactivity and selectivity to the catalyst/DNA interactions can help to tailor a new generation of enantioselective DNA hybrid catalysts. Expanding the scope of reactions is also of interest, as very few non-Lewis acid reactions have been performed with these hybrid systems, so aziridinations and other reactions have been performed and the latest results will be presented.

SERMACS 1269

Tuning the frequency of localized surface plasmon resonances

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Localized surface plasmon resonance research has been extended from noble metals to doped metal oxide nanoparticles. Unlike noble metal nanoparticles, the carrier density of metal oxide semiconductors can be tuned by doping. The ability to tune the plasmon frequency offers potential applications in optoelectronics and sensing. Here we present the tuning of the plasmon frequency of tin(IV) indium oxide nanoparticles through the near-IR by doping with gallium(III). Doping with gallium(III) results in fine-tuned control of the resonant frequency, as well as well-defined Vegard behavior in the nanoparticles. The LSPRs and optical band gaps are characterized by UV-Vis-NIR spectroscopy, while the crystal structure and Vegard behavior are studied via pXRD.

SERMACS 1270

Understanding ORR/OER catalysis in alkaline media using $MnFe_2O_4$ and $LaNiO_3$: Towards epitaxially grown bifunctional catalysts

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The efficient catalysis of oxygen reduction (ORR) and evolution (OER) is highly sought-after chemistry in relation to the effective implementation of fuel cells. Currently the most effective catalysts for these reactions are platinum metal and RuO_2, which are costly to implement and have poor stability in alkaline solutions. A significant amount of ORR and OER research has focused on elucidating the reactivity of transition metal oxides (TMOs) that use metals such a Mn, Co, Fe, and Ni. TMOs with the spinel and perovskite structure have shown activity towards ORR and OER, respectively. The mechanisms for ORR and OER are complicated due to the involvement of four protons, four electrons, and O_2 double bond cleavage and formation. To gain a better understanding of these mechanisms within the spinel and perovskite structure, $MnFe_2O_4$ and $LaNiO_3$ grown via molecular beam epitaxy (MBE) have been evaluated electrochemically and structurally for their catalytic properties. MBE provides precise control over stoichiometry and exposed crystal faces in materials, meaning the effect of these variables on catalysis can be measured. Achievement of a single material that can effectively catalyze both reactions simultaneously is the goal of this project. The growth of hetero-composite films via MBE, with a perovskite matrix and spinel pillars, could function as an effective bifunctional catalyst.

SERMACS 1271

Exceptionally high C_2H_2 adsorption affinity in robust ultramicroporous metal–organic frameworks

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Two robust ultramicroporous metal–organic frameworks (MOFs) were synthesized by combining $[M(pdt)_2]^-$ (M = Cu, Ni; pdt = pyrazine-2,3-dithiolate) building units with Cu^{2+} ions; they are denoted **NKMOF-1-Cu** and **NKMOF-1-Ni**. Experimental gas adsorption measurements revealed that both MOFs exhibit exceptionally high C_2H_2 uptake at ultra-low pressures. The zero-coverage isosteric heat of adsorption (Q_{st}) value for C_2H_2 in **NKMOF-1-Ni** is close to 60 kJ mol^{-1}, which is among the highest reported in the literature. In contrast, the low-pressure uptake and Q_{st} for other gases such as C_2H_4, CO_2, and CH_4 in this MOF are much lower. Ideal adsorbed solution theory and column breakthrough experiments indicate that **NKMOF-1-Ni** displays the highest selectivity yet for C_2H_2/CO_2 and C_2H_4/CH_4 mixtures. Grand canonical Monte Carlo simulations revealed that C_2H_2 adsorbs at two main binding sites in both MOFs: (1) between the pyrazine units and (2) between the MS_4 units. Single-crystal X-ray diffraction measurements for C_2H_2 in **NKMOF-1-Cu** at low pressure revealed the same primary binding site as predicted through modeling. Periodic density functional theory calculations for C_2H_2 localized at the two sites in both MOFs produced adsorption energies that are comparable to the corresponding experimental C_2H_2 Q_{st} values.

SERMACS 1272

Physical and electrochemical properties of copper deficient $CuCrO_2$ for application in Li-ion batteries

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Transition metal oxides are often used in conjunction with carbon black as the cathode material in Li-ion batteries. While these materials are extensively studied and used in commercial production, studies on defect states of these materials and how their properties are influenced is scarce. Here we report the synthesis of delafossite and propose synthetic approaches for inducing defects. Through electrochemical and synthetic lithiation, adjusting synthetic parameters, and modification of paste and film development, the effects on and electrochemical properties were studied. The pH of the solution during synthesis as well as using acidic or basic solutions to wash the product is shown to impact the concentration of Cu vacancies and phase of the sample. Doping synthetically with lithium at varying concentrations, as well as electrochemically lithiating the sample, influences the observed physical and electrochemical properties of the material based on EDS and pXRD data. TEM is being explored more extensively to determine if such results are predominately caused by a change in the size distribution of the nanoparticles, or whether synthetic conditions cause the material to be amorphous or crystalline. In the presence of $LiClO_4$, CV presents drastic changes in faradaic current which signifies increased electron transfer within the system. Lithiation of the material and synthetic conditions also influence the charge and discharge of the system via chronopotentiometry. Further studies of defects states in delafossite will aid in developing a firm understanding of how these states influence other properties. These findings may be used to aid researchers in developing more efficient cathodic materials for Li-ion battery development and production.

SERMACS 1273

Using thiazolothiazoles as highly stable and highly fluorescent bridges for electrochromic and membrane voltage sensing applications

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The electrochemical and spectroscopic properties of thiazolothiazole compounds are well-suited for a variety of optoelectronic applications involving fluorescent sensing and electrochromism. Symmetric, alkylated dipyridinium TTzs are a viologen-like compound which show reversible, two-electron reductions and on/off fluorescence with high quantum yields. Similarly, asymmetric, donor-acceptor TTz derivatives have also been developed that demonstrate strong, positive solvatofluorochromism with Stokes shifts between 40 and 130 nm depending on solvent polarity. These asymmetric TTzs demonstrate fluorescence quantum yields greater than 0.9 and large changes in their dipole moments ($\Delta\mu$ = 13 - 18 D), thus making them good candidates for cellular membrane voltage sensing. In vitro cell studies indicate good membrane staining, minimal background noise, enhanced photostability, and promising cell membrane voltage sensitivities. Given their bright fluorescence and high stability, TTzs can be expected to serve as effective conjugated bridges in a wide variety of similar applications.

SERMACS 1274

Materials discovery via family expansion: Structure prediction in the wadeites and superwadeites

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A very desirable goal within solid-state chemistry is the ability to predict a structure, either conceptually or computationally, prior to its discovery. This is typically achieved conceptually through the elucidation of a family of compounds, whose understanding can then be used to predict new compounds within the family. The Wadeite structure type, named after $K_2ZrSi_3O_9$, is a versatile structure type with formula $A_2BT_3O_9$(A = alkali metal; B = tetravalent cation; T = Si, Ge). The B cation has been reported to be main group, transition metal, and actinide elements. Of the lanthanides, only Ce, Pr, and Tb commonly adopt a tetravalent configuration, with Ce(IV) being readily obtained under flux growth conditions. We have synthesized $A_2CeSi_3O_9$(A = Rb, Cs) and $Cs_2CeGe_3O_9$crystallizing in the Wediete structure type. Changing the B cation to a trivalent rare earth results in a new family of compounds, dubbed the superwadeites, that are related to the Wadeite structure by polyhedral substitution. Elucidation of this structural family allows for the prediction of the existence and structure of $Cs_2Ge_5O_{11}$. DFT calculations support that $Cs_2Ge_5O_{11}$ is a stable compound. Ultimately, this compound is grown via a solid-state reaction and its structure is refined via Rietveld refinement.

SERMACS 1275

Design strategies to enhance amidoxime chelators for uranium recovery

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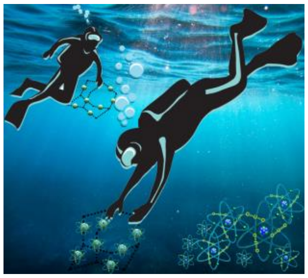
To move nuclear as a primary energy source, uranium resources must be secured beyond what terrestrial reserves can provide. Given the vast quantity of uranium naturally found in the ocean, adsorbent materials have been investigated to recover this vital fuel source. Amidoxime (AO) has been found to be the state-of-the-art functional group for this purpose, however, improvements must still be made to overcome the issues with selectively capturing uranium at such a low concentration found in the ocean. Herein, we report PAF-1 as a platform to study the effects of two amidoxime ligands. The synthesized adsorbents, PAF-1-CH_2NHAO and PAF-1-NH$(CH_2)_2$AO, with varying chain lengths and grafting degrees, were investigated for their uranium uptakes and kinetic efficiency. PAF-1-NH$(CH_2)_2$AO was found to outperform PAF-1-CH_2NHAO, with a maximum uptake capacity of 385 mg/g and able to reduce a uranium spiked solution to ppb level within 10 minutes. Further studies with PAF-1-NH$(CH_2)_2$AO demonstrated effective elution for multiple adsorption cycles and showed promising results for uranium recovery in the diverse composition of a spiked seawater solution. The work presented here moves forward design principles for amidoxime-functionalized ligands and provides scope for strategies to enhance the capture of uranium as a sustainable nuclear fuel source.



SERMACS 1276

Monodisperse perovskite oxide nanocrystals with tunable size and composition for enhanced oxygen reduction reaction

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Due to the distinct electrical properties, ternary perovskites, such as barium titanate ($BaTiO_3$), have attracted much attention during the past decades. Perovskite oxide materials can be synthesized with various techniques, such as solid-state reactions, wet chemical method (sol-gel, hydrothermal), chemical vapor deposition, and molecular beam epitaxy. Most of the approaches suffer from large crystal grains with wide ranges in shape and size, or expensive and energy-inefficient. How to synthesize perovskite materials with low-cost, low temperature and within nanometer scale thus become the focus of much research effort. Herein, by using star-like poly(acrylic acid)-block-polystyrene (PAA-*b*-PS) copolymers as template, we propose a strategy for synthesizing perovskite nanoparticles (NPs), $BaTiO_3$ and $PbTiO_3$. The coordination between the bimetallic precursors and the functional groups of PAA (carboxylic acid group) enables the confinement of NPs within PAA block, offering an approach to modulate the size of NPs by simply tuning the molecular weight of PAA block. By annealing the hybrid composite comprising $BaTiO_3$ NPs and graphene, the size of the synthesized $BaTiO_3$ NPs can be maintained, and the crystallinity can be improved. A significantly enhanced oxygen reduction reaction performance is observed after doping 5 mol% of cobalt with $BaTiO_3$ NPs. This work demonstrates a new type of highly efficient perovskite oxide catalyst for electrochemical energy technologies.

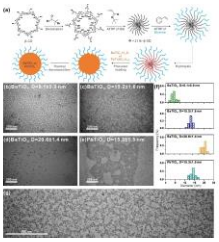

Figure (a) Scheme of the synthesis of perovskite oxide nanoparticles (NPs) with star-like PAA-*b*-PS diblock copolymers as nanoreactors. TEM images of PS-capped $BaTiO_3$/ $PbTiO_3$ NPs obtained by utilizing star-like diblock copolymers as nanoreactors with diameters of (b) 8.1 nm (c) 15.2 nm (d) 20.6 nm, and (e) 15.3 nm. (f) Statistics of size distribution of the synthesized NPs. (g) TEM image of the monodisperse $BaTiO_3$ NPs with smaller magnification

SERMACS 1277
PbTiO3 nanosheets from a layered titanate precursor

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$PbTiO_3$ is known for being a piezoelectric material that exhibits ferroelectricity with a high Curie temperature compared to other perovskite materials. For this reason, research on the formation of nanomaterials of $PbTiO_3$ is of great interest for applications such as high temperature piezoelectric ceramics as well as non-volatile random-access memories (RAMs). Freestanding nanosheets of tetragonal $PbTiO_3$ were synthesized via a hydrothermal approach. The resulting sheets have promising properties such as a low band gap (2.13 eV) and a high c/a ratio (1.049). The formation of this material has proven challenging due to the preference of lead to form basic carbonates when exposed to CO_2 and the lack of stability of the nanosheets in water when exposed to light. This synthetic approach will be expanded to the $BaTiO_3$ and $SrTiO_3$ systems. In this presentation, the synthesis, characterization, and stability of the $PbTiO_3$ nanosheets will be discussed.

SERMACS 1278
Fluorinated imidazolium paramagnetic ionic liquids

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Paramagnetic ionic liquids (PILs) have been demonstrated as a new type of magnetic fluid. PILs are neat magnetically susceptible liquids distinguished from ferrofluids and magnetorheological fluids which are heterogeneous mixtures of magnetic particles and carrier fluids. We have synthesized PILs by incorporating magnetically susceptible elements into the anion, cation or both. Many advantages to PILs have been demonstrated such as high thermal stability, low vapor pressure, and liquid-liquid separation using a magnetic field. Using microwave synthesis, perfluorination of the imidazolium cation has been achieved and paramagnetism has been instilled by varying magnetically susceptible anion complexes, [M = Fe, Dy, Gd, Ho]. These fluorinated PILs were prepared and characterized using ^1H NMR, ^{13}C NMR, ^{17}F NMR, FTIR, DSC, and TGA. Magnetic susceptibility was determined using the Evan's method.

SERMACS 1279
Synthesis, structural, and photophysical properties of series of closo-decaborates with 1-pyridinium-10-x substituents

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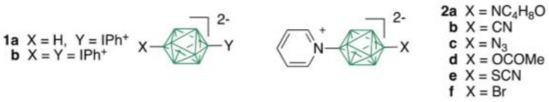
Boron clusters are sigma aromatic compounds that have been applied in photonics, medicine, and liquid crystals.We have previously demonstrated that selective activation of the apical B-H bond towards nucleophilic substitution using $PhI(OAc)_2$. Using this methodology, [*closo*-$B_{10}H_9$-1-IPh]$^-$(**1a**) is substituted with strong nucleophiles morpholine, CN^-or N_3^-, then reacted with $PhI(OAc)_2$, followed by pyridine, to give **2a**–**2c**, respectively. Monosubstitution of [*closo*-$B_{10}H_8$-1,10-$(IPh)_2$]$^-$(**1b**) with $MeCO_2^-$, SCN^-, or Br^-, followed by separation from starting material and doubly substituted by-products, and subsequent reaction with pyridine gave **2d–2f**. This presentation will discuss the scope and limitations of this chemistry, as well as UV-vis and single crystal XRD studies augmented with DFT calculations to determine the substituent effect on the cage-to-pyridine excitation energy and on the boron cluster geometry in **2a**–**2f**.



SERMACS 1280

Designing MOFs for trace CO_2 capture

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Metal-organic frameworks (MOFs) have emerged as a fascinating class of materials with a wide range of potential applications. Much of the interest in MOFs stems from their well-defined, porous structures and molecular building blocks that offer a high degree of structural and functional group tunability. Our group has been interested in the design of MOFs containing reactive transition metal species for applications in heterogeneous catalysis and trace CO_2 capture. This presentation will describe our recent work with MOFs containing nucleophilic transition metal hydroxide functional groups. These bio-inspired materials adsorb CO_2 at atmospheric concentrations and function via a CO_2/HCO_3^- chemisorption mechanism that is aided by cooperative hydrogen bonding interactions.

SERMACS 1281

Conformal, ultra-thin MOF-based films: Characterization of growth, porosity, and electronic transport

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For potential integration in electrochemical device structures, we have investigated the deposition process and electrochemical properties of thin films based on copper-paddlewheel metal-organic frameworks, specifically MOF-14 and MOF-399. These films were fabricated by sequential, alternating, solution-phase deposition of the inorganic and organic ligand precursors. Morphological characterization undertaken with atomic force microscopy to study the film growth mechanism showed that both the MOF-14 and MOF-399 chemistries produced conformal films via a van der Merwe-like growth mechanism. This is in contrast to other surface-anchored MOFs, notably the iconic and related copper-paddlewheel HKUST-1 MOF, that follow a Volmer-Weber growth mechanism with isolated crystallites that nucleate and ripen. The chemical and thermal stability films based on the MOF-14 and MOF-399 systems has been investigated. Resulting from this study, chemical etching has been undertaken to pattern the film and determine the physical thickness of the film utilizing atomic force microscopy. Film thickness is controlled by the number of deposition cycles with linear film growth of 1.4 and 2.2 nm per layer for the MOF-14 and MOF-399, respectively. To investigate the inherent porosities of these ultra-thin conformal MOF analog films, cyclic voltammetry redox probe characterization using ferrocene was conducted. Consistent with the larger pores for the MOF-399 system, larger peak currents are observed for the MOF-399 analog films compared to MOF-14. Additionally electrochemical impedance spectroscopy was used to determine the electronic transport properties of the film. This is particularly relevant for their utilization as active or passive interfacial components within hierarchical structures for electronic applications, such as sensors or low-k dielectrics.

SERMACS 1282

Gas-phase synthesis of hierarchically structured and responsive metal-organic frameworks

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Metal-organic frameworks (MOFs) are versatile materials and have enjoyed widespread study and use as tunable scaffolds for energy storage, catalysis, and separations. Our lab is focused on developing new approaches for the synthesis and characterization of hierarchically structured and responsive MOFs and related coordination polymers. We demonstrate the synthesis of 1- and 2-dimensional coordination polymers composed of di-Mo complexes. These materials exhibit anomalous gas adsorption characteristics, redox activity, and photo-tunable charge transport. Notably, we demonstrate the versatility of chemical vapor deposition and the unique opportunities this method presents for the preparation of layered 2-dimensional MOFs. We show that single crystal device studies allow for not only detailed investigation of charge transport mechanisms within these materials, but also *in situ* identification of the unique switching behavior of these MOFs when exposed to optical, electronic, and chemical stimuli.

SERMACS 1283

Light harvesting and energy transfer in a porphyrin-based metal-organic framework

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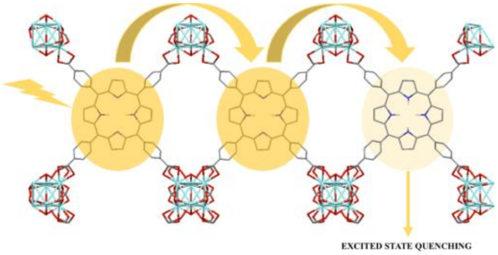
We present synthesis and photophysical characterization of a water stable PCN-223(freebase) metal organic framework (MOF) constructed from meso-tetrakis(4-carboxyphenyl)porphyrin (TCPP). Photophysical properties of the synthesized crystalline material were studied by using a wide range of steady-state and time-resolved spectroscopic techniques. Excitation energy transfer (EET) in MOF was investigated by studying the pH dependence of photoluminescence quenching. Quenching experiments performed on TCPP and PCN-223 demonstrated that the extent and the rate of quenching in MOF is significantly higher than monomeric ligand. Based on these results, we propose that upon photo-excitation, the excitation energy migrates across neutral TCPP linkers until it is quenched by a N-protonated TCPP linker. The N-protonated linkers act as trap states that deactivate the excited state to the ground state. Variable temperature measurements aided in understanding the mechanism of singlet-singlet EET in PCN-223 MOF. The rate of energy transfer and the total exciton hopping distance in PCN-223 were calculated to quantify the energy transfer characteristics of PCN-223. Nanosecond transient absorption spectroscopy was used to study the triplet excited state photophysics in both free ligand and PCN-223 MOF. Furthermore, femtosecond transient absorption spectroscopy was employed to get a better understanding of the photophysical processes taking place in ligand and MOF on ultrafast timescales. Efficient energy transfer (Förster radius = 54.5 Å) accompanied with long distance exciton hopping (173 Å) was obtained for PCN-223 MOF.



