Crystal growth and analysis of select oligothiophenes

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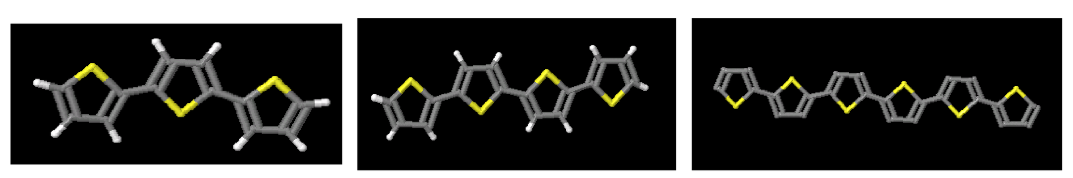
Introduction

As of 2006, solar energy accounts for approximately 0.1% of all the energy produced in the United States. Both high costs and a 12-18% average efficiency rate in commercial panels provide a steep entry with limited gains for the consumer. However, certain promising organic materials may provide an avenue of higher efficiency and cheaper production costs in future solar panels. Conjugated organic polymers, such as the polythiophenes, possess conjugated backbones, which give them electrical and optical properties that make them promising candidates for electrical devices such as transistors and photovoltaic cells. In addition, these organic polymers are cheap to produce and incorporate into electronic devices in comparison to current materials, such as silicon. Because defects and packing morphologies affect the transport of charge in conjugated polymers, an investigation into the effects of these phenomena on the real-world efficiency of these materials is important. However, polymers are complex molecules with a wide variety of morphologies, making them difficult to characterize. Thiophene oligomers serve as a model system to characterize different packing morphologies available to these conjugated polymer materials.

Thiophene Oligomers



Terthiophene, Quaterthiophene and Sexithiophene, respectively.

The creation of a library that correlates Raman microscopy data with crystal structure data obtained from x-ray diffraction provides a picture of the effects of crystal morphology and growth defects on the overall electrical properties of these model oligomers.

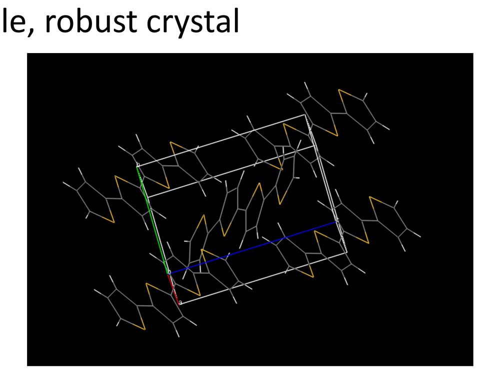
X-ray Diffraction (XRD)

Single Crystal Diffraction

Non-destructive technique which diffracts x-rays off a single, robust crystal sample.

Benefits

- Provides detailed information about crystal structure, including unit cell information, bond angles and packing morphologies
- Provides simulated powder diffraction patterns to match against experimental powder diffraction results



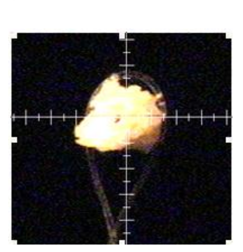
Representative model of packing structure produced by single crystal diffraction of quaterthiophene

Powder Diffraction

Diffracts x-rays off a well-ground, homogenized sample.

Benefits

- Relatively short data collection time
- Requires a minimal sample of substance
- Provides a powder pattern that can be matched against known sample patterns



Homogenized powder sample of quaterthiophene mounted for diffraction

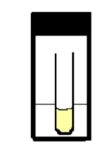
Acknowledgments

CCI: Center for Chemical Innovation

Crystal Growth Techniques

Vapor Diffusion

- Uses two liquids, one in which the compound is soluble and one in which the compound is insoluble
- Two liquids must be miscible
- Insoluble liquid must have higher vapor pressure
- The compound is dissolved into the soluble liquid to form a saturated solution
- An inner vial containing the saturated solution is placed inside an outer container filled with the insoluble liquid and left to sit for up to a week
- As outer liquid evaporates and mixes with the inner liquid, compound solubility is reduced and crystals form
- Vibrations and movement are avoided during crystal growth