SERMACS 1284

Modulating guest based photophysics in metal organic frameworks

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Porous metal organic frameworks (MOFs) have been shown to effectively encapsulate a wide range of transition metal guests including metallloporphyrins and transition metal polyimines. These functionalized materials provide outstanding platforms for the development of solar photocatalysts and light harvesting devices. Of particular interest in the development of photoactive materials in MOFs is the ability of the pore to modulate the photophysical properties of the guest. We have now developed a wide range of new MOFs templated by Ru^{2+} polymines that have unique photophysics relative to complexes in solution. These included greatly extended ^{3}MLCT lifetimes and shifted emission maxima. These properties are directly related to confinement which controls both excited state photochemistry and ground state conformations of the guest. We have also examined metalloporphyrin photophysics in porphyrin@MOF systems in which both the singlet and triplet excited states are modulated by the nature of the pore-porphyrin interactions. Here, these results will be discussed in the context of specifically tunable photoactive MOF materials.

SERMACS 1285

Self-assembled reversed bilayer vesicles through pnictogen bonding: Step one in the design of a truly artificial cell

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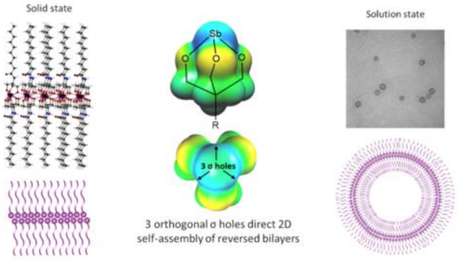
Pnictogen bonding is part of a broader class of secondary bonding interactions shared by many of the heavier p-block elements. Despite a strong redundancy in the underlying phenomenon, the supramolecular design of systems that utilize chalcogen, pnictogen or tetrel bonding can be more challenging than with halogen bonding as the same 1:1 topological analogy with hydrogen bonding does not exist for these other groups as it does for the halogens. Despite this, the ability of these elements to engage in more than one simultaneous supramolecular interaction can have important utility in the design. In particular, multiple pnictogen bonds can be used to actively direct the formation of reversed bilayer vesicles. Efforts to control the vesicle size trough modifications of monomeric building blocks will be discussed. Water stability has been introduced and the application of these vesicles as nanocontainers is being explored in order to address questions pertaining to membrane permeability.



Self-assembly of reversed-bilayer membranes and vesicles through pnictogen bonding between antimony alkoxide cages.

SERMACS 1286

Electronic properties and photophysics of photochromic frameworks

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Materials capable of adaptation based on external stimulus have recently attracted attention in the advanced technology sector. Modulated by temperature, pressure, pH, applied voltage, or light; chromic compounds can be applied as "smart" windows or sensors, self-healing coatings, optical switches or controlled drug delivery systems. Recently, we reported our use of metal-organic frameworks (MOFs) as a tool to study fundamental changes in the photophysical- and electronic properties of photochromic molecules immobilized in porous frameworks. In this presentation, we disclose our findings on the photoisomerization kinetics of photochromic MOFs and the established correlations of their electronic structure as a function of excitation wavelength. A combination of UV-vis and diffuse reflectance spectroscopies were used to study the photoisomerization kinetics, and pressed-pellet conductivity measurements were used to correlate the observed spectroscopic data with light-based cycling of conductivity values. The findings suggest that photoswitch immobilization into porous scaffolds can drastically change their electronic and photophysical properties which opens new avenues for technological applications.

SERMACS 1287

Syntheses of copper tetrachalcogenide metallate (Mo/W) nanoparticles and their applications towards energy storage

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Supercapacitors represent a compromise between high burst power of traditional capacitors and high energy density of traditional batteries, with good device life time (charge-discharge cyclability). Layered materials, such as transition metal dichalcogenides and graphite, are often used in supercapacitor application for their topotactic redox couples and large accessible surface areas after exfoliation. To further improve the potentials of layered materials, we look to ternary chalcogenides that separate the roles of the metals, one for structure stability and the other for providing accessible redox events. In particular, we synthesized nanoparticles of Cu_2MX_4 (X = S, Se and M = Mo, W) nanoparticles and examined their electrochemical characteristics towards supercapacitor applications.

SERMACS 1288

Ruthenium(II)-polypyridyl doped zirconium(IV) metal–organic framework UiO-67-Ru films for solid-state electrochemiluminescence

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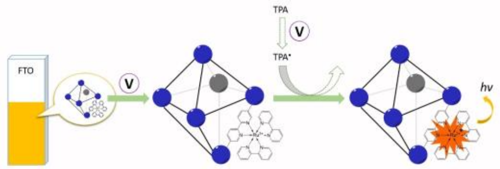
Electrochemiluminescence (ECL), an electrogenerated chemiluminescence, is a highly sensitive technique with wide bioanalytical applications that combines the advantages of both electrochemistry and chemiluminescence. Solid-state ECL has particularly drawn increasing attention due to their advantages over solution-phase ECL, such as reducing consumption of expensive reagent and enhancing the ECL signal. Herein we report the ruthenium(II)-polypyridyl doped zirconium(IV) metal-organic framework (MOF) film, UiO-67-Ru, for solid-state ECL. The UiO-67-Ru thin films were solvothermally prepared on conducting fluorine-doped tin oxide (FTO) glass slide and characterized by powder X-ray diffraction (PXRD) and scanning electron microscopy (SEM). With tripropylamine (TPA) as coreactant, UiO-67-Ru@FTO exhibited high ECL intensity and good stability. A linear relationship was found between ECL intensity and TPA concentration in a wide range of 0.04-20 mM. Additionally, UiO-67-Ru@FTO was successfully used for dopamine detection, implying its great potential for real-life application.



Solid-state ECL in UiO-67-Ru film on FTO

SERMACS 1289

Redox reactivity of soft and porous materials

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Over 20,000 unique structures of metal-organic frameworks (MOFs) have been reported, with nearly all examples featuring metal-carboxylate or metal-azolate bonds. Due to the highly ionic nature of these binding motifs, MOFs are electrical insulators, with very few exceptions. On the other hand, traditional coordination polymers often incorporate metal-ligand motifs with greater covalency, leading to semiconductor electronic properties. The one-dimensional architectures of coordination polymers produces amorphous structures lacking accessible pores, however. Here, we present synthetic approaches that combine the chemistry of one-dimensional and higher-order coordination polymers to access a new family of permanently porous materials with band-type electronic structures. Furthermore, we harness the intrinsic lability of the metal-ligand motifs. More broadly, the dynamic bonding will be used to study the fundamental impact of dynamic bonding on band-type electrical properties and achieve electrochemically actuated self-healing behavior in materials with future use in energy storage and conversion.

SERMACS 1290

History and introduction to forensic DNA testing

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This talk will outline how Forensic DNA testing has been a crucial tool in criminal investigation since 1986 and its evolution from the use of restriction enzymes and the use of a type of repetitive DNA variation called VNTRs (Variable Number of Tandem Repeats) to the analysis of another type of repetitive DNA variation called Short Tandem Repeats and to also include mitochondrial DNA and genetic variation termed Single Nucleotide Polymorphisms (SNPs). The introduction of techniques such as the polymerase chain reaction and DNA sequencing by the method of Sanger will be discussed as well as the recent invention of massively parallel sequencing of DNA (next generation sequencing). Chemistry has enabled these developments that have enabled the application of molecular sciences all around the world and made evidence of items that would otherwise not be useful in criminal investigation by any other means. Chemistry is behind the availability of kits, standards and reagents and techniques that enable forensic DNA testing. Informatics in the shape of national forensic DNA databases and other DNA databases has extended the applications of DNA testing across time and geographical boundaries in the service of criminal investigation and also exoneration of the innocent.

SERMACS 1291

The comparison of MtDNA control region haplotypes between individuals of known maternal lineage and ancient skeletal remains from the flevaeis plot archaeological Site in rhodes

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DNA analysis can be utilized on human skeletal remains found at crime scenes or archaeological sites to distinguish between individuals and determine identifying characteristics. At the Flevaeis Plot archaeological site in Rhodes, two graves were uncovered each containing six to seven skeletons that were estimated to be 1,368 to 2,341 years old. Rhodes' tumultuous history and occupation by different peoples indicates the potential for maternal lineages from several cultures to be within the skeletal remains, namely those of Greek, Roman, Mediterranean, Persian, and Arab descent. This project utilized hypervariable region I (HVI) sequences from studies of contemporary populations of the ethnic groups indicated above as a reference. HVI was sequenced from Flevaeis plot bones and compared to the revised Cambridge Reference Sequence (rCRS) haplotypes in Mega X to determine whether there was sufficient sequence similarity with variants from known populations to infer maternal lineage. A comparison of substitutions within the HVI sequences of the bones and the known populations indicate potential origin in Italian, Iraqi, and Cyprian ethnic groups. In addition, the position of one of the bones in a phylogenetic tree indicates shared ancestry with individuals of the Iraqi populations.

SERMACS 1292

Case study analysis of DNA evidence: An examination of criminal defense and prosecution systems in south georgia

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While the literature documents indigent/criminal defense investigators participation in the criminal justice system from penal confinement to prosecutorial employment, limited information exists regarding courtroom procedures for admissibility and presentation of DNA evidence. This preliminary study will examine what the prosecutor, public defender and expert witnesses do regarding DNA evidence. Case studies will be used to identity, examine, and discuss how DNA evidence is used in hearings, evidence, and trails for defendants in South Georgia. Factors determining DNA and its usage at the investigative stage to trial phrase will be examined. Data was collected via a mailed questionnaire developed for this study. The results from the case studies will determine how DNA evidence is used by criminal defense investigators, prosecutors, and experts in major cases in South Georgia as prior research had not demonstrated specific data. Further, the research identifies and provides how various professionals in criminal justice previously absent from the literature. Case study results will address the e potential ramifications of how DNA evidence is used and presented as evidence in a dual criminal justice system of criminal defense and prosecution.

SERMACS 1293

Development of cannabis sativa autosomal and organelle genotyping methods for forensic and intelligence purposes

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Cannabis sativa L. (marijuana) is the most commonly used illicit drug in the United States and significant illegal traffic from Mexico exists at the US border. Cannabis specific autosomal short tandem repeat (STR) methods can serve as a tool for individualizing and associating samples. Chloroplast DNA (cpDNA) has the distinct advantage of being useful for biogeographic and crop type determination; however, there have been limited cpDNA studies in C. sativa. Lastly, massively parallel sequencing (MPS) technology is an emerging technology in the field of forensic genetics that can be applied to targeted sequencing of C. sativa. This project explores the forensic genetic issues associated with the identification and origin determination of C. sativa. For this purpose, a novel 13-loci autosomal STR multiplex was developed and optimized for C. sativa individualization according to standard recommendations. Additionally, C. sativa cpDNA was explored to allow for genetic determination of biogeographic origin, discrimination between marijuana and hemp, and association between cases for C. sativa samples. Five distinct populations were evaluated using two cpDNA hotspot regions, rpl32-trnL and trnS-trnG. And finally, as a proof of concept, a custom panel for MPS was designed to interrogate 12 cannabis-specific STR loci by sequence rather than by size. A simple workflow was designed to integrate the custom PCR multiplex into a workflow compatible with the Ion Plus Fragment Library Kit, Ion Chef, and Ion S5 system. Results revealed intra-repeat variation in eight loci where the nominal or size-based allele was identical, but variances were discovered by sequence. In addition, full concordance was observed between the MPS and capillary electrophoresis data. Results provide the forensic genetic community a comprehensive genetic tool (STR, cpDNA, and MPS) that allows for the individualization of cannabis samples, the association of different cases as well as origin determination of samples for forensic and intelligence purposes.

SERMACS 1294

Forensic epigenetics, a powerful technique to determine body fluids and phenotype

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Determining the type and origin of body fluids in a forensic investigation can provide important assistance to criminal investigations. For example, in situations such as sexual assault or child abuse, the presence of DNA from skin cells may indicate innocent contact while the determination of blood or semen may be indicative of criminal behavior. We have developed a set of epigenetic markers which produce unique and specific patterns of DNA methylation that can be used to identify blood, semen, saliva and vaginal epithelial cells. This new method easily fits within the workflow of a standard forensic DNA laboratory. Our procedure involves the testing of DNA extracted from human samples, which is then amplified using bisulfite modified PCR. Specific primers amplify the region of interest, and the quantitative methylation profile of each locus is determined by pyrosequencing. The versatility of these new markers is presented by showing the results of validation studies on sensitivity, human specificity, stability and mixture resolution. We also will present data on the development of an alternative QPCR method that can determine body fluids using high resolution melt techniques. Lastly we present additional results on the utilization of pyrosequencing for age and other phenotypic information such as smoking status. The results of these methods can provide important information to law enforcement and triers of fact in criminal casework.

SERMACS 1295

Interactive experience with microwave technology in teaching and research labs

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Microwave technology has become a common tool for chemical synthesis with many academic institutions incorporating microwave-assisted experiments into their teaching and research labs. Early introduction to innovative instrumentation, such as microwave reactors, teaches students to embrace ideas on the cutting edge of chemistry, better preparing them for technologies they will encounter in their careers. This workshop will include a review of microwave theory, provide a pedagogical comparison of both single and multi-mode technologies available for the teaching lab, and highlight several examples of experiments that have been adapted for microwave technology with an emphasis on green chemistry principles. Participants will receive hands-on training to understand how microwave-assisted chemistry can fit into any teaching lab.

CEM

SERMACS 1296

Selective microwave heating of organic reaction mixtures

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Dudley Lab research contributes to the development of emerging and enabling technologies for chemical synthesis. This seminar will focus on the use of microwave electromagnetic radiation to produce the thermal energy needed to accelerate dynamic chemical processes. Thermal chemical reaction mixtures are typically subjected to convective heating. The physics of convective heat transfer underlies all of physical organic theory, which guides our fundamental understanding of thermochemical processes. Microwave energy, in contrast, produces heat by a dielectric heating mechanism, which needs to be understood in order for us to gain maximum benefit from this new technology. On behalf of our collaborative research team, I will describe a physical model for selective heating in homogeneous solution and reaction systems in which microwave-specific rate enhancements have been documented both qualitatively and quantitatively. Recent efforts to apply this model advantageous in chemical synthesis will be highlighted.

SERMACS 1297

Microwave initiated nanomanufacturing towards energy applications

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Nanomaterials, such as carbon nanotubes (CNT), metal oxides, and polymers, possess superior mechanical, thermal and electrical properties, lead to broad applications in composite materials, smart structures, chemical sensors, energy storage and nano-electronic devices. However, the high cost and difficulty in getting large scale, high quality nanomaterials remain challenges. We demonstrate a facile and scalable microwave approach for the direct growth of CNT, nanostructured metal chalcogenides on a wide range of substrates, including conducting polymers, graphenes and graphite powders and so on. The microwave initiated nanomaterial growth will take only 20-30 seconds under the microwave irradiation at room temperature in air, no need of any inert gas protection, and additional feed stock gases, usually required in CVD approach. Preliminary results demonstrated the as-produced nanocomposites can be used for hydrogen evolution reaction (HER) and electrochemical energy storage such as supercapacitor applications.

SERMACS 1298

One-pot microwave assisted Suzuki coupling synthesis of substituted isoxazoles: Efforts to minimize self-coupling byproducts

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Isoxazole derivatives have been shown to exhibit a broad range of biological activities. Unfortunately, previous methods of synthesizing 3,5-diarylisoxazole derivatives have resulted in poor reaction rate, poor yield, and unfavorable environmental effects. We aim to overcome these issues by optimizing microwave-assisted Suzuki coupling with a green solvent and reusable catalyst. It is expected that microwave heating will greatly increase the reaction rate while Suzuki cross-coupling should produce few side products, thereby increasing the yield of our desired isoxazole product. Finally, using the green solvent mixture alongside a reusable catalyst will greatly minimize the chemical waste resulting from this reaction. To test and optimize this reaction method, the synthesis of two isoxazole compounds, 3-phenylisoxazole and 3-(4-methoxyphenyl)-5-phenylisoxazole, were studied. Synthesis of 3-phenylisoxazole was successful at small scales; however, issues of pressure and solvent volume surfaced when the reaction scale was increased. We will discuss our attempts to optimize this reaction method through exploration of various reaction conditions.

SERMACS 1299

Green synthesis of five and six membered nitrogen containing heterocycles

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Five and six membered nitrogen containing heterocycles are found in a broad array of organic compounds. They have also shown exceptional biological activities towards various diseases. These small organic molecules are also very prominently used as sensor in various chemosensing applications. Conventional methods for the synthesis of heterocycles often make use of hazardous chemicals and multi-step processes. Due to recent environmental regulations, eco-friendly greener procedures have been targeted to synthesize important synthons through short reaction time and increase reactions yields. This talk will address the microwave assisted synthesis of nitrogen containing heterocycles and its targeted applications.

SERMACS 1300

Microwave induced solution-combustion synthesis of complex metal oxides

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The continued exploration of selective microwave heating has provided a new avenue for a variety of applications where traditional thermal heating fails to produce the desired final product. In ceramic chemistry, microwave technology provides selective heating in synthesis of materials that require additional acceleration without increasing the overall thermal gradient in the process. The disposition of Plutonium (Pu) is a high-priority issue for DOE missions in nuclear materials management and environmental cleanup at nuclear sites. To broaden the options available for addressing this challenge, a solution-based synthesis route for fabricating a durable Pu-doped Gd 2 Zr 2 O 7 ceramic is proposed. Gd 2 Zr 2 O 7 exhibits high structural stability to heavy ion bombardment, indicating that the material can withstand sustained Pu alpha decay events. While such desirable characteristics have spurred further research into Gd 2 Zr 2 O 7 (and similar pyrochlore systems), an experimental study on the self-propagating solution combustion synthesis involving the doping of Gd 2 Zr 2 O 7 with surrogates of Pu will be presented.