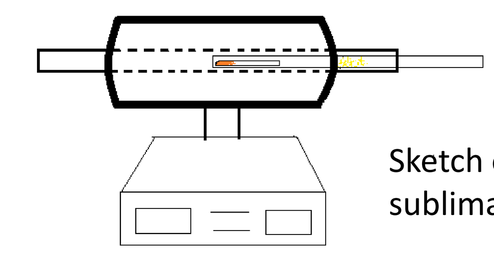


Schematic of vapor diffusion setup

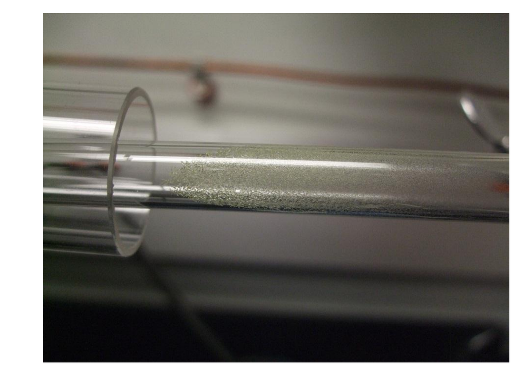
Toluene/Pentane vapor diffusion setups for terthiophene, quaterthiophene and sexithiophene

Zone Sublimation

- Compound is placed in a sealed vacuum tube
- Sealed vacuum tube placed inside a tube furnace
- Tube furnace set to hover around the boiling point of the substance
- As the compound vaporizes, it will move outwards from the center of the tube as a result of the temperature gradient created
- Crystals will begin to form in the outer (cooler) portions of the vacuum tube

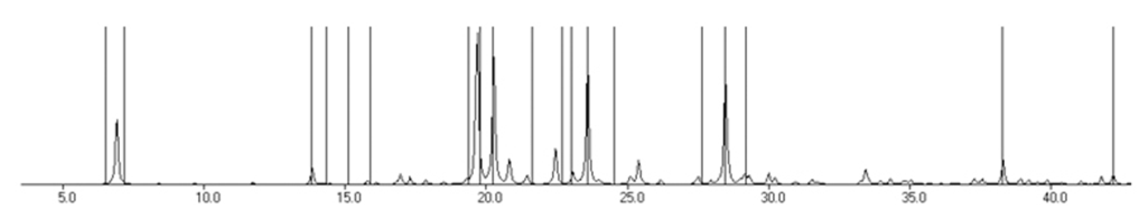


Sketch of a zone sublimation setup

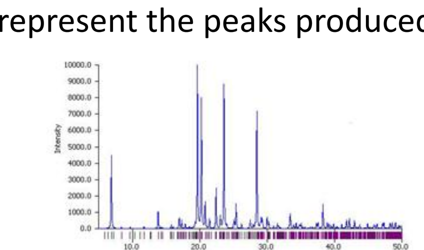


Sexithiophene crystals in a vacuum tube grown by zone sublimation

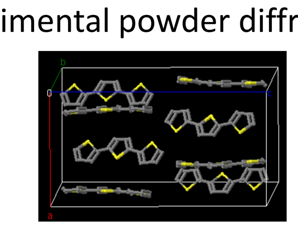
Results: Terthiophene (Zone Sublimation)



Powder results for terthiophene grown by zone sublimation. The graph represents the simulated powder pattern produced by single-crystal diffraction of the sample. The vertical lines represent the peaks produced by experimental powder diffraction of the same sample.