SERMACS 1301

What I did for summer vacation: Experiences of a high school student in a college research lab

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The experiences of a local high school student working in a chemistry research lab are presented. As part of the Department of Education's Upward Bound Program, the presenter worked in the lab of a mentor at Southeastern Louisiana University. The student was able to test planned experiments for the University's General Chemistry laboratory course, work with college peers on their projects, learn valuble sythetic techniques and chemical principles, as well as produce publishable results for the lab group.

SERMACS 1302

How yogurt can be used to teach biochemistry

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This lab activity was designed to strengthen our Food and Nutritional Science students' knowledge of biochemistry concepts and the relationship between these concepts and food science. We designed a laboratory experience that teaches biochemistry concepts using yogurt as a model, and we linked those concepts to food safety, an important area of food science. The learning objective of this laboratory exercise was for the students to be able to 1) Explain enzyme activity; 2) Explain the role of lactase in fermentation; 3) Explain the chemical changes that convert milk into yogurt; 4) Explain the lac operon; 5) Distinguish between the bacterial strains in yogurt; 6) Explain the relationship between fermentation and food safety; 7) Apply aseptic techniques in the laboratory; 8) Estimate bacterial counts from colony counts; 9) Analyze laboratory results and draw conclusions. The students employed a colorimetric method to measure the lactase activity of bacterial strains found commercial yogurts and were encouraged to relate the activity to bacterial lactic acid production, fermentation, and food safety. Students were assessed with pre- and posttest exams, via laboratory

reports, by class performance, and using the Intrinsic Motivation Inventory (IMI). Students scored highly on classroom performance and laboratory report scales (mean > 90%). A mean increase of five questions answered correctly revealed a substantial improvement in understanding of antibiotics and inhibitor modes of inhibition. IMI scores indicated that students were motivated during the activity. This exercise could be used as a template for how to introduce complex concepts in biochemistry and molecular biology in a simplified way using food, particularly yogurt, as a model for Food Science students as well as students from other majors.

SERMACS 1303

Investigating the effects of laboratory learning environment on students' learning outcomes in a general chemistry course

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This study determined the effects of the five different laboratory partnerships established in General Chemistry laboratories and students' study group interactions outside the classroom on their social interactions and the perceived quality of their Chemistry learning. The investigation addressed two areas of academic and psychological outcomes. Five different laboratory partnerships were designed and implemented for the first year General Chemistry students (N = 2122) for four consecutive semesters. Chemistry lab sections were randomly designated into one of the five different laboratory partnerships; (1) Free choice- students found their own partner, (2) Random assignment- lab partners were assigned randomly, (3) Side-to-side assignment – kept Math ACT score constant among student pairs (4) High-low assignment- kept Math ACT score variable among student pairs (5) Lecture section based assignment-students paired with partner in same lecture section; if same lecture section not available, then pairs were kept with same professor. In General Chemistry lectures, students were encouraged to involve in study groups outside the classroom with their laboratory partners and student contact information was provided. In this study, student lecture grades and survey findings were used to measure students' Chemistry performance and their attitudes about their lab partners and study group partners. Data collected were analyzed using Analysis of Covariance (ANCOVA). Results showed that the covariate, students' pre-mathematics performances, was significantly related to their General Chemistry performances, $F(1, 1807) = 883.0$, $p < .001$, $h^2 = .33$; There was a significant effect of the designated laboratory partnership on students' General Chemistry performances after controlling for their pre- mathematics performances, $F(4, 1807) = 3.6$, $p = .006$, $h^2 = .01$. Also, it was found that the Chemistry exam performances of students in "Side to side" partnership type was significantly different from the students in the 'Free choice' and 'Lecture based' partnership types. In addition to this, how student attitudes change according to their laboratory partnership and how it affects to their study group interactions outside the classroom, and academic performances will be discussed.

SERMACS 1304

Hands-on electrospray ionization-mass spectrometry for undergraduate biochemistry students: Peptide identification by ladder sequencing

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Mass spectrometers are ever-increasingly powerful, user-friendly and affordable. Thus, the addition of mass spectrometry laboratory experiments into the undergraduate laboratory curriculum is both now feasible and an effective tool to teach students to use instrumentation as it relates to various subdisciplines of chemistry, including biochemistry. Here, an experiment demonstrating the use of a high-resolution electrospray ionization mass spectrometer (ESI-HRMS) for the identification of peptide sequences and the differentiation of peptide isomers was developed and implemented in a biochemistry laboratory course for third-year chemistry major undergraduate students in Mississippi State University. As a pre-lab assignment, students were tasked to predict the mass-to-charge ratios and the fragmentation patterns for five given peptides using an online fragmentation prediction tool (Protein Prospector's MS-Product tool, prospector.ucsf.edu). Next, students analyzed two unknown peptides using ESI-HRMS. The theoretical and experimental results were then compared to reveal the identity of the two unknown peptides. The success rate of recognizing the unknown peptide sequences was 87.5%. This laboratory experiment provided students with hands-on experience using a research-grade ESI-HRMS instrument to solve a bioanalytical problem—specifically, identification of the primary structure of a peptide of unknown sequence. According to the student responses on an anonymous survey questionnaire, students were appreciative of the opportunity to perform this experiment.

SERMACS 1305

NSF Noyce program: REMAST (recruit and engage math and science teachers) at Newberry College, phase I (2009-2015) and phase II (2015-2020) through year 5

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Newberry College, a 4-year institution with an enrollment of 1,100 students, prepares secondary biology, chemistry, and mathematics teachers. With NSF Noyce Phase I (2009-2015; DUE-0934802) funding, the RE-MAST program at Newberry College met the goal to more than double the STEM secondary-certified teachers over a five-year period. Based on the findings from the RE-MAST Phase I program, the NSF Noyce REMAST Phase II program (2015-2020; DUE-1439839) goals were established as to 1) recruit 9 to 16 additional STEM majors into teaching; 2) provide educational support for Scholars; 3) provide professional development (PD) opportunities for Mentors, scholars, Teaching Fellows, and grant personnel; and 4) pursue an innovative research agenda related to teacher retention, or persistence of math and science teachers in the teaching profession. During this 10th year of the REMAST program at Newberry College and the 5th year of Phase II, the overall design and status of the program will be presented.

SERMACS 1306

Food chemistry applications through baking and sensory analysis in a summer research apprentice program

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The average American consumes about 9.5 pounds of chocolate per year and spends $20 billion annually on baked goods, including muffins. Approximately 15 million Americans have some type of food allergy or sensitivity, with milk and gluten in the top eight. During a summer research apprentice program for high school students, we engaged participants in an active learning food chemistry experiment. The purpose of the experiment was to compare the sensory acceptability parameters and nutritional values for two different recipes for chocolate muffins – one recipe with traditional ingredients [gluten flour (G) and dairy (D)] and the other with non-traditional ingredients [gluten-free flour (GF) and non-dairy (ND)]. We baked a previously validated G/D chocolate muffin recipe adapted the same recipe for GF/ND. Four batches of muffins were prepared for a sensory acceptability test. The GF/ND muffins had sensory acceptability test scores similar to those of the G/D muffins. The calculated nutritional values were likewise comparable between the G/D and GF/ND muffins recipes. By conducting this experiment, the students learned how starch, gluten, sugar and leavening agents chemically interact when combined with milk, eggs, and butter. They also explored what happens when gluten, dairy, and solid fat are replaced in a chocolate muffin recipe. The students realized that baking with GF/ND versus G/D was relatively straightward and palatable, but not healthier. This food chemistry experiment thus provided students with the opportunity for hands-on, practical application of basic food chemistry principles through baking, sensory testing and nutritional values assessment.

SERMACS 1307

Pt(0) nano-dispersed in a range of organically modified silicates as catalysts for the hydrosilylation of imines and oximes

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Platinum(0) nanoparticles dispersed and stabilized in organically modified silicates (ORMOSILs), namely triethoxysilane (HTEOS) or methyltriethoxysilane (MTES), resulting Pt@HTEOS and Pt@MTES respectively, are investigated as catalysts for the hydrosilylation of oximes and imines. In this study, the reaction conditions are optimized and the scope explored, using a wide range of substrates with diverse electronic and steric features.

SERMACS 1308

Consumer considerations of local value-added dairy products in North Carolina's original research triangle cities

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The domestic and global dairy markets promise exciting opportunities for companies willing to adapt to a continuously evolving consumer market. North Carolina's dairy industry contributes over 3,000 jobs to the state's economy. This includes all actors in the dairy value chain. Although product diversification and value-addition have become important aspects of business planning, today's savvy consumers are questioning the effects of dairy consumption with a wide range of concerns, from environmental sustainability and animal welfare to health and wellness. Accordingly, this study was motivated by the growing interest in on-farm production of value-added dairy products such as cheese, yogurt, butter, and ice cream and by the lack of information regarding the market potential for such products. The study examines consumer behavior in North Carolina's original Research Triangle cities of Raleigh, Durham, and Chapel Hill towards value-added local dairy products with regard to consumers' willingness to pay. Primary data was collected from food consumers using a well-structured questionnaire in the study target areas (Raleigh, Durham and Chapel Hill) in North Carolina. The purposive sampling technique was used to select respondents before conducting a conjoint analysis to assess consumer willingness to purchase locally produced yogurt. With consideration toward the changing consumption patterns of dairy products, this study will give local North Carolina farmers greater insight into diversifying production practices that could boost revenue. The results of the study would likewise be of relevance to the USDA, fluid milk processors and dairy farmers in general.

SERMACS 1309

Optimized growth medium for the selective enumeration and differentiation of *Lactobacillus* ssp. *bulgaricus*

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The probiotic characteristics and resultant health benefits attributed to *Lactobacillus delbrueckii* ssp. *Bulgaricus*, a well-known bacterial species used alongside other lactic acid bacteria in yogurt and cheese production, are well-documented in the literature. In addition, consumers of yogurt typically enjoy its desirable organoleptic properties that are a result of the symbiotic relationship between *L. bulgaricus* and *Streptococcus thermophilus*. It has been argued that a minimum level of ≥ 6.00 log CFU/g of probiotic microorganisms such as *L. bulgaricus* should be present in order for the various health benefits associated with the consumption of probiotic products to be achieved. However, the standard growth medium such as deMan Rogosa Sharpe (MRS) used for general enumeration of lactic acid bacteria often underestimates the true count of *L. bulgaricus*. In addition, identification and differentiation of *L. bulgaricus* are particularly difficult when other lactic acid bacteria are present. An optimized growth medium is thus needed to accurately enumerate and differentiate *L. bulgaricus*, especially in mixed cultures. We optimized modified reinforced clostridial medium (mRCM) for the selective enumeration and differentiation of *L. bulgaricus* by adding 0.01% uracil, 0.2% Tween 80, 0.025% CaCl2, 0.5% fructose, 0.5% dextrose, 1% maltose and 0.25% pyruvate to RCM. The addition of 0.008% aniline improved the morphology and differentiation of *L. bulgaricus* colonies in a mixed bacteria culture. Cell recovery and bacterial counts of *L. bulgaricus* in tested yogurt brands were higher in mRCM-PYR than in the conventional MRS medium as mRCM-PYR highly inhibited the growth of the other bacterial species (*Streptococcus thermophilus*, *Lactobacillus acidophilus*, *Bifidus* and *Lactobacillus reuteri*) present in the yogurt. Our results demonstrated that mRCM-PYR was more effective in culturing, enumerating and differentiating *L. bulgaricus* than the conventional medium. Consequently, mRCM-PYR can be recommended as a more reliable growth medium for the accurate enumeration and differentiation of *L. bulgaricus*.

SERMACS 1310

Preliminary assessment of food safety knowledge and practices at a university food service establishment in Bulgaria

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The objective of this study was to observe food service workers at a university establishment in Bulgaria in order to assess the workers' level of awareness and knowledge of food safety practices and sanitation/hygiene regulations. The study was conducted at a university cafeteria at the University of Food Technologies in Plovdiv, Bulgaria and included observations of food handlers and students who have had some practical training in food service. The observations were conducted during the various stages of food processing including - storage, pre-processing, final processing (cooking), distribution, cleaning, and quality control. With regard to the observations on personal hygiene requirements, it was noted that not all workers used gloves and others did not wash their hands in advance. There was an obvious lack of knowledge regarding temperature danger zones, ideal refrigeration measures and temperature control during cooking. However, regulations related to sanitizing and cleaning equipment and contact surfaces were followed. To the best of our knowledge, no studies related to the food safety knowledge of food service workers in Bulgarian restaurants have been published. Consequently, our observations would indicate that continued research into risk perceptions and safe food handling practices in food and catering establishments in Bulgaria is warranted in order to enhance sanitation and hygiene practices that will ensure food safety and quality.

SERMACS 1311

Peer mentoring: Analysis of success and web resources for STEM tutoring centers

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Peer mentoring is a key aspect of undergraduate education. The mentees improve in technical proficiency, receive encouragement, increase their social and academic confidence, develop study and communication skills, and make new friends. The mentors reinforce their knowledge of the subject, improve in leaderships skills, increase in confidence, and enlarge their circle of academic friends. Peer mentoring has many variations in STEM: Learning Assistants (LA), Peer-led Team Learning (PLTL), Supplemental Instruction (SI), and Tutoring. The amount of money spent on peer mentoring can be very large. Often, the efforts are overseen by separate offices at an institution, making it difficult to be sure which approach is best under given circumstances. Tools to help the faculty and administration evaluate the various approaches would be very welcome. We have created Excel spreadsheets that allow rapid production of data tables and graphs for evaluation of the utility of the peer mentoring effort, and presentation of this data to the administration. Outputs include numbers of students, time, day and week of visit, unique student visitors by course and section of course, comparison of grades and DFW rates for those who attended and did not attend tutoring. We have also created a website that aggregates resources available for those starting STEM tutoring efforts.

SERMACS 1312

Green oxidations using oxoammonium salt for the undergraduate laboratory and student research

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Oxoammonium cations are derived from TEMPO (2,2,6,6-tetramethylpiperidinyl-N-oxyl) and similar compounds. TEMPO and its derivatives are stable nitroxide radicals that are easily prepared or commercially available.A one-electron oxidation of a nitroxide produces an oxoammonium cation, providing an active oxidizing agent. The oxidations are mild, efficient, and provide an environmentally friendly method for the oxidation of a variety of substrates. Typically, oxoammonium cations have been used for oxidation of alcohols and aldehydes to produce carbonyl containing products. The oxoammonium salt oxidation protocol has been used in the undergraduate lab for the oxidation of 9-fluorenol to the corresponding ketone. The experiment gives students an opportunity to examine and consider green chemistry principles. Results from incorporating this experiment and strategies for implanting green chemistry principles in the laboratory curriculum and research experiences will be presented.

SERMACS 1313

Get involved with the ACS division of chemical education

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Want to know more about the Division of Chemical Education, learn how you can get more involved with DivCHED, learn about educational resources for chemistry, find out how to apply for travel awards, or meet and network with people from your region, nationally, and around the world who have similar interests? The Division of Chemical Education aims to serve as a means of focusing and enhancing the interest and efforts of all constituencies involved in the teaching and learning of chemistry at every level. If you have an interest in chemistry education, we want you involved in DivCHED. Come visit our poster to learn more about the Division and all we have to offer, meet representatives from the Division, and let us know what you think the Division can do to better meet the needs of our members.

SERMACS 1314

Wheetrometer project: Low cost, lab built instruments for UV / VIS / near-IR spectrophotometry

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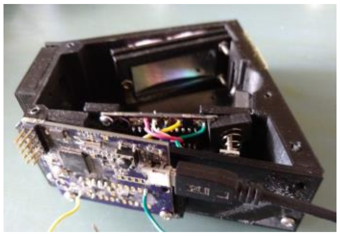
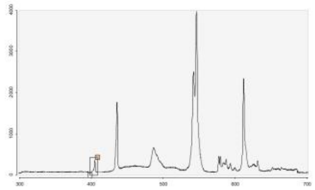
We describe visible and uv-vis spectrometers that can be built for ~$250 USD by anyone with access to a hobby-grade 3d printer. We also describe our work toward a low-cost deuterium / halogen light source for use with the spectrometer. The spectrometer incorporates a 0.15 mm slit, collimating mirror, reflection grating, focusing mirror, CCD array detector and electronics. In addition to the hardware, we developed firmware and a user interface that can be downloaded free of charge. The instrument is controlled from a host computer over usb. The user interface allows input of parameters such as integration time and data averaging. Spectra can be displayed and zoomed in the user interface. Spectra can be stored as CSV files and retrieved when desired. While the software was written for windows, it should be possible to compile for mac or linux. A wavelength calibration routine is built in to the user interface. Calibration is based on known wavelengths of emissions from commercial fluorescent lamps. The useful wavelength range and resolution depend on the choice of gratings. At the time of abstract submission, we were working with 1200 line/mm gratings, giving spectrometers that measure wavelengths ranging from 300 to 700 nm with ~2 nm resolution. A 600 line/mm grating should double the range and resolution. The resolution of light intensity measurements is 12 bit (4095 steps).



3D Printed uv-vis spectrometer.



Emission spectrum of CFL recorded using WheeTrometer.

SERMACS 1315

Determination of the density of eggs as they age to improve a general chemistry laboratory experiment

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It is known that as eggs age their density changes. In Wingate University's General Chemistry I Laboratory, students in different laboratory groups will have eggs of differing freshness and will determine the density of the egg during their first week of lab during the Fall semester. Eggs are purchased within a month of classes starting in July and also the week that classes start in August. In the lab, students are given eggs labeled A and B, not knowing when each egg is purchased. The goal is to determine which egg is freshest based on the density found. However, results have shown very little difference in the density of an egg within a month making it difficult for students to make a correct determination of the freshness of the eggs. The density of eggs was studied in this project to determine the number of months needed to see a significant difference in the density of an egg. The density is found by just floating the egg in a salt water solution and determining the density of the salt water.

SERMACS 1316

Teaching GOB organic chemistry as a general science core class for non-science majors

Daniel R. Zuidema, *dan.zuidema@covenant.edu, Janet Jian. Covenant College, Lookout Mountain, Georgia, United States*

In the last few years, we have taught GOB organic chemistry as a course that fulfills the general science core requirement for non-science majors. In this report, we will provide ACS standardized exam assessment data, details on how the course is run, and student feedback.

SERMACS 1317

Tandem reduction and cyclization of 2-nitrophenylacetylenes as a preparation of indoles

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The indole core is a moiety present in many bioactive molecules, both natural and artificial. While many methods are known for the preparation of this moiety, new approaches add to the synthetic chemist's toolbox. One method relies on the cyclization of 2-alkynylanilines to form indoles. The scope of this method can be extended while maintaining its efficiency if a nitro group precursor is reduced before the cyclization event, preferably in one pot. This poster will share the results of investigating sequential reduction of the aromatic nitro group under mild conditions before intramolecular nucleophilic attack to the indole unit.