Powder pattern for terthiophene taken from the Cambridge Structural Database

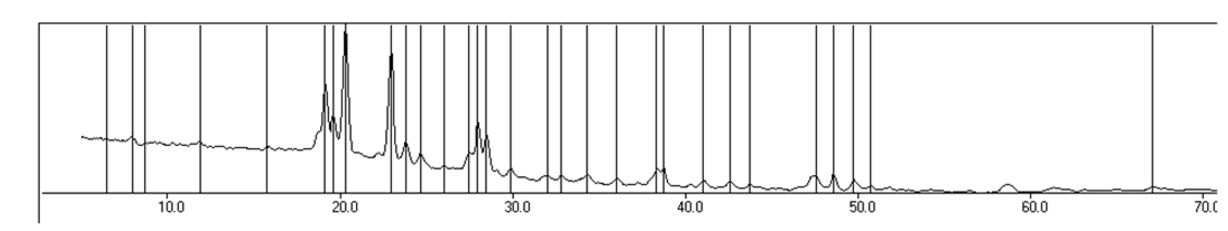


Packing structure for terthiophene sample produced by single crystal XRD

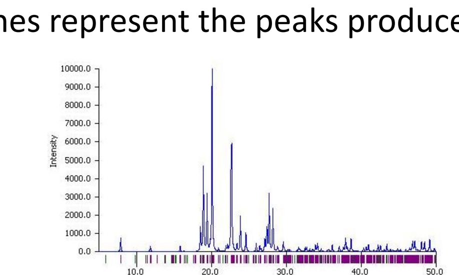
a	15.225
b	5.635
c	25.848
α	90
β	98.15
γ	90

Unit cell information for terthiophene

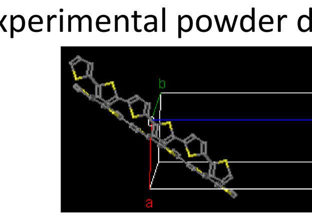
Results: Sexithiophene (Zone Sublimation)



Powder results for sexithiophene grown by zone sublimation. The graph represents the simulated powder pattern produced by single-crystal diffraction of the sample. The vertical lines represent the peaks produced by experimental powder diffraction of the same sample.



Powder pattern for sexithiophene taken from the Cambridge Structural Database

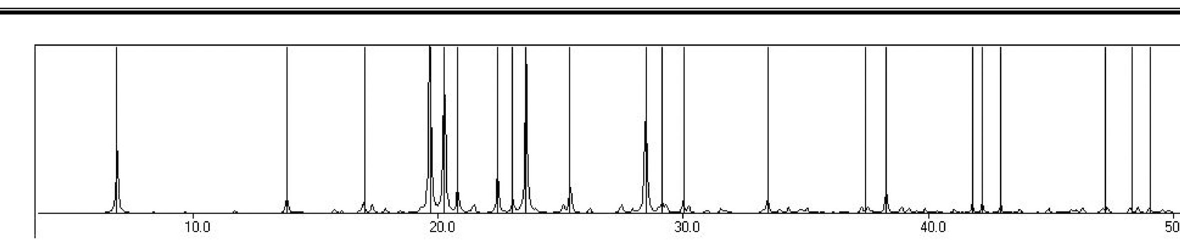


Packing structure for sexithiophene sample produced by single crystal XRD

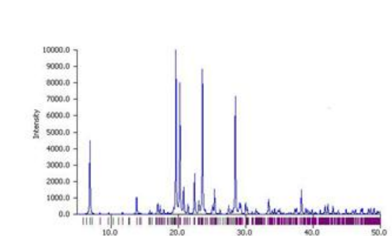
a	90
b	44.708
c	7.851
α	90
β	90.76
γ	90

Unit cell information for sexithiophene

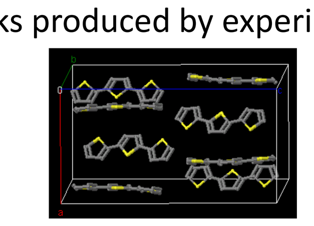
Results: Terthiophene (Vapor Diffusion)



Powder results for terthiophene grown by vapor diffusion in a toluene/pentane setup. The graph represents the simulated powder pattern produced by single-crystal diffraction of the sample. The vertical lines represent the peaks produced by experimental powder diffraction of the same sample.



Powder pattern for terthiophene taken from the Cambridge Structural Database



Packing structure for terthiophene sample produced by single crystal XRD

a	15.225
b	5.635
c	25.848
α	90
β	98.15
γ