SERMACS 1318

Small business development center assistance for existing and prospective small business owners

***Becky Brownlee**, rbrownlee@georgiasbdc.org. University of Georgia Small Business Development Center, Savannah, Georgia, United States*

The Small Business Development Center (SBDC) provides tools, training and resources to help small businesses grow and succeed. The University of Georgia SBDC is part of America’s Small Business Development Centers which provides these same services throughout the United States. This presentation will show current and future business owners the free SBDC resources available and general business information.

SERMACS 1319

Intellectual property and contract considerations for start-ups

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Ideas fuel our information economy. Entrepreneurs must know who owns those ideas and how to create and extract value from them. They must know when their intellectual property warrants protection, and they must understand contracts issue that arise whether internally with owners and employees or externally with suppliers and customers. With a basic understanding of intellectual property and contract law, entrepreneurs can protect and capitalize on their ideas, as well as their skills, for success in this rapidly changing economy.

SERMACS 1320

Managing your online presence

***Chase Cowart**, ccowart@georgiasbdc.org. University of Georgia Small Business Development Center, Savannah, Georgia, United States*

Every business has, or should have, a website and social media accounts. Your overall online presence could very well be your first impression. Actively managing that presence can help ensure it’s not also your last impression. This presentation will discuss tactics and platforms that can be used to ensure that you’re putting the best foot forward for your career and your business.

SERMACS 1321

Sales as a career alternative in the chemical industry

***Joseph P. Stoner**, joestoner@bellsouth.net. Retired, Atlanta, Georgia, United States*

Sales skills are important skills for everyone. There are many career options for the young chemist in sales. The importance of sales skills will be covered. Ways for a young person to get sales experience will be reviewed. Different types of chemical business areas will be reviewed and how the aspiring young person can get involved in sales. How sales skills interact with technical skills, marketing skills and management skills will be discussed. The sales process will be reviewed and how different personality styles fit into sales skills will be covered.

SERMACS 1322

Board of directors and scientific advisory board: Know the needs for your start-up company

***James Skinner**, jim@jskinner.com. Terregena Inc., Franklin, North Carolina, United States*

As the scientific founder of a new company, you know your technology, you’ve identified a problem, and your technology will correct it. Now it’s time to lift your company from the lab to commercialization. How do you organize your new company? Who are the officers? You and your team are steeped in science and technology, but have little or no business experience, especially entering a market in the form of the product or service derived from your technology. Founders of new companies need to surround themselves with the best and the brightest in terms of business experience, particularly a Board of Directors and Scientific Advisory Board. Experienced industry executives and scientists can assist you in addressing the many challenges that you will face and provide you and the company with the credibility to secure the funding required to bring your technology to commercialization. The roles played by these boards and their importance in making your new company successful will be discussed.

SERMACS 1323

Functionalized shell-shell-core (SSC) nanopesticide for mosquito control

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For centuries, mosquito-borne diseases (dengue, malaria, etc.) have been one of the leading causes of morbidity and mortality world-wide. For example, dengue alone puts nearly half of the world populations at risk, and with impending climate change mosquito-borne diseases are poised to increase globally. Reducing exposure to mosquitoes has been a leading focus of mosquito-borne disease control strategies. In addition to habitat control, where possible, current mosquito control strategies include usage of high-volume high-dose pesticides. However, increases in and concerns over insecticide resistance (IR), coupled with unintended risks to human health and nontarget species, have led to the search for novel tools and strategies to combat mosquito-borne diseases. These innovative methods may include turning to the past for future solutions. Silver (Ag) and its compounds, known to have antimicrobial properties, have been used for medicinal purposes for thousands of years. It may be possible to find new ways to use Ag to develop a more sustainable tool for mosquito control. Indeed, using surface modified silver nanoparticles (AgNPs) at a concentration of 0.5 mg/L we observed significant oocidal, larvicidal, pupicidal and adulticidal effects against *Aedes aegypti* L. Encouraged by these results, our ongoing work explores coupling low concentration functionalized AgNPs with Deltamethrin (DM), a widely used type-II pyrethroid that is losing effectiveness against mosquitoes, forming a shell-shell-core (SSC) nanosystem. Further, we aim to characterize the SSC molecule in detail using complementary microscopic, spectroscopic, and light scattering techniques, and test for inhibitory effects against different life stages and populations of *Ae. aegypti*, including both the susceptible and resistant strains. Successful development of SSC nanosystem will open new ways for controlling other mosquito- and vector-borne diseases.

SERMACS 1324

Analysis of factors affecting the removal of polyacrylamide from water by UV persulfate method

***Jing Huang**, 972586389@qq.com, Dianhai Yang, Weihai Pang. Tongji University, Shanghai, China*

As an important water-soluble polymer, polyacrylamide (PAM) can be used as a flocculant in solid-liquid separation, a conditioning agent for sludge dewatering, a formula, and a water purification agent such as activated carbon. In the three water treatment industries, such as sewage treatment, raw water treatment and industrial water treatment, the potential hazards and their secondary pollution to the environment are often easily overlooked. Under the action of degradation, the PAM main chain in the wastewater is broken and a large amount of oligomers are generated, which further produces a large amount of acrylamide (AM) monomer and causes damage to the peripheral nervous system of humans and animals. The UV persulfate method was used to remove polyacrylamide (PAM) in water. The effects of persulfate dosage, pH value, initial PAM concentration and chloride ion (Cl^-) on the removal of PAM were studied. The removal effect of polyacrylamide was compared by TiO_2/H_2O_2 method. The test results show that removal rate of the PAM can reach 90.5%, the initial mass concentration of PAM is 100 mg/L, the persulfate dosage is 0.75 mmol/L, and the pH is 9.0.

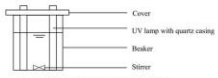

Figure 1. Schematic diagram of the test device

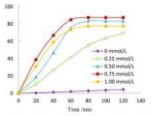

Figure 2. Effect of persulfate dosage on PAM removal rate

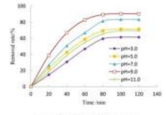

Figure 3. Effect of pH on PAM removal rate

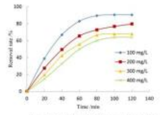

Figure 4. Effect of initial PAM concentration on PAM

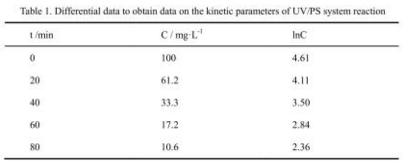

Table 1. Differential data to obtain data on the kinetic parameters of UV/PS system reaction

t /min	C / mg·L^{-1}	lnC
0	100	4.61
20	61.2	4.11
40	33.3	3.50
60	17.2	2.84
80	10.6	2.36

SERMACS 1325

Electrospinning of nanofiber polystyrene and silica layered mats for the visible colorimetric detection of polycyclic aromatic hydrocarbons in water

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Aquatic ecosystems are a critical part of maintaining life on the planet. There are, however, many sources of contamination within the oceans—a large source of which being pollutants from oil spills. A common class of such pollutants is polycyclic aromatic hydrocarbons (PAHs), many of which are suspected of causing cancer and are regulated by the Environmental Protection Agency (EPA). Here, a polymer-based sensor is used for the detection of PAHs at concentrations similar to those in the environment. The sensor is composed of two distinct layers, one of polystyrene (PS) and another of silica (SI). A hydrophobic PS mat prevents evaporation of water, while the non-polar PAHs travel through the nanofibers. The SI fibers, sitting above the PS, provide a substrate for the colorimetric chemistry to take place. To produce the nanofibers, electrospinning was employed. Formaldehyde, combined with an acid, condenses the fused benzene rings of the PAHs to form brown colored quinoid compounds. To provide a theoretical connection, computer modeling of the system will be done with finite element analysis. This on-site and novel sensor provides an alternative to the traditional, expensive analytical equipment (HPLC, GC-MS), and allows for enhanced water monitoring of carcinogenic pollutants.

SERMACS 1326

Hygroscopic properties of marine aerosol particles and their role in cloud droplet formation

Rachel Bramblett, *rachel.bramblett@uga.edu, Amanda A. Frossard. Chemistry , University of Georgia, Athens, Georgia, United States*

One of the largest uncertainties in predicting Earth's current and future climates is the connection between aerosol, cloud, and radiative properties. The composition and size of an aerosol particle influences how it interacts with solar radition, including its ability to activate into a cloud droplet. Surface active compounds, or surfactants, have been observed in ambient atmospheric aerosol particles and may increase the ability of particles to activate into cloud droplets by decreasing their surface tension or have the opposite effect by decreasing hygroscopicity. The effect of surfactants on particle activation into cloud droplets was up until recently neglected in cloud microphysical models. Marine aerosol particles comprise the largest contribution to natural aerosol existing in Earth's atmosphere. In order to improve our understanding of specific properties of this aerosol and its activation into cloud droplets, we used a Humidified Tandem Differential Mobility Analyzer (HTDMA) to measure hygroscopic growth factors across a range of discrete submicron particle diameters. In this study, we measured the growth factors of aerosol particles generated from (i) authentic seawater and (ii) mixtures of sea salt and standard organics and surfactants. We observed a decrease in the hygroscopic growth factor of the aerosol particles from the authentic seawater solution, compared to that of pure aqueous sea salt particles. We also measured the effect of surfactants and organics on the hygroscopic growth factor of these laboratory generated particles.

SERMACS 1327

Seasonal measurements of atmospheric PAHs in the Atlanta metropolitan region via passive air sampling

Katia Del Risco, Drasti Patel, ***Kathryn Zimmermann***, *kzimmermann@ggc.edu. Georgia Gwinnett College, Lawrenceville, Georgia, United States*

Polycyclic aromatic hydrocarbons (PAHs) are products of incomplete combustion processes, are considered probable human carcinogens, and have the physiochemical properties associated with bioaccumulation. Thus, PAHs pose risk to both human health and environmental organisms. Measurements of 16 EPA priority PAHs were conducted using passive air samplers (PAS) at four sampling sites within the Atlanta metropolitan region (two urban, one suburban, and one rural site). Preliminary results of gas-phase concentrations of PAHs for two seasonal sampling periods will be reported and discussed.

SERMACS 1328

Encapsulated oxygen releasing compounds in biodegradable micromaterials for environmental remediation

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Anoxia is one of the primary detrimental effects resulting from eutrophication and harmful algal blooms in natural water systems. Low oxygen concentrations in environmental waters leads to fish kills and can have long-lasting effects on local economies and tourism. Innovative remediation methods are advantageous for these complicated environmental events. In this study, we present a unique micromaterial that has potential application for anoxic water mitigation. Calcium peroxide was encapsulated within biodegradable silk fibroin, collagen, and whey protein concentrate core-shell micromaterials by an electrospraying technique. Oxygen release from the constructed micromaterials was monitored as a function of time using dissolved oxygen probes in sealed bottles. Structures of the micromaterials were characterized by SEM, FTIR, UV-Vis, and fluorescence spectroscopy. The encapsulated collagen and whey protein concentrate micromaterials were soluble in water and released oxygen as a function of time at pH 7. In contrast, silk fibroin micromaterials were stable at neutral pH, but began to degrade at pH 4 to 5 and released encapsulated calcium peroxide over time. Encapsulated composites of collagen, whey, and silk fibroin demonstrated different oxygen release rates compared to the singular encapsulated micromaterials. We propose that these materials will aid in oxygenation of the sediment-water interface and prevent internal loading of limiting nutrients such as phosphorus.

SERMACS 1329

Investigation of hygroscopic properties of giant cloud-condensation nuclei with an aerosol optical trap and humidified tandem differential mobility analyzer

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Understanding the links between aerosol particles, clouds, and radiative properties remains a large uncertainty in predicting Earth's changing energy budget. The ability of a particle to act as a cloud condensation nuclei (CCN) is dependent on both its size and composition. Giant CCN may also have an influence on cloud and precipitation microphysics, and the properties controlling their growth are largely unknown. Natural aerosol particles, such as sea salt and pollen and fungal spore particles have also been observed to behave as giant CCN, in addition to CCN at smaller size ranges. Here, we compare the hygroscopic growth and evaporation of aerosol particles generated from fungal spore and pollen fragments to those generated from seawater and model laboratory aerosol particles. Anemophilous and entomophilous pollen fragments were investigated for chemical and hygroscopic growth differences. We

measured the hygroscopic growth of individual, course mode aerosol particles using an aerosol optical trap combined with Raman spectroscopy. We compare those measurements to the growth factors of size-resolved, submicron aerosol particles using the Humidified Tandem Differential Mobility Analyzer (HTDMA). Using the two instruments, we can understand the hygroscopic growth of particles from the submicron CCN range into the coarse mode giant CCN sizes. Fragmented pollen exhibit an increase in hygroscopicity, and can act as CCN as a result.

SERMACS 1330

Impacts of the mountain valley pipeline: Longitudinal changes in the baseline assessment of Mill Creek, Bent Mt., Virginia

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The Mountain Valley Pipeline (MVP) is a 303-mile natural gas pipeline that is planned to cross more than 1000 bodies of water from West Virginia to Virginia. Substantial modifications to the stream channels and surrounding areas are expected because of the nature of the installation process. Evidence suggests that the magnitude of the impacts will be significant; therefore, the objective of this study is to capture the long-term impacts of the MVP on the water chemistry and stream ecology of Mill Creek. Water chemistry analyses (alkalinity, total water hardness, anions, cations, and metals) provide insight into the health of the streams and will be monitored to show changes due to the pipeline construction and restoration period. Before installation baseline water samples have been collected at multiple sites along Mill Creek and analyzed for alkalinity, total water hardness, and presence of anions. Alkalinity and total water hardness values were determined through quantitative analysis using titrations. An ion chromatography method was developed to quantify anions, including chloride, nitrate, sulfate, and phosphate ions. After the completion of the pipeline this data will be used as reference to assess the impact and recovery time of Mill Creek.

SERMACS 1331

Heavy metal pollution and loss of metal metabolism in eastern oysters (*Crassotrea virginica*) from the Elizabeth River, Virginia

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Oysters that grow in heavily contaminated zones of the Elizabeth River in southern Virginia have high mortality rates. Instead of surviving the typical eighty years of an oyster’s lifespan, they often die within their first two years. These oysters are exposed to high levels of arsenic, cadmium, lead, and other heavy metals, which suggests that they are dying due to heavy metal poisoning. In the present work, we analyzed the metal content for multiple metals both in the shell and the soft tissue of oysters from locations in the Elizabeth River. Soft tissue was separated from the shells surgically. After cleaning, both the shell and the soft tissue were dissolved separately in a mixture of concentrated nitric acid and hydrogen peroxide and the resulting solutions were filtered and analyzed using ICP-OES. Oysters that showed high amounts of cadmium in their soft tissue had very different amounts of sodium and potassium than oysters which did not have cadmium, indicating that they were not regulating these biologically important metals as well. Similarly, the shells of such oysters did not show the typical ratio of magnesium to strontium that healthy oysters usually have. These results suggest a loss of metabolic ability to store or secrete metals that oysters typically use to maintain their lives, and could be contributing to the high mortality rate.

SERMACS 1332

Change in wax profiles for CCD colonies

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Colony Collapse Disorder (CCD) is a phenomenon during which the population of a beehive very rapidly diminishes from a large and robust population to very few surviving bees, or none at all. Many possible causes for it have been suggested, including the overused of certain agricultural pesticides and global warming. No single cause, however, has been definitively linked with the phenomenon. Nonetheless, identifying and counteracting CCD is a matter of great commercial importance, because a huge amount of the world food supply is dependent upon pollination by honeybees. In the present study, we are examining the composition of wax secreted by the honeybees involved in a CCD event. Wax samples from different developmental stages of the hive were removed and hydrolyzed by saponification to release the long-chain fatty acids, then esterified to make esters with methanol. The fatty acid esters were then analyzed by GC-MS. Wax that had been laid down long before the CCD event showed a profile of odd-numbered long-chain fatty acids that was consistent with percentages reported in literature for healthy hives. Wax that had been laid down in a time period much closer to the CCD event showed an aberrant distribution of these same fatty acids. These results are suggestive of a possible bioindicator of CCD. If so, it would allow apiarists more time to find a way to help the hive, and stop the CCD event before it occurs. Our lab continues examining more samples to find if the pattern occurs in other CCD event hives.

SERMACS 1333

Development of an extraction technique for surfactants in ambient aerosols and estuarine water from Skidaway Island, GA

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Surfactants are surface active organic molecules that lower the surface tension of a solution. They have natural and anthropogenic sources that contribute to their concentrations in atmospheric aerosol particles and coastal seawaters. Surfactants in atmospheric aerosol particles may influence the ability of a particle to grow into a cloud droplet. In seawater, surfactants play a role in bubble bursting processes at the ocean surface and contribute to the emission of primary marine aerosols. Thus, it is important to characterize the concentration and composition of surfactants in the environment. This study demonstrates an efficient extraction technique using multiple solid phase extraction cartridges to separate and concentrate surfactants from seawater or aerosol samples. The composition of the extracted surfactants is characterized with electrospray ionization coupled with an ion trap mass spectrometer (ESI-IT-MS). Using surfactant standards, we measured extraction efficiencies of at least 75%, 75%, and 50% for anionic, cationic, and nonionic surfactants, respectively. We applied these techniques to characterize surfactants in atmospheric aerosol particles and estuary water collected from the Skidaway Institute of Oceanography outside of Savannah, Georgia during May and June of 2018. Here we compare the surfactant mass spectral signatures in aerosol particles over a range of particle sizes and in the estuarine waters over daily cycles.

SERMACS 1334

Biosorption of copper(II) to ground peanut hulls: pH dependence and regeneration capacity

Stephen Adom, *syowusu1@catamount.wcu.edu, Carmen L. Huffman. Western Carolina University, Cullowhee, North Carolina, United States*

Current methods for heavy metal remediation can be costly and may have numerous drawbacks including environmental pollution. Bioremediation, which is the process in which heavy metal (or metalloid) species, compounds, or particulates are removed from solution using a biological material (the biosorbent), has been proposed as an alternative remediation technique. Research findings have shown that peanut hulls are an effective biosorbent material. The hulls have been shown to adsorb copper (II) ions in the concentration range of 10-1000 ppm. This is likely due their high content of cellulose and lignin, which have many alcohol groups that are weak cation binding sites. Batch (equilibrium) studies have been performed to determine the surface coverage of copper onto peanut hulls. Concentrations of copper were measured using flame atomic absorption spectroscopy, and data was fit using the Langmuir model to calculate the adsorption capacity. The optimal pH for the effective adsorption of copper ions onto peanut hulls has been studied. Low pH decreases adsorption capacity due to the competition between H^+ and copper ions for binding sites on the hulls, while high pH causes copper ions to precipitate as copper hydroxide, which cannot be adsorbed onto the hulls, lowering the adsorption capacity. Additionally, the regeneration of the hulls has been studied. Desorption occurs in highly acidic solutions since H^+ ions compete with copper ions for binding sites. Adsorbed H^+ on hulls is then desorbed by mixing the hulls with strong base and rinsing with ultrapure water. This process should allow the reclaimed hulls to be used for additional remediation cycles.

SERMACS 1335

Assessment of environmental adversity of chemicals in traditional laboratory experiments: Best practices and benefits

Koushik Banerjee, *kb7071@hotmail.com. Polk State College, Winter Haven, Florida, United States*

Traditional undergraduate laboratory experiments involve the generation of huge amounts of environmentally adverse chemicals, in particular, heavy metals. Such chemicals, once used in experiments are expensive to dispose of and are adverse to the environment. Miniaturization of conventional experiments can lead to the generation of less amount of environmentally adverse waste. Elimination and reduction of usage of expensive chemicals also reduced the cost of experiments in these laboratories. Herein, best practices and case studies that lead to an evaluation of environmental adversities of selected chemicals and ways to eliminate or minimize them will be presented.

SERMACS 1336

Chemostratigraphy of the Big Harris River system using trace metal and particle size analyses

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Chemostratigraphy is the technique of sediment characterization and correlation using subtle variations in the elemental composition of the sediments. The chemostratigraphic study of the Big Harris River near the town of Shelby, NC involves a chemical analysis of the sediment at varying strata depths to determine the concentration of the trace metals in the sediment by x-ray fluorescence spectroscopy. The trace metal analysis provides a unique chemical fingerprint of the stratigraphic sections. Particle size analysis will also be performed. Principle component analysis is used to classify strata to determine how sediment flows throughout the river system. Preliminary results will be presented.

SERMACS 1337

Hydrogen molybdenum tungstate bronze films for reduction of carbon dioxide to formate

Dane W. Scott, ***Mohammad Basjunaid***, *BAJUNAID@mail.etsu.edu. Chemistry, East Tennessee State University, Johnson City, Tennessee, United States*

This work focuses on electrodeposition of hydrogen bronze films. The hydrogen bronzes undergo a color change upon intercalation of the oxide matrix with hydrogen or group I cations. This is a one electron reduction process. Notably, this study focuses on the use of the electro-deposition process in preparing films of hydrogen molybdenum oxide and hydrogen tungsten oxide (molybdenum and tungsten bronzes). The goal of this work is to satirize formate dehydrogenase. The result is application of molybdenum and tungsten bronzes mimicking formate dehydrogenase to reduce carbon dioxide to formate. A yellow peroxymolybdic tungstate acid solution was used for electrodeposition of hydrogen molybdenum tungstate films. The silver chloride electrode was used as a reference, a titanium mesh was used as a large counter electrode and carbon paper was the working electrode. Electrodeposition was carried out at -2.0 V between 20 minutes and 2 hours to determine the effect of film thickness on reduction of carbon dioxide. These films were characterized by film thickness, conductivity and XPS. Reduction experiments were carried out using 0.1 M sodium bicarbonate used as the electrolyte. The cathode and anode were connected by a sodium sulfate salt bridge. The cathode contained the reference electrode and hydrogen bronze working electrode. The anode was a platinum wire mesh. A typical reduction experiment involved saturating a 0.1 M solution of sodium bicarbonate with CO_2 gas and bubbling carbon dioxide for one hour during reduction. Applied potentials from -0.2 and -1.4 V were used. Formate was determined by ion chromatography to determine Faradaic efficiency.

SERMACS 1338

Preparation and characterization study of modified multi-walled carbon nanotubes using iron oxide

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Finding alternative sources for freshwater is an important task for the water crisis in nowadays. However, there are still a lot of challenges for developing a sustainable technology to turn saltwater to freshwater with high performance, environmentally friendly and economically feasible at large scale. Biofouling causes by natural micro-organisms is one of the most common problems in water filtrations. Conventional membrane materials, such as activated carbon, are less robust and infeasible in self-cleaning function which requires chemical treatments for cleaning and recycling. In nanomaterials, carbon nanotubes (CNTs) are composed of cylindrical graphite sheets rolled up like chicken wire like structure hollow from inside. This type of material has been widely used for water desalination before as a low energy solution, and the inner hollow cavity make it ultra-efficient for transporting water molecules and great for desalinating water. Moreover, studies have been shown that CNTs have an anti-biofouling characteristic which make CNTs is a good candidate material for sustainable water purification technologies. However, CNTs has a lower surface area than conventional membrane materials. Therefore, the aim of our study is modifying the traditional CNTs by doping it with high surface area iron oxide. This study is performing a thorough study about this new composite by evaluating the surface areas, morphology, and structure at various ratio between CNTs and iron oxide. We are hoping to determine the best ratio formula for this material with high surface area, robustness, and longer lifetime for large scale water purification systems.

SERMACS 1339

Sonochemical degradation of metribuzin in aqueous solutions

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Metribuzin is a widely used herbicide that is commonly used in agriculture to control broadleaf and grassy weed species. Like other triazine herbicides, there is concern about its persistence in the environment and its potential to contaminate surface and ground waters. The sonolytic removal of this herbicide from wastewater was investigated in this study. Metribuzin in aqueous media was subjected to ultrasound using different sources; a low power cleaning bath and a 20 kHz probe type horn. Enhanced rates of metribuzin degradation occur with both systems. Using the low power cleaning bath, a solution of metribuzin that was sonicated under argon for six hours, decreased to 38% of the initial concentration. Degradation rates significantly increased using the 20 kHz probe type horn. High-Performance Liquid Chromatography (HPLC) and Gas Chromatography Mass Spectrometry (GCMS) were used to analyze the sonicated solution for metribuzin levels and degradation products. The decrease in metribuzin concentration resulted in the formation of the metabolites diketometribuzin (DK) and deaminated diketo-metribuzin (DADK). Spike recoveries for the HPLC method ranged from 98% - 112%. The optimum experimental conditions, as well as rate constants of the degradation will be presented.

SERMACS 1340

Synthesis, isolation, and evaluation of oxidative behavior of aqueous fullerene oxide ($c_{60}o$) suspensions

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Current and impending industrial applications of engineered nanomaterials have spawned a growing scientific and public interest in the environmental and health impacts of these materials. Fullerenes are among the most attractive carbon nanomaterials and have wide-spread applications including electronics, automobile, aircraft, and energy. Stable aqueous suspensions of fullerenes (known as nano-C_{60}) are poorly understood complex systems where with subtle effects of their specific synthetic method and surface chemistry dominate its stability and reactivity. Nano-C_{60} has been shown to induce toxicity in numerous cell cultures and whole animal systems. However, contradictory reports in the literature make it difficult to interpret the mechanism by which C_{60} toxicity is induced. Nano-C_{60} suspensions are demonstrated to rely on the [6,6]-closed epoxide derivative of the fullerene (known as $C_{60}O$) for stability and it is possible that $C_{60}O$ plays a key role in the oxidative behavior of the system. Therefore, elucidating the extent and mechanism of oxidative toxicity caused by these materials will have profound implications for both designing environmentally friendly waste disposal methods and understanding fullerene/biological interactions in the environment. This work is focused on the synthesis of $C_{60}O$ enriched fullerene samples, isolation of $C_{60}O$ using semi-preparative high-performance liquid chromatography (HPLC), evaluation of colloidal properties, and to monitor the oxidative response using a probe molecule: dihydrorhodamine 123 (DHR123). Excellent peak separation was achieved, between C_{60} and $C_{60}O$, by using a mixture of toluene/n-hexane mobile phase in a Nacalai Cosmosil Buckyprep packed semi-preparative column. Isolated $C_{60}O$ has been used to prepare aqueous colloidal suspensions of $C_{60}O$. Results of fluorescence assays for monitoring oxidative behavior of these $C_{60}O$ suspensions with the probe molecule DHR123 will be discussed.

SERMACS 1341

Vermicompost from stormwater pond phycoremediation: Multidisciplinary (EPA-P3) STEM project

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Constructed wetlands (CWs) and stormwater management ponds (SWMPs) are popular best management practices for reducing flood risk and removing pollution from stormwater runoff. The challenge this project addresses is how to effectively manage CWs and SWMPs to provide the known benefits of flood prevention and pollutant removal, while also minimizing the potential for unintended consequences such as methylmercury production, eutrophication from excessive algae growth. CWs and SWMPs can increase property values by providing water views (Sander and Polasky, 2009); however, these ponds are often plagued by algal blooms, which are considered an eyesore and malodorous nuisance (Monaghan et al., 2016). Excessive algae growth can also exacerbate the potential for methylmercury production if the pond becomes eutrophic. Algae growth is commonly combatted by algaecide application. This project provides a viable alternative control strategy (eliminating the need for algaecides), which is cost effective and simple to implement, with the added benefit of removing pollutants as well as the excess nutrients which cause the blooms. The research and design goals of the project are to 1) Evaluate phycoremediation as a strategy for reducing nutrient and metal pollution from CWs and SWMPs. 2) Design and demonstrate a vermicomposting method for freshwater algae. 3) Evaluate the composting of stormwater pond algae in terms of feasibility, and costs/benefits to people, prosperity, and the planet. 4) Create recommendations for waste stormwater algae composting methods based on results of measurements, modeling, statistical, and economic analysis. 5) Educate the Virginia Wesleyan University community and local school children on sustainability and the P3 approach. To our knowledge, this is the first study to evaluate phycoremediation for nutrients and metals in stormwater ponds and the first study to use algae as a vermicompost amendment.

SERMACS 1342

Sink or swim: Biotic influences on carbon cycling in a vegetated barrier island ecosystem

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Climate change and sea level rise are difficult and persistent issues that are innately tied to the carbon (C) cycle. The International Panel on Climate Change has reported the effects of global C cycling on climate change through the fluxes of three main reservoirs: continental lands, open ocean, and the atmosphere. They currently have no model for fluxes in marginal zones, like vegetated coastal systems such as barrier islands. This study quantifies C cycling in vegetated coastal ecosystems impacted by warming temperatures, rising seas and storm disturbances. Within the expanding shrub communities of Virginia barrier islands we examined the role of soil, groundwater and leaf litter along with it’s microbial consumption. Samples were collected from Morella cerifera shrub thickets of various ages and grasslands. Soil was analyzed for percent organic matter (OM). Groundwater samples were analyzed for dissolved organic C (DOC) and microbial bioavailability of said C through bioassay. M. cerifera litter leachate samples were inoculated with groundwater and incubated for a month in fresh and saline solutions before being analyzed for DOC. Results showed that island soil has minimal OM, and concentrations of labile dissolved C are high under the shrub thickets and low under grasslands. Analysis of leachate samples, indicate high C-input that is rapidly consumed by active microbial communities. This suggests that coastal shrub-dominated systems rapidly export C to the groundwater, where it is highly labile, potentially reducing to < ⅓ of original concentration within a month by native microbial communities in ideal conditions. Although the fate of C-laden groundwater is still unknown in situ, we feel that coastal vegetated ecosystems offer significant potential for adjustments in climate change projections, a necessity for more accurate predictions of our future.

SERMACS 1343

Geochemical fingerprinting reveals effects of urbanization and geology on natural water across Middle Tennessee

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This analysis details an application of geochemical fingerprinting to distinguish the primary difference in two reservoirs from various physiographic regions of Tennessee. Geochemical fingerprinting of water samples is the utilization of multiple analytes or analyte ratios to describe a particular body of water. The geology of Middle Tennessee offers an unusually sharp boundary between radically different underlying rock stratigraphy: the Cumberland Plateau rests on Pennsylvanian Sandstone (primarily silica), while the Highland Rim is Mississippian Limestone (rich in calcium carbonate). The difference between the two types of bedrock is expected to manifest in differences in the water in contact with the rock. Ion Chromatography (IC) was utilized to determine important analytes including calcium, magnesium, sodium, fluoride, chloride, nitrate, and nitrite. Multiple samples within each reservoir were gathered to investigate spatial and temporal variation within each reservoir as well as differences between the two reservoirs. Detailed multivariate and GIS analysis of the analyte concentrations allows the estimation of how land-use patterns, including the effects of agriculture and urbanization, may alter the chemistry of the water bodies. These differences are expected to prove useful for future investigations of the sources and sinks of natural waters throughout middle Tennessee.

SERMACS 1344

Concentrations and sources of trace metals in water and sediments of the South Fork New River, Ashe County, North Carolina, and their potential effects on aquatic biota

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Ore Knob Copper Mine located in Jefferson, North Carolina, operated from 1850 to 1962; the mine tailings from the mining operations were dammed and put in Ore Knob Branch. The dam eroded and released the tailings into Peak Creek, which resulted in the Environmental Protection Agency putting the mine on the National Priority List in 2009. The residents were given private wells and springs as remediation, but not much was done for the aquatic biota with in the South Fork New River and other major tributaries. In this research project bioavailable trace metal concentrations in water (cobalt, copper, zinc, and iron) and channel bed sediment (arsenic, cobalt, zinc, manganese) will be determined by inductively-coupled plasma optical emission spectroscopy, total metal concentrations in channel bed sediment will be determined by X-ray fluorescence spectrometer and sediment grain size and organic matter composition in the channel bed sediment will be determined by Mastisizer 2000 laser particle size analyzer and Vario EL III elemental analyzer. Water and sediment samples were collected along the channel bed of the South Fork and North Fork New River and the New River. Water and sediment samples were collected from surrounding tributaries; Peak Creek, Dog Creek, and Kings Creek. The sediment samples will be digested with aqua regia to remove potential trace metals from the surface of the sediment particle. Spatial distribution plots of the bioavailable concentrations for water and sediment will be created. The total-recoverable metal concentrations in the water will be compared to the North Carolina standards. The dissolved metal concentrations in the water will be compared to the acute and chronic USEPA freshwater aquatic biota criteria. The concentration within the sediment will be compared to guidelines provided by MacDonald et al.

SERMACS 1345

Chemical ecology made easy: Teaching students about the link between toxin chemistry and HABs

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Teaching students about chemical ecology and the role of phytoplankton in the marine environment can be challenging due to a perception by students and teachers that the content is too challenging or irrelevant to their lives. Here, students learn that chemistry is linked to all marine life and affects where they choose to live and what eats them. We will provide two examples of K-12 activities that incorporate chemistry while teaching students about dinoflagellates and Harmful Algal Blooms (HABs). The first example is about the role of primary producers in coral reef food webs and how ciguatoxin can bioaccumulate in some organisms that humans eat. The second activity is about the potential for HABs to render valuable shellfish resources in New England unsafe for human consumption due to saxitoxin bioaccumulation in tissues. Students learn how data on HAB cells and resting cysts are collected and subsequently used to ensure seafood safety and predict bloom magnitude. Students construct some of the molecules involved and gain an appreciation for the complexity and similarity of some chemical structures. Modifications for visually impaired students are provided. The activities conform to Next Generation Science Standards and Ocean Literacy Principles. The ultimate goal of such outreach efforts is to encourage students to have a greater understanding of and appreciation for the marine environment and to consider STEM careers.

SERMACS 1346

Leveraging engineering for student success in chemistry

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Through leveraging engineering to solve community-based issues of importance to students, teachers can authentically engage their classes in the science and engineering practices as put forth by the Georgia Standards of Excellence and the Next Generation Science Standards. This session will focus on the *why* and the *how* of identifying issues important to your students, incorporating the engineering design process, and grounded the entire process in standards-based instruction. Participants will engage in hands-on learning in utilizing simple circuitry and basic programming; no prior experience is required.

SERMACS 1347

Classroom demonstration on ocean acidification

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I present a relatively inexpensive demonstration of ocean chemistry's response to increasing atmospheric carbon dioxide. Using relatively common/inexpensive aquarium pump and pH meter in conjunction with an inexpensive atmospheric CO_2 meter interfaced to an open-source Arduino microcontroller, students' respiration of carbon dioxide in the classroom is bubbled into natural or artificial seawater in a small container during the 60-min activity. Participants regularly record the atmospheric CO_2 concentration and seawater pH to investigate the tight coupling of these two measurements. Related content is also presented that may be shared during the activity in-between student measurements/observations. Documentation of the activity with building instructions and example source code will also be available.

SERMACS 1348

Implementing culturally responsive curriculum in the chemistry classroom

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The curriculum presented in the chemistry classroom can often appear distant and irrelevant to some students, especially to those students that feel marginalized due to cultural differences. Accessing students' backgrounds and interests through implementation of culturally responsive curricula improves student engagement. I will describe examples of projects, such as an examination of the Flint, Michigan water crisis, that allow students to relate to different cultures outside the classroom walls. Consequently, students are exposed to social issues that connect to the science content, which also aids in content retention.

SERMACS 1349

One spot synthesis of highly regioselective 2,3-dihydrobenzofurans acetate through palladium catalyzed annulation of acrylic ester as synthons

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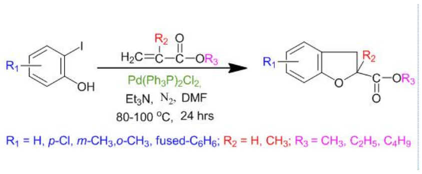
Benzofurans are interesting compounds because of their natural occurrence and biological activities. Compounds containing the benzofuran moiety are widely distributed in nature. They are used as versatile intermediates in organic and natural product synthesis. They have also shown a range of biological activities. The biological properties have attracted chemists in developing an efficient synthesis of DHBs. Recently, our research group has developed methods for the synthesis of benzo-fused heterocyclic compounds, e.g. isoindolines, isoquinolinone, benzo[b]furans and indolium chloride by palladium catalyzed reactions with terminal alkynes and alkenes. A convenient one pot synthesis alkyl 2, 3-dihydrobenzofuran-2-ylcarboxylates through metal mediated reaction.



SERMACS 1350

Brønsted base mediated *trans* hydroboration of alkynamides

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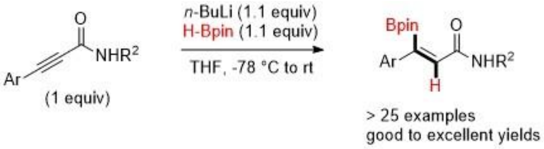
Vinylboronates are an invaluable class of organic compounds and serve as substrates in a variety of synthetically useful transformations. For example, Suzuki-Miyaura cross-coupling of vinylboronates and organohalides is a fundamental C-C bond forming transformation in any organic chemist's toolbox. Furthermore, organoboron functional groups are becoming increasingly common in medicinal and biological applications. Classical methods to synthesize vinylboronates, such as the hydroboration of alkynes, typically afford the *cis* addition product. Methods affording the *trans* addition products are scarce and typically rely on transition metal catalysts. In this work, we describe a transition metal-free Brønsted base mediated *trans* hydroboration of alkynamides. This reaction proceeds with complete regio- and stereoselectivity, affording the corresponding (*E*)-β-borylacrylamides in good to excellent yields. Synthetic scope and product application will be discussed.



SERMACS 1351

Low-waste synthesis of long-chain alkylbenzenes on superacidic mesoporous catalysts

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Currently commercial production of long-chain alkylbenzenes is accomplished by means of Friedel-Crafts alkylation of benzene using Lewis acids. However, such approach poses a serious threat to the environment due to generation of large volume of toxic waste. The objective of this work was to develop a low-waste synthesis of long-chain alkylbenzenes. Phosphotungstic acid (PTA) with Keggin structure is a well-known solid superacid with pKa ≈ -13. However, PTA's low surface area and solubility in polar solvents limit its use in heterogeneous catalysis. This problem was solved by covalent immobilization of PTA on the surface of silica gel. Superacidic mesoporous materials were synthesized by co-condensation of tetraethyl orthosilicate with PTA in acidic media. Various surfactants were used as pore-forming agents. FT-IR spectra of the materials contained characteristic band of PTA at 957 cm^{-1}. TEM images revealed mesoporous structure of the catalysts and presence of embedded PTA clusters. Mesoporous material had high BET surface area and high concentration of acidic catalytic sites. The catalysts were successfully tested in liquid-phase alkylation of 1,3,5-trimethylbenzene by dec-1-ene at various temperatures. The catalyst obtained with Pluronic P123 as a template demonstrated the highest activity and resulted in the highest conversion of dec-1-ene into the products. It was also determined that this catalyst was more effective than zeolite HY. High thermal and chemical stability of the obtained mesoporous materials also enabled their recyclability. Catalysts remained active during three subsequent cycles of alkylation.

SERMACS 1352

Novel chromium(III) photocatalysts for radical cation cycloadditions

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Radical cation cycloadditions have been extensively studied using different photosensitizers or photocatalysts. Our group has been developing unique transformations enabled by the formation of radical cation intermediates, accessed via electron transfer using $[Cr(Ph_2phen)_3]^{3+}$ excited by visible light. A (4+2) cycloaddition using electron rich alkenes has been thoroughly investigated, showing differential reactivity from the ruthenium or iridium photocatalysts more commonly employed. A chromium(III)-photocatalyzed cyclopropanation reaction with diazo reagents and electron-rich alkenes has also been developed. Utilizing photocatalysis for this transformation can address problems of chemoselectivity and β-hydride elimination that have been observed in the carbene manifolds. Most recently, a direct (3+2) cycloaddition using vinyl diazo reagents, electron-rich alkenes, and either chromium or ruthenium photocatalysis has been described. The development of novel chromium photocatalysts toward expanding the scope of reactivity will be discussed. Comparisons between new chromium(III) photocatalysts and $[Cr(Ph_2phen)_3]^{3+}$ will also be highlighted.

SERMACS 1353

Transition metal catalyzed asymmetric dearomatization of heteroarenes

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Non-aromatic nitrogen containing heterocycles such as dihydropyridines, tetrahydropyridines and piperidines are common structural motifs in drug molecules and natural products. Because of their widespread presence in bioactive molecules, synthesis of such heterocycles has attracted significant attention of synthetic community. Despite these efforts, methods for the catalytic enantioselective synthesis of dihydropyridines and piperidinesis is still limited. We will discuss our efforts toward the synthesis of non-aromatic heterocycles through dearomatization of heteroarenes using transition metal catalysis. Factors that influence the dearomatization reaction yield, enantioselectivity as well as our proposed mechanism of these reactions and chemoselective reactions of the dearomatization products will also be discussed.

SERMACS 1354

Stereoselective synthesis of olefins using swellable organically modified silica nano-reactors

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Swellable organically modified silica (SOMS) is capable of behaving as a nano-reactor to facilitate synthetic organic reactions of importance, such as the synthesis of biodiesel synthesis, peptides, and therapeutic drugs. The use of SOMS nano-reactors to facilitate synthetic organic reactions results in unparalleled increases in reaction yield and decreases in reaction time. For example, SOMS nano-reactors are capable of completely conversion of plant-based oil into biodiesel fuel in less than 10 minutes. Currently, our research group seeks to explore the use of SOMS nano-reactors to facilitate olefin synthesis via the Wittig reaction. The Wittig reaction is often used in organic synthesis as a method of carbon-carbon double bond formation and can be used to synthesize a large diversity of important molecules. However, the use of the Wittig reaction presents challenges. A chemist choosing to synthesize an olefin via the Wittig reaction will likely need to isolate their desired product from a mixture of isomeric (*E* and *Z*) products. Unfortunately, the presence of isomeric products greatly diminishes the yield of the desired olefin and necessitates purification before the desired product is obtained. As such, the ability to stereoselectivly synthesize the *E* or *Z* product remains highly desirable, yet unattainable. The authors will present recent advancements in the use of SOMS nano-reactors to facilitate the stereoselective synthesis of olefins using the Wittig reaction.

SERMACS 1355

One-pot enol silane formation-Mukaiyama aldol reactions promoted by trimethylsilyl trifluoromethanesulfonate

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Ketones, esters, amides, thioesters, and aldehydes can be converted into enol silane nucleophiles in the presence of trimethylsilyl trifluoromethanesulfonate and an amine base. Recent results show that these reaction conditions can be manipulated to yield either the aldol condensation product (i.e., the alpha,beta-unsaturatedcarbonyl) or the aldol addition product (i.e., the beta-silyloxycarbonyl compound) as desired. Control experiments verify the importance of the putative enol silane intermediate. In the case of ester enolates, the ester itself may be employed as solvent to render the procedure more environmentally friendly. Crossed aldol reactions between disparate nucleophiles can be controlled through judicious choice of reaction partners.

SERMACS 1356

Swelllable organically modified silica facilitated organic synthesis

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Traditional methods of organic synthesis often require lengthy reaction times, extensive purification, and significant use of hazardous chemicals. And while advancements in instrumentation have broadened the applications of synthetic organic chemistry, the underlying chemical principles of reactivity remain unchanged since the discipline's inception. To date, a synthetic organic chemist seeking to synthesize a product through the combination of reactants must accomplish this task, in its most simplistic form, by combining the reactants and a solvent in a flask followed by mixing. Through this process, the chemist hopes the reactants will collide with sufficient velocity and in the correct, three-dimensional, orientation such that a reaction will take place and the new product will be synthesized. The use of swellable organically modified silica (SOMS) nano-reactors seeks to overcome the reactivity challenges of conducting synthesis using traditional methods by ensuring reactivity through the restriction of reactants to nano-sized reactors. For example, in a traditionally conducted organic synthesis, reactants that are diluted with solvent and stirred in a reactor face the same reactivity challenges that you and I would face if we were trying to find each another while bobbing in an ocean that covers the surface of earth. The reactant molecules are magnitudes smaller than the reaction vessels that contain them and even well dispersed reactant molecules must navigate a large ocean of solvent to achieve reactivity. However, the chances of reactivity can be greatly enhanced if the reactant molecules are restricted to nano-sized reactors. The author will present the development of SOMS nano-reactor facilitated organic synthesis and present their use to facilitate the synthesis of biodiesel fuel, pharmaceuticals, peptides, and other synthetic organic reactions.

SERMACS 1357
Selected synthetic transformations of a polycyclic diene toward novel oxa-bowls

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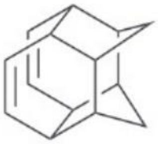
The polycyclic diene **1** was initially proposed as a precursor to the corresponding, yet still unknown bishomohexaprismane. We will discuss selected synthetic transformations of this versatile framework: The inherent cyclooctadiene subunit may be exploited toward the synthesis of novel organometallic complexes and the functionalization of one or both double bonds delivers intriguing scaffolds. We will present crystal structures of selected diene derivatives and summarize our attempts toward an oxa-bowl.



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SERMACS 1358
Palladium-catalyzed synthesis of α-trifluoromethyl benzylic amines via fluoroarylation of *gem*-difluoro-2-azadienes enabled by phosphine-catalyzed formation of an azaallyl–silver intermediate

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The development of biologically relevant and structurally diverse chiral a-trifluoromethyl amines is of great significance in medicinal chemistry as these compounds have been shown to be particularly useful due to the influence of fluorine on the pKa, bioavailability, and pharmacokinetics. We report a palladium-catalyzed method for the synthesis of a-trifluoromethyl benzylic amines through the vicinal fluoroarylation of *gem*-difluoro-2-azadienes. We identify an a-trifluoromethyl azaallyl–silver species, which has been characterized *via* NMR spectroscopy, as the likely nucleophilic partner in the cross-coupling. XPhos is proposed to play a dual role in the transformation. First, the phosphine serves as a phase transfer catalyst that promotes the addition of AgF to the difluoroazadiene, generating the nucleophilic α-trifluoromethyl azaallyl–silver intermediate. Second, XPhos forms the active Pd catalyst, which couples the aryl iodide substrates to the *in situ*-formed azaallyl–silver species. Critical to the success of several challenging cross-couplings, such as sterically hindered or electron-poor aryl iodides, was modification of the azadiene's activating group from a benzophenone imine to a benzylidene.

SERMACS 1359
Synthesis, isolation, and characterization of alpha-oxo gold carbenoids

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Alpha-oxo gold(I) carbene complexes have attracted substantial attention, as they are proposed as intermediates in many gold-catalyzed atom transfer reactions. Despite significant progress in the field of gold(I) catalysis, there remains uncertainty around the involvement of gold carbene species in these atom transfer reactions. Alternatively, recent theoretical models indicate the involvement of alpha-oxo gold carbenoids as the intermediate species, as opposed to a carbene complex. Herein, we report the synthesis, isolation, and characterization of gold alpha-pyridinium and alpha-sulfonium carbenoid complexes that, through kinetic analysis, can provide elusive mechanistic data regarding the mechanism of gold-catalyzed oxidation of alkynes.

SERMACS 1360
Regioselectivity influences in platinum-catalyzed enol ether formation

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Enol ethers are important structural components existing in an array of naturally occurring and pharmacologically active molecules, and are employed as nucleophiles in a range of transformations. General approaches toward accessing this functional group include condensation of a carbonyl with an alcohol, alcohol/alkenyl halide cross coupling, allyic ether isomerization, and hydroalkoxylation of alkynes. The latter reaction subset represents a direct and convenient method, although a primary consideration is the regioselectivity of the addition. Therefore, methods that can facilitate these transformations selectively would be a potentially attractive addition to the existing synthetic approaches. Herein we highlight the ability to generate these heterocycles regioselectively via a platinum-catalyzed hydroalkoxylation pathway. We anticipate these studies could have broader implications in our understanding of the platinum carbene reaction manifold, which has been widely employed toward the syntheses of heterocycles and carbocycles.

SERMACS 1361

Trifluoromethyl fragmentation approach to accessing ?-fluoro Michael acceptors

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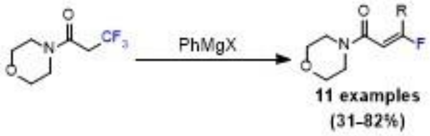
Fluorine incorporation leads to substantial improvement in the biological properties of organic compounds. It is reported that fluorinated compounds exhibit higher lipophilicity, bioavailability, membrane permeability, and metabolic stability. The monofluoroalkene is of particular interest because monofluoroalkenes are bioisosteres for peptide bonds. Fluoroalkenes are substantially more resistant to hydrolysis by peptidases and proteases *in vivo*compared to peptide bonds. Although there are numerous methods to synthesize α-fluoroalkenes, access to the β-fluoroalkenes is more limited. Two methods are available to convert alkynes into β-fluoro-α,β-unsaturated esters and amides using gold catalysts, and another approach requires stoichiometry chromium for a reductive coupling to create β-fluoro-α,β-unsaturated amides. There is still a need for additional approaches to access these β-fluoroalkenes. Our method uses 3,3,3-trifluoropropanamide as a substrate for nucleophilic addition by Grignard reagents and allows stereoselective access to both the (*E*)- or (*Z*)-β-fluoro-α,β-unsaturated amides. This approach is a one-pot reaction in which the Grignard reagent functions as a base and a nucleophile. This method provides direct access to an important class of bioisosteres of peptide bonds.



SERMACS 1362

Deoxyhalogenation of alcohols to alkyl halides using a silatrane moeity and acetyl chloride

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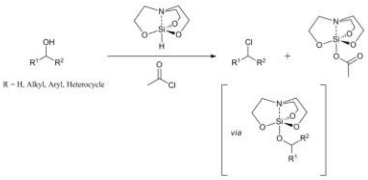
The conversion of alcohols to alkyl halides is an important step in the synthesis of value added chemicals. Taking advantage of the unique chemistry of a silatrane moeity - a hypervalent silicon species - alcohols can be converted to the corresponding alkyl halides using acetyl chloride as the source of the chlorine atom. Preliminary studies have shown that the an alkoxysilatrane intermediate of both primary and secondary alcohols readily react with acetyl chloride to yield alkyl chlorides in isolated yields of up to 87%.



SERMACS 1363

Intermolecular allylic C–H etherification of internal olefins

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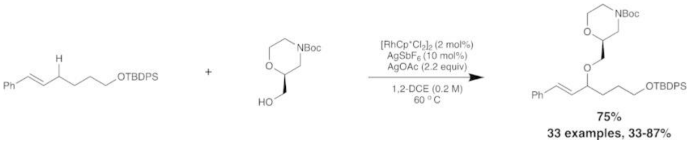
Group IX Cp* catalysts have proven indispensable in directed C–H functionalization, performing a wide variety of cross-couplings with aryl C–H bonds. Here in we report the non-directed intermolecular allylic C–H etherification of internal olefins with alcohols as the coupling partner. The transformation is proposed to proceed via a Cp*Rh-π-allyl intermediate. The reaction is tolerant of oxidatively sensitive alcohols, and several biologically relevant motifs are tolerated in both the olefin and alcohol. Mechanistic studies supporting the proposed mechanism will be presented in context of our recently disclosed allylic C–H amination mechanistic studies.



Allylic C–H Etherification of Internal Olefins

SERMACS 1364

C–H functionalization of aromatic alcohols utilizing readily attachable and cleavable molecular scaffolds

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Bond formation via metal-catalyzed selective C—H functionalization is well appreciated and often relies on the directing capability of the substrate. The appropriate positioning of a Lewis basic functional group can present the metal catalyst center at a specific site, enabling activation of otherwise unreactive C—H bonds. Utilizing pyridine- and quinoline-based acetal scaffolds as alcohol surrogates, our group has accomplished the *ortho*-olefination and arylation of aryl alcohols via Pd-catalyzed C—H functionalization. These scaffolds can be directly attached and removed post-functionalization in high yielding recovery. Pyridylacetal-directed *ortho*-olefination will be discussed, as well as telescoping efforts highlighting the conversion to olefinic products without any intermediary purifications. The utility of the quinoline based hemiacetal in *meta* C—H arylation, by combining functionalization with the transient norbornene strategy to produce biaryl compounds, will also be highlighted. Based on this premise, current and future work focusing on streamlining this process towards new modes of C—H functionalization will be briefly discussed.

SERMACS 1365

Regioselective CP*Ir(III)-catalyzed allylic C–H sulfamidation of terminal olefins

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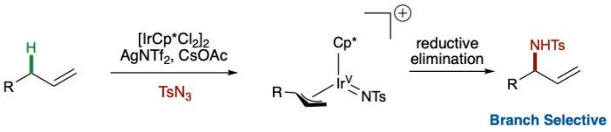
C–H functionalization provides an attractive alternative to allylic substitution reactions, which require pre-functionalized olefin substrates. In this study, we report the development of Cp*Ir(III)-catalyzed allylic C–H sulfamidation of terminal olefins, using sulfonyl azides as the nitrogen source. Mechanistic studies suggest that the reaction proceeds through a Cp*Ir(III)-π-allyl intermediate, which is subsequently oxidized to the Cp*Ir(V)-nitrenoid before C–N reductive elimination. The reaction has good functional group tolerance, and displays exclusive regioselectivity to give the branched products from terminal olefins. A brief survey of the synthetic utility of these products will also be presented.



SERMACS 1366

Convergent synthesis to access an enantiopure indenyl ligand scaffold

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Chiral Cp*-based catalysts have been utilized as extremely useful tools to induce enantioselectivity in a catalyst-controlled manner. In this work, we present a new synthetic route to access a class of chiral indenyl ligands. The synthesis is convergent, modular, and begins from inexpensive, commercially available starting materials, allowing for rapid access to a library of ligands. Synthesis of the corresponding metal complexes and initial evaluation of their activity as catalysts for enantioselective C–H functionalization reactions will be described.

SERMACS 1367

Patent law for chemists: What you need to know

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In a world of instantaneous information exchange and rapidly evolving technology, private companies, universities, solo inventors, and many others have increasingly begun to appreciate the growing importance of intellectual property. Chemists today should understand the basic principles of patent law from an inventor perspective, including the steps, costs, and other requirements for applying for (and receiving) a United States Patent. A more complete understanding of other issues, in particular those common to universities, are relevant to patent issues as well, including inventorship, assignment of rights, patentable subject matter, and foreign filings. Case studies relating to specific patents will be employed in this symposium in order to better illustrate key concepts. In addition, chemists today may see patents in a number of different contexts, and it is important to know and understand both the relevance and the impact these patents can have on a growing field or particular technology. This symposium will also give chemists the tools they need to understand the evaluation of intellectual property, and to better appreciate the legal framework undertaken by patent attorneys in any analysis thereof. Use of intellectual property is also a necessary consideration. Thus, this symposium will also address the different ways that a patent owner can use intellectual property, offensively or defensively, and otherwise leverage it as an asset.

SERMACS 1368

Patent law for chemists: what you need to know

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Already sumitted.

SERMACS 1369

Characterization and analysis of binding interactions between photactive Cr(III) diimine complexes and DNA

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For the past several years, the Wheeler Lab has investigated and characterized novel tris-diimine Cr(III) complexes to be utilized as a potential source of photoactivated chemotherapeutic agents. These complexes have the ability to photooxidize guanine, when excited by UV light, leading to DNA strand scission and, in some cases, permanent adduct formation. Complexes that contain different types of ligands are studied to understand the two different proposed binding interactions, including: intercalating diimine ligands (e.g., dipyridophenazine, DPPZ; 11,12-dimethyldipyridophenazine), and a range of "ancillary" ligands (e.g., 1,10-phenanthroline, phen; 3,4,7,8-tetramethylphenanthroline, TMP; 1-methylimidazole, 1-MeImid). Spectrophotometric titration is utilized to quantify binding affinity (K DNA) using the McGhee-Von Hipple algorithm for non-cooperative binding due to the reduced absorptivity of intercalated Cr (III) complexes, associated with pi stacking with DNA bases. Isothermal titration calorimetry (ITC) data is employed to verify the contributions of enthalpy and entropy to the thermodynamics of binding, as well as to verify the K DNA values obtained by spectrophotometric titration. Equilibrium dialysis and circular dichroism (CD) demonstrate unique differences in the binding affinities of the Λ and Δ Cr (III) enantiomers as a function of ancillary ligand identity.

SERMACS 1370

Determination of deoxynivalenol and ochratoxin A in North Carolina grown organic wheat grains

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The main safety issue of cereal grains is mycotoxin contamination. This study quantified the contents of deoxynivalenol (DON) and ochratoxin A (OTA), two frequently occurring mycotoxins, in organic wheat samples collected from six counties in North Carolina by enzyme-linked immunosorbent assay (ELISA) and high performance liquid chromatography (HPLC). By ELISA, all samples were DON and OTA positive, and the DON contents in the flour and bran samples were 0.7-2.35 ppm and 5-8 ppm, respectively, while OTA in the flour and bran samples were 9.54-25.55 ppb and 21.67-32.55 ppb, respectively. By HPLC, the DON detected in flour and bran were 0.24-0.47 ppm and 0.35-0.83 ppm, respectively; all flour samples were OTA negative, but 5 out of 6 bran samples were OTA positive (0.48-1.28 ppb). The results indicate that the organic wheat produced in North Carolina during 2018 season were contaminated by DON and OTA to various degrees. However, the concentrations of these two mycotoxins determined by ELISA were significantly higher than those determined by HPLC. However, more studies with larger sample number are needed to obtain more representative results. To avoid overestimation or underestimation, it is important for researchers and regulatory agencies to conduct collaborative multi-lab studies to develop and standardize analytical methods and detailed procedures for accurate DON and OTA quantification.

SERMACS 1371

Investigating antioxidant activity of sulfur and selenium-containing complexes

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Oxidative DNA damage is a leading cause of cancer and other diseases related to damaged DNA. DNA oxidation can occur when DNA is exposed to Reactive Oxygen Species (ROS) such as hydrogen peroxide. One way in which ROS production may be limited or prevented is through the availability of antioxidants to react with ROS and form an unreactive product. We are currently investigating sulfur and selenium-containing compounds as potential antioxidants in a mechanism wherein the antioxidant of interest may coordinate with a biologically available metal (Fe^{2+}), thus preventing the formation of ROS and extensive DNA damage. The potential antioxidant compounds of interest are *N,N'*-dimethylimidazole thione (Dmit), methimazole (MetIm), 2-mercaptoimidazole (MerIm), and *N,N'*-dimethylimidazole selone (Dmise). Results from gel electrophoresis, capillary gel electrophoresis (CGE), polymerase chain reaction (PCR), and Ultra-Performance Liquid Chromatography (UPLC) Quadrupole Time-of-Flight Mass Spectrometry (QTof-MS) show these sulfur and selenium-containing compounds are successful in limiting ROS-induced DNA oxidation. Additionally, the compounds exhibit the ability to prevent DNA oxidation at lower concentrations than the naturally occurring antioxidant glutathione that is produced *in vivo*.

SERMACS 1372

Bacterial exometabolomics by high-resolution mass spectrometry

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The intestinal microbiome is vastly diverse in nature and plays an important role in overall health. Characterizing the enteric exposome, including microbiome-derived metabolites, lipids, fatty acids, and other biochemicals that interact with the epithelium, is critical to understand the host-flora relationship. Distinguishing secreted bacterial compounds from those of environmental or host origin can be challenging but is essential to define the microbiome's effect on health. Here we exhibit both liquid chromatography-high-resolution mass spectrometry (LC-HRMS) and paper spray ionization (PSI)-HRMS approaches for the analysis of the bacterial exometabolome, using several native intestinal bacterial species as an experimental model. We show a PSI-HRMS workflow to differentiate between conditioned versus unconditioned media and identify bacteria-derived biochemicals using a rapid (30 sec) direct analysis analytical method. Also demonstrated is the isolation, purification, and LC-HRMS chemical profiling of outer membrane vesicles containing secreted bioactive compounds responsible for a variety of important extracellular functions.

SERMACS 1373

Characterization of red blood cell derived extracellular vesicles using Raman spectroscopy

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Raman spectroscopy provides precise signature of the molecular content of the analyte by measuring the nonelastic scattering caused by the radiating laser. It has been a method of choice due to the label free detection, requires no sample preparation and provides Raman fingerprints corresponding to the constituents of the sample. In this study, Extracellular vesicles (EV) derived from the Red blood cells (RBCs) have been used. EV's are produced in response to various stimuli have been potential indicators in diagnosis of health conditions and are interesting area of study. Like all other cell types, RBC's also release EV's (exosomes and micro vesicular bodies) due to aging and disease conditions. The extracellular vesicles derived from the Red Blood Cells slightly differ in size and protein expression and exhibit almost similar Raman spectral signatures. This study demonstrates the ability of Raman spectroscopy to differentiate with the use of multivariant statistical tool. Multivariant statistical tools have been used to analyze the raman data and distinguish the vesicles into exosomes and micro vesicles. This study paves a way for the noninvasive method to study extracellular vesicles in combination with the identification oxyhemoglobin and methemoglobin content in the extracellular vesicles which could also be determined from the Raman spectra.

SERMACS 1374

Feasibility study of using ion mobility-mass spectrometry to detect RNA modifications

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Specific RNA modifications have been used as biomarkers for monitoring a variety of abnormal biological activities. To detect a specific RNA modification, it requires a selectivity to distinguish the targeted RNA modification from as many as 160+ different types of RNA modifications that have already been discovered and reported in the literature. Some of the RNA modifications are isomers, which represent a bigger challenge to the current analytical methods being used to detect RNA modifications. In this study, our goal is to explore the potential of coupling ion mobility spectrometry (IMS) as an extra dimension of measurement to the current liquid chromatography-mass spectrometry (LC-MS) technique. Specifically, we compare the ion intensity and the outcome from collision-induced dissociation (CID) of selected RNA modifications under two different modes of operation, one without IMS and the other one with IMS, in the Waters Synapt G2 High Definition Mass Spectrometer. We found the IMS did not significantly lower the signal intensity despite of the relatively high gas pressure inside the ion mobility cell. Also, we found the reported ion heating in IMS could be beneficial for CID experiments. Based on the results of this study, we demonstrated the coupling of IMS to LC-MS can improve the detection of specific RNA modifications.

SERMACS 1375

Profiling the epitranscriptome in glioblastoma

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The central dogma of molecular biology describes the flow of genetic information from DNA that is copied to RNA which provides the formula for proteins. The discovery of post-transcriptional modifications (PTMs) to nucleic acids expanded the complexity of what is occurring in the regulatory layers that lies between DNA and proteins. A new field of study, epitranscriptomics, was created in part by the discovery that certain RNA modifications have reader, writer, and eraser proteins that enable reversibility which is indicative of a role in gene expression. RNA modifications are decorations on the chemical structure of the four canonical RNA bases, sugar, or even the phosphate group that makes up the monomeric units of RNA known as a nucleotide. Over 140 of these distinct modifications have been discovered in eukaryotes. These evolutionarily controlled modifications require a significant energy cost to maintain cellular functions and overall health, suggesting their importance. Conversely, disruptions or alterations in modifications that lead to gene under-or- over expression occurs in disease states, such as found in the N6-methyladenosine (m6A) mRNA modification that is implicated in the self-renewal and tumorigenesis of glioblastoma (GBM). The arduousness in RNA modification research has been limited methodologies for detecting, quantifying and identifying specific RNA molecules that carry RNA modifications. In this analytical study, ultra performance liquid chromatography in tandem with high resolution mass spectrometry (UPLC-HRMS) was employed for the comprehensive profiling of the epitranscriptome in glioblastoma cell lines U87 and LNZ308, as well as patient derived primary cells MGG6, MGG8 and PN157. UPLC-HRMS was carried out in a Water's Acquity LC system equipped with a polar end-capped reverse phase Acquity HSS T3 column and a Thermo Fisher Scientific Q Exactive Plus. Positive identification of 40

modified RNS were confirmed by MS/MS fragmentation. In addition, accurate mass analysis (< 5ppm) with reproducible retention times expand the profile to include 16 more low abundant modified RNAs. Biological and technical replicates were used to account for biological variability. This novel characterization will allow for the targeting of known enzymes or proteins associated with the up or down regulated PTMs in glioblastoma which may help illuminate possible mechanisms of gene expression regulation.

SERMACS 1376

Applying standard additions to chronoamperometric reactive oxygen species measurements in cancer cells

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Matrix effects typically hamper accurate measurement of reactive oxygen species (ROS) in cancer cells. A Prussian Blue (PB) zinc oxide carbon nanotube composite was used to analyze ROS. The Fe in PB, which can result in ROS artifacts via Fenton reactions, were minimized by keeping its content low (~0.04 atom%). MCF-7, BT20 and 4T1 breast cancer cell lines were oxidatively stressed, and the resulting ROS species (H_2O_2, ●OH, etc.) were assayed. This technique offers advantages over standard enzyme-linked immunosorbent assays (ELISA) in terms of speed and precision of the measurements. The composite's low toxicity makes it amenable to *in vivo* sensing applications. Aspects of control experiments evaluating the Fe content in these cell lines to assure its non-interference with sensing performance will be discussed.

SERMACS 1377

Evaluating self-segregation of semen components via SERS

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The purpose of this study is to demonstrate Surface-Enhanced Raman Spectroscopy (SERS) as a means of non-destructive, confirmatory identification of semen with a higher accuracy than currently implemented methods in forensic analysis. Previously in our lab, a method was developed and optimized to grow silver nanoparticles (AgNPs) on commercially-available nylon swabs, which allows for evidence collection directly onto a SERS-compatible substrate. However, since bodily fluids are comprised of a large number of components, they form heterogeneous stains; this results in stark variation of spectra collected along the stains. As such, there is not yet a standardized protocol for conducting Raman spectroscopy on semen collected on these swabs. Our goal is to understand component separation that occurs as semen dries on various SERS-active substrates, with capillary forces characteristic of the coffee-ring effect as the basis for segregation behavior. Preliminary studies using Raman spectral imaging show simulant stains assume concentric coffee rings, with ring diameter being inversely proportional to the hygroscopicity of the component. This study will also help determine other physical parameters of each semen component that contribute to separation, which may facilitate future studies of the efficacy of AgNP-coated swabs in analyzing other complex bodily fluids.

SERMACS 1378

Iron bioavailability in a novel soy-based cookie

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Iron deficiency anemia (IDA) is the most common worldwide nutrient deficiency; five to 10 million people in the United States and 2 billion people worldwide are affected. IDA is highly prevalent among women and children, and in children it can cause permanent cognitive delays. Soybeans are a rich source of iron, but high in phytic acid (PA). PA is an antinutritional factor that chelates iron tightly thereby decreasing iron bioavailability. Wheat flour contains phytase, an enzyme that degrades phytic acid; it has the potential to increase iron bioavailability from PA. Four recipes for soy-flour based cookies were developed. Two recipes contained different levels of wheat flour in an effort to decrease chelation of iron from phytic acid; one recipe was absent of spices, and the fourth was all soy flour. The purpose of this research project was to determine iron and phytic acid content of the cookies with varying levels of wheat flour. Iron was quantified using the inductively coupled plasma (ICP) instrument and PA quantification was done using a spectrophotometric assay for each of the cookie recipes. A sensory study using Just-About-Right scales was also completed to determine if the addition of wheat flour affected consumer perception of bitterness, sweetness, and aftertaste. Hedonic scales were used to assess overall consumer acceptance of each treatment. Both chemical analysis and sensory data were obtained with the intent of using the cookies in a future clinical trial to assess efficacy of them in improving iron status in women at risk of IDA.

SERMACS 1379

Wax oleogel: Prospect of a healthy saturated fat substitute

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Oleogelation is a novel and effective technology to structure liquid oil into semisolid fat. Oleogel, an organic system comprised of oil trapped in a three-dimensional network formed by a structuring agent, presents itself as a promising solution to substitute saturated fat. Among several studied structuring agents, waxes appear to be the most promising. The objective of this study was to find the best ratio of oil/wax as stable oleogels to replace saturated fats in food products Five vegetable oils (sunflower, safflower, flaxseed, avocado, and grapeseed) were structured with three waxes (candelilla, carnauba, and rice bran). The addition of each structurant was defined in preliminary studies. For each wax two different proportions were tested, 3 and 6% for candelilla and rice bran wax, and 4 and 8% for carnauba wax. The stability of oleogel was analyzed by its oil binding capacity (OBC), visualization evaluation and peroxide value under two different temperatures (room and 35 C) at two different times (day 1 and day 7). The fatty acid composition of the oils was analyzed by gas chromatography. Among the waxes, candelilla wax structured all the oils for both amounts (3 and 6%), producing an oleogel with higher stability even at higher temperatures and after seven days. Although the rice bran wax had structured the oils for both amounts (3 and 6%), the rice bran oleogels were not stable on the first day for both conditions (room and 35C) and showed the lowest OBC for all oils. OBC was dependent on oil composition. The oleogel structured with carnauba wax was stable only with 8% of addition, under both conditions by seven days into the experiment. The results of this study thus demonstrated that that oleogelation is a viable method for producing stable lipids that can be used as a saturated fat substitute.

Vegetable oils structured with 4% of carnauba wax in the first day of storage at room temperature.

SERMACS 1380

Quantifying the atrazine degradation ability of mycelium utilizing high performance liquid chromatography (HPLC) and quadrupole time of flight mass spectrometry (QTOF-MS)

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Mycelium contain enzymes that are capable of breaking down atrazine (AT) into metabolites and simpler organic compounds. Their ability to break down these compounds makes them an important tool for bioremediation. Methods were created to determine the amounts of AT, desethyl atrazine (DEA), hydroxyatrazine (HA), desethyl-desisopropyl atrazine (DEDIA), and desisopropyl atrazine (DIA) found in the soil-mycelium matrix. Fieldwork was required to harvest the mycelium and extraction procedures were used to obtain the compounds of interest. Analysis was performed using high performance liquid chromatography (HPLC) and ultra performance liquid chromatography (UPLC) with UV detection. Quadrupole time of flight mass spectrometry (QTof-MS) was used to verify chromatography peaks as well as determine other atrazine metabolites the enzyme reactions formed in the soil. Recovery studies were done for each of the compounds and the overall atrazine degradation was studied by manipulating atrazine dose, mushroom species, time mycelium are present in soil, and photolysis time. It has been determined that mycelium are capable of reducing the amount of atrazine in soil by up to 97%, with DEA and HA being the most prevalent metabolites. Additionally, most AT degradation occurs within the first few weeks of mycelium growth.

SERMACS 1381

Development of an analytical method to detect commonly used herbicides, glyphosate and AMPA

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Because of the difference of pricing, choosing between organic and conventional produce can be a difficult decision that often leaves many wondering if purchasing organic is worth the extra cost. Unfortunately, determining the validity of organic claims on various types of produce is a complex issue that has many different existing methods and applications. This study focuses on development of a simple, yet efficient method to extract and detect glyphosate and aminomethylphosonic acid (AMPA) from conventional corn and potato samples in order to compare them to the extracts from the corresponding organic produce. High performance liquid chromatography (HPLC) coupled with an ultra violet-visible (UV-Vis) detector was used as the primary method of detection for the derivatized herbicides. The herbicides were extracted from homogenized samples of produce using a methanol solution as well as an acetonitrile solution and a mixture of various inorganic salts. All unwanted components of the organic layer were removed via a SPE cartridge, leaving behind only the desired glyphosate or AMPA. The extracted herbicide was then derivatized with fluorenylmethyloxycarbonyl chloride (FMOC-Cl) in the presence of a borate buffer at a pH 9 while being stirred and slightly heated. A cosolvent extraction using diethyl ether and hexanes was used to remove majority of excess FMOC-Cl and produce cleaner chromatograms with well-defined peaks. This simple method of extraction allows for the detection of the herbicides that are present in concentrations as low as 0.100 ppm.

SERMACS 1382

Identification of microplastics in green sea turtle (*Chelonia mydas*) gastrointestinal contents

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Persistent and increasing anthropogenic debris is a global concern posing negative effects on the ocean. Plastic debris is invasive and long lasting due to a slow degradation period. Ingestion of plastic debris, both directly and indirectly, by sea turtles has been widely documented in various ocean basins, primarily through strandings, to understand more robustly lethal and sublethal effects. Mote Marine Laboratory's Stranding Investigation Program (SIP) has responded to strandings of 5 species of sea turtles since 2003, averaging 120 responses per year, with approximately 50% being green sea turtles, *Chelonia mydas*. The gastrointestinal (GI) tracts of SIP recovered green sea turtles have not been well examined since their benthic diet of algae and seagrass make plastics difficult to detect. However, given the ubiquitous presence of microplastics (<5 mm) ingested by green sea turtles around the world, and the increasing presence found in SIP recovered loggerhead and Kemp's Ridley sea turtles, the SIP examined recovered green sea turtles more thoroughly for the presence of plastics. Using a KOH digestion method, the GI tracts, both tissue and contents, of 5 stranded green sea turtles recovered by the SIP from Sarasota and Manatee counties, Florida, were examined for microplastics. Further analyses are set to be conducted on the collected samples at the University of the South. Techniques such as IR spectroscopy, MicroRaman spectroscopy, and Epimicroscopy can be used to chemically characterize and identify plastics collected from the GI tracts of green sea turtles. Ingested microplastic presence by green sea turtles in this area of the Gulf of Mexico has yet to be established. Understanding the presence/absence will lead to a better awareness of the volume of pollution in the area, subsequently aiming to detect better, identify, and counter the sublethal effects plastics have on green sea turtles.

SERMACS 1383

Secondary metabolite profiling and natural product discovery from cyanobacterial blooms of North Carolina

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The growing prevalence of harmful cyanobacterial algal blooms (CHABs) in North Carolina water bodies has been facilitated by increased nutrient loading and warmer temperatures. Urban stormwater retention ponds and related runoff features in regions that experience high rainfall can harbor these favorable conditions to support prolific CHABs. While they are most commonly known for the potent toxins they produce, these microscopic chemical factories have been identified as a modern source of bioactive secondary metabolites replete with potential leads for pharmaceutical research. Implementation of semi-targeted UPLC-QToF-based metabolomics analysis coupled with annotated GNPS molecular networking has enabled rapid and more comprehensive evaluation of cyanobacterial blooms in North Carolina water bodies. A multi-species cyanobacterial bloom model system in King's Highway Pond, Wilmington, NC was profiled throughout the summer bloom season and across several years. Bioassay-guided fractionation of bloom material from multiple years and comprehensive structure elucidation resulted in the discovery of new bioactive and potentially ecotoxic members of multiple classes of cyanopeptides

SERMACS 1384

Exploring a multi-spectral analytical scheme for color dye identification

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Color powders are used on a day-to-day basis in color run races, gender reveals, and religious rituals. Due to their potential for causing accidental fires and adverse health effects via inhalation and dermal absorption, analytical methods aimed at the identification of dyes and characterization of their risks have been developed. The dye extracts of color powders known as India Green and CC Blue were characterized using quadrupole/time-of-flight mass spectrometry (q/TOF-MS), liquid chromatography coupled to mass spectrometry (LC-MS), and proton nuclear magnetic resonance (H-NMR). The MS techniques offer useful structural clues for analyzing the multiple constituents of the dye mixtures through chromatographic separation or tandem MS. They overcome the difficulty of H-NMR in dye mixture analysis while benefitting from the unique capability of H-NMR in providing information on the number and type of hydrogen atoms found in the dye structure. Vibrational spectroscopic techniques based on Raman and infrared (IR) can be used for confirming the chemical identity via spectral database search or assigning functional groups to assist in MS and NMR interpretation. X-ray fluorescence (XRF) and X-ray microanalysis methods will yield elemental ratios of dyes or their elemental concentrations. The X-ray methods can easily determine if an organic dye is sulfonated and which counterions might be present in dyes. Aqueous leachate of the color powders was also analyzed by gas chromatography-mass spectrometry (GC-MS) to assess the possibility of environmental contamination via dye dissolution. Pyrolysis of extracted dyes in the temperature range of 250-600 degree Celsius followed by GC-MS analysis allows for evaluation of the thermal stability of dyes and the identification of volatile fragments lost at characteristic pyrolytic conditions. Analytical characterization of dyes will lead to a better understanding of their properties and ensure human health and safety for consumer products with dyes.

SERMACS 1385

Investigation of toxic heavy metals in coffee samples by graphite furnace atomic absorption spectroscopy

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The purpose of this study was to investigate the level of lead, cadmium, and chromium in coffee samples produced in different parts of the world. All coffee samples purchased from local stores and treated with a mixture of nitric and perchloric acid before analysis. The thermal behavior of Cd, Cr and Pb during pyrolysis and atomization stages were investigated with and without matrix modifier. The concentrations of cadmium, chromium and lead ranged from 0.02 to 0.13 mg/kg, 0.04 to 1.7 mg/kg and 0.02 to 1.48 mg/kg, respectively. The concentrations of Cd and Cr were well below the maximum permissible levels. The precision was better than 6% for 95% of the samples.

SERMACS 1386

Valorization of lignin through a mild organosolv treatment of biomass

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Lignin is the most abundant biopolymer which has a main role in maintaining rigidity of the cell walls in lignocellulose plants. Due to numerous economic and environmental benefits, there has been much attention focused on valorization of lignin. During this process, the lignin polymer breaks down to small and highly valuable fragments that can potentially be used in industries such as biofuels and resin production. Among different methods, organosolv treatment which uses an organic solvent and acid for fragmentation of lignin seems very promising because of economic and environmental benefits associated with this method. Nevertheless, the use of relatively high temperature and pressure in such treatments and lack of a comprehensive organosolv lignin characterization are still important obstacles that need to be addressed. Here, we introduce a mild and environmentally friendly ethanosolv treatment of switchgrass biomass for valorization of lignin using phosphoric acid as a catalyst. Analysis of resulting low molecular weight products using GC-MS as an analytical tool shows a variety of phenolic monomers and dimers present in ethanosolv treated switchgrass biomass. To confirm that the observed products originated from lignin, we also conducted the ethanosolv treatment on a lignin isolated from switchgrass. Analysis of isolated lignin before ethanosolv treatment did not show the presence of any monomers or dimers that were observed in ethanosolv treated biomass. However, post ethanosolv treatment, monomers were observed and identified. Furthermore, the presence of the same fragments when lignin instead of biomass is treated by ethanoslov process confirms that these observed fragments are lignin-originated. All of the monomers observed in ethanosolv treated lignin were also observed in the biomass samples. Additionally, one dimer was observed in both samples however several dimers were observed only in the biomass samples perhaps indicating that these dimers existed as dimers in the biomass. The organosolv fragmenation of lignin using this approach is a mild and environmentally friendly method which makes it very promising for valorization of lignin. Furthermore, a comprehensive GC-MS characterization of ethanosolv treated switchgrass biomass using this methodology will be presented that can be served as a guide for the better understanding of structure and valorization of lignin.

SERMACS 1387

Is goldenseal stable under different storage conditions? Targeted and untargeted approaches to study the effects of storage conditions on stability of *Hydrastis canadensis* (Goldenseal)

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Hydrastis canadensis, commonly known as goldenseal, is a perennial herb that is native to southeastern Canada and eastern United States. The extract of goldenseal is bioactive due to the alkaloids present and has been used as a folk medicine for treatments of infection. However, these types of medicinal plants may also face degradation if not stored properly. The purpose of the study is to analyze the stability of known and unknown metabolites of goldenseal during exposure to different storage conditions, using untargeted metabolomics and mass spectrometry. The research project focuses on identifying the chemical changes in the content of goldenseal using under different temperature conditions (40°C ± 5°C as high temperature, 20°C ± 5°C as room temperature, and 4°C ± 5°C as low temperature) or different light : dark cycles (16 hours : 8 hours, 12 hours : 12 hours, and 0 : 24 hours), or different sample conditions (powdered version of the roots, and actual roots). This shelf-life project is a six-month study, where each month is treated as one-time mark.

SERMACS 1388

Electrochemical detection of dopamine with doped and undoped silicon nanowires

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Dopamine (DA) is an important neurotransmitter in the brain that governs a variety of physiological functions. Monitoring its concentration is useful for disease management and diagnosis. This study explores the utility of 60 nm diameter, 30-µm length silicon nanowires (SiNWs) deposited onto glassy carbon electrodes (GCEs) to quantify DA concentrations in aqueous solution. Electrocatalytic activity of the SiNW/GGE sensor was monitored with cyclic voltammetry (CV) and chronoamperometry (CA). CVs of the SiNW/GCE sensor at 0.01-10 mM DA concentrations were used to determine the oxidation and reduction potentials of DA. The interplay of factors affecting sensing efficacy, such as SiNW surface loading, solution pH, and n- and p-doping of SiNWs were investigated to optimize sensitivity and selectivity.

SERMACS 1389

Comparison of the observed size-dependent melting point of CdSe nanocrystals to theoretical predictions

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Cadmium selenide nanocrystals were observed to have a size-dependent melting point which was depressed relative to the bulk melting temperature. The observed size-dependent melting point ranged from 500-1478 K, while a model based on the surface area to volume ratio predicted that is should range between 774-1250 K. The nanocrystals were heated in situ in the electron microscope, and the melting point was almost immediately followed by the vaporization of the CdSe nanocrystals, allowing for straightforward determination of the melting temperature. The differences between the observed melting point of CdSe nanocrystals and the values predicted by the surface area to volume ratio model indicates that additional factors are involved in the melting point depression of nanocrystals.

SERMACS 1390

Surface-enhanced resonance Raman scattering of rhodamine B in thin films of multilayer $Ti_3C_2T_X$ MXene nanosheets

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Surface-enhanced resonance Raman scattering (SERRS) of rhodamine B, excited at 532 nm, was measured on multilayer two-dimensional (2D) titanium carbide (*ml*-$Ti_3C_2T_x$) nanosheets. The $Ti_3C_2T_x$ MXene nanosheets, prepared with a milder LiF/HCl etchant, showed a stronger enhancement effect of SERRS than did *ml*-$Ti_3C_2T_x$ nanosheets which had been prepared using a harsher hydrofluoric acid (HF) etchant. It is proposed that the milder LiF/HCl method resulted in *ml*-$Ti_3C_2T_x$ nanosheets with smaller interlayer separation which increased the occurrence of plasmonic hot spots. The more rigorous HF etchant process resulted in larger separation between layers and smaller particles. LiF/HCl-etched nanosheets drop-cast onto a glass slide supported an approximately linear SERRS response from Rhodamine B over the concentration range 0.5 - 5 x 10^{-6} M.

SERMACS 1391

Size-dependent electrochemical deposition of Au on Au nanoparticles

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Electrochemical deposition (ECD) of metals involves the reduction of simple metal ions or metal complexes to the metallic form onto a conductive electrode surface. It traditionally occurs by the well-known nucleation and growth mechanism, where the formation of a supercritical (or stable) nucleus of metal atoms occurs first under a constant overpotential. These nuclei then grow larger in a second step by the reduction of the simple metal ions or metal complexes on the nucleus surface which leads to the formation of metal nanoparticles (NPs). Metal ion (or complex) reduction to form the initial nucleation sites has a higher activation energy compared to the continued growth of the formed nucleation sites. Metal nucleation therefore requires higher overpotential compared to the growth of the nucleation sites. There has been a great deal of work measuring the overpotential needed to induce nucleation on various electrode surfaces and structures, but less attention given to the growth step. Here, we describe the ECD (growth) of Au on different-sized Au NPs attached to indium tin oxide (ITO)-coated glass electrodes through a (3-aminopropyl)triethoxysilane (APTES) linker. ECD of Au occurs by the electrochemical reduction of $AuCl_4^-$. As the size of the Au NP decreases, the deposition ($AuCl_4^-$ reduction) potential becomes more positive (lower overpotential). The deposition of Au on a bare Glass/ITO/APTES electrode occurs at a potential of 300 ± 10 mV (vs Ag/AgCl), which corresponds to the potential required for Au nucleation on the electrode. In comparison, the deposition potentials for growth (vs Ag/AgCl) on 4 nm, 15 nm and 50 nm diameter Au NPs are 757 ± 8 mV, 630 ± 30 mV and 500 ± 60 mV, respectively. The deposition potential on 4 nm sized Au NPs showed the most positive shift of ~450 mV from that of the nucleation potential. This shows that the potential for growth of Au depends on the size of the Au NP nucleation site. This could be due to the smaller Au NPs acting as better catalysts for $AuCl_4^-$ reduction or due to a size-dependent thermodynamic shift in the standard reduction potential, which is known for metal NPs. Anodic stripping voltammetry (ASV) and electrochemical surface area-to-volume (SA/V) measurements confirm that the Au NPs increased in size following ECD at potentials corresponding to the growth potential for the different size Au NPs. Au NPs attached directly onto Glass/ITO by electrophoretic deposition (EPD) shows similar trends.

SERMACS 1392

Combination of a Prussian blue modified electrode with a glucose oxidase encapsulated xerogel for the detection of glucose

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Prussian Blue has been shown to be highly effective in the detection of hydrogen peroxide. Literature has several examples of successful biosensor systems that rely on enzymatic activity to produce hydrogen peroxide. In addition, several recent publications have discussed biosensor systems with the key enzyme encapsulated with a xerogel. All of these systems rely on metal electrode materials which have a relatively high operating potential which allows for a greater possibility of interferences. In this research, a highly sensitive Prussian Blue modified electrode is combined with a xerogel in which glucose oxidase has been encapsulated. This new system provides an electrochemical system with low operating potential and high sensitivity. This electrochemical system shows excellent performance in the detection of glucose in physiologically relevant concentrations.

SERMACS 1393

Glucose oxidase and Prussian blue nanoparticles encapsulated within a xerogel for the detection of glucose

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Recent literature reports examples of electrochemical biosensor systems based on the encapsulation of enzymes and metal nanoparticles into a xerogel for the detection of biologically important compounds, such as glucose. While these systems are very successful with acceptable detection limits and linear ranges. However, Prussian Blue modified electrodes have been shown to be better than metal electrodes for the detection of hydrogen peroxide. Here, a biosensor system where a xerogel in formed with both glucose oxidase and Prussian Blue nanoparticles.

SERMACS 1394

Electrochemical characterization of potassium chromate in buffered acidic solutions for water purification

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Chromium exists in the environment in three main forms: hexavalent, trivalent, and chromium metal. While trivalent chromium, Cr(III), is non-toxic and an essential dietary element, hexavalent chromium, Cr(VI) is highly toxic to humans and is mostly formed through industrial processes. Cr(VI) is a key element in chrome plating and leather tanneries, often used as an oxidant or pigment in dyes. Due to the high mobility of Cr(VI), removal is challenging and Cr(VI) easily seeps into ground water systems causing contaminations and hazards for human consumption. Considering the danger associated with Cr(VI), the reduction of hexavalent chromium in an environmentally friendly manor needs to be addressed. The general approach to this work is to reduce Cr(VI) into Cr(III) through electrochemical proton-coupled electron transfer (PCET) reactions in water. Experimentally, no reduction is observed in water for Cr(VI) within the potential range of 0.7 to -0.7 V vs Ag/AgCl. However, in acidic solutions, reduction is observed and becomes more prominent with an increase in acidity and proton availability. A variety of acidic buffers are used to control the pH of the solution to uncover the separate influence of pH and acid specificity on chromate reduction. Understanding the reduction of Cr(VI) to non-toxic Cr(III) through PCET reactions will lead to novel energy efficient and environmentally friendly water purification methods.

SERMACS 1395

Initial investigation of Prussian blue electrode applications with cholesterol and galactose

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Prussian blue modified electrodes have been developed into an inexpensive alternative to traditional biosensors based on precious metals. Prior research in our lab has focused on Prussian Blue electrodes for the detection of glucose specifically. This system relies on the encapsulating of an enzyme within a xerogel formed on the modified electrode surface. We hope to expand the functionality of Prussian Blue electrode systems to other relevant molecules through encapsulating other oxidase enzymes, including galactose oxidase and cholesterol oxidase, on the surface of the Prussian Blue electrodes. Furthermore, we examined if there is a relationship between various silanes, used in the formation of the various xerogels, and the performance of Prussian Blue electrodes.

SERMACS 1396

Statistical modeling for identifying dyes on fibers found at crime scenes

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Fully appreciating significance of fiber evidence in forensics arises from understanding the ubiquity of fibers, as well as the variety of fiber manufacturing processes. Fibers readily shed from products, leading to cross-transfer, an important principle of forensic science. Fibers may be transferred between individuals or between a particular environment and an individual's clothing or other belongings. Comparison of questioned fibers found at a crime scene to those of known origin is thus critical to determining associations between suspects, victims, and the crime scene. Fiber identification is often performed with UV-visible microspectrophotometry (MSP), a quick and non-destructive approach for spectral comparisons. UV-visible spectra of fibers may consist of a large number of wavelengths distributed over the spectrum. Commonly, the number of wavelengths is larger than the number of samples (*i.e.*, fibers), thus leading to a 'Big Data' problem. Modern inferential statistics have evolved to include powerful sparse regression methods, whose solutions have few, but significant non-zero coefficients. Lasso is a sparse regression method which reduces the number of parameters by placing a penalty on the L_1-norm, improving prediction accuracy for prediction of significant variables. In this study, logistic regression using a Lasso penalty will be used to create an unbiased model for predicting dye composition of fibers. This technique will be compared to more conventional statistical methods, such as Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA), for prediction accuracy.

SERMACS 1397

Use of DRIFTS in the identification of accelerants in fire debris

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The analysis of fire debris is vital to fire investigations. Because arson has one of the lowest clearance rates according to the Armstrong forensics laboratory, advancements in the area of fire debris analysis could help increase the number of solved cases. Infrared spectroscopy provides characteristic quantitative and qualitative spectra and is virtually non-destructive to the samples. In this experiment the use of Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) to analyze samples of fire debris was done in order to test for the use and identification of accelerant in a particular burn study. This was accomplished by running 4

different types of burn studies 3 times: wood chips with no accelerant, wood chips with gasoline, wood chips with kerosene, and wood chips with ethanol. Each sample was analyzed on the Perkin Elmer Spectrum 2 FTIR with DRIFTS Accessory, collecting 10 replicate scans per each sample. The spectra collected will then be examined visually and using statistics to determine the presence of the different accelerants in each sample. To help differentiate accelerants in the debris samples, Spectrum 10 spectroscopy software was used to determine characteristic peaks in the spectra.

SERMACS 1398

Comparative study between feed forward neural networks and least absolute shrinkage and selection operator for the degradation detection of polyester-urethane audio magnetic tapes

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Audio magnetic tapes manufactured using polyester urethane were used as the main recording medium in the late twentieth century and store invaluable quantities of information. However, with time these tapes become non-playable due to degradation of the magnetic layer. Playing a degraded tape can cause an extensive damage to the tape, as well as to the play back device. For this reason, about 40% of the 21.5 million tapes in U.S. cultural heritage institutions house are in unknown conditions.[1] Our laboratory has found that Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR FT-IR) combined with multivariate statistical analysis can be used to determine the playability of polyester urethane audio magnetic tapes. This is a fast and non-destructive technique, which can be used to determine the playability status without playing the tape. This would facilitate the identification of non-playable tapes from playable ones and makes the baking and digitalization process easier and faster. In the present study, we acquired replicate spectra from 206 audio magnetic tapes of various brands and models and compared the results to playability testing. Principal Component Analysis (PCA) was initially applied as a dimension reduction technique,[2] and the Least Absolute Shrinkage and Selection Operator (LASSO) was employed as a model selection tool.[3] Classification was carried out using feed forward neural network.

SERMACS 1399

N-donor heterocycles for trivalent actinide and lanthanide separations

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Heterocyclic N-donor ligands are being designed, synthesized, and evaluated in efforts toward improved separations of trivalent actinides from lanthanides. Candidates are screened for stability, solubility, and solvent extraction efficiency and selectivity of Am(III) over Eu(III). Compounds exhibiting sufficient extraction and selectivity, as well as solubility in one or more of the solvents tested (e.g., toluene, 1,4-diisopropylbenzene, and trifluoromethyl-phenyl-sulfone) undergo systematic analysis to determine the effects of varying conditions and evaluate their potential as extractants. Data are used to define and validate theoretical models and guide the design process. This project is centered on evaluating both symmetrical and non-symmetrical bis-triazinyl pyridine (BTP), bis-triazinyl bipyridine (BTBP) and bis-triazinyl phenanthroline (BTPhen) scaffolds. For the tridentate ligands, 3,3'-dimethoxy-phenyl-bis-1,2,4-triazinyl-2,6-pyridine (MOB-BTP) is being used as a benchmark to compare solubility and extraction efficiency. Results have confirmed that substituents on a ligand backbone tend to play a major role in extracted complex solvation. Surveying a wide variety of structures from synthetic, theoretical and analytical approaches, we intend to provide new directions for designing prospective N-donor ligands.

SERMACS 1400

Prediction of diesel fuel physicochemical parameters using partial least squares regression and mid-infrared spectroscopy data

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Eight diesel fuel brands collected from several stations within the Atlanta metropolitan area in the State of Georgia were class-identified using FTIR/ATR data and partial least squares discriminant analysis (PLS-DA). Physicochemical variables (initial boiling point, 10% distillation, 50% distillation, 90% distillation, endpoint, % residue, sulfur content (ppm), flashpoint, API gravity and cetane) of our samples were determined by the Georgia Department of Agriculture (Georgia, Tifton). Ten spectra per fuel brand were collected over the 650 – 4000 cm^{-1} mid-infrared region, resulting in an 80 x 3351 matrix. The underlying structure of the 80 x 3351 matrix was analyzed by principal component analysis, then refined by PLS-DA. The dummy variables in PLS-DA were later replaced by the physicochemical variables. Of the 80 spectra, 48 were used to build a prediction model, while 32 were used as a test set. Randomized physicochemical variables were created from Microsoft Excel and used as input to test the extent of correlations between the diesel fuel spectra and the randomized variables. Based on the t1/u1 plots, the PLS model using physicochemical variables showed good correlations between the variables and diesel fuel spectra ($R^2 = 0.8212$) with 99% correct predictions. The randomized variables showed very little correlations ($R^2 = 0.1486$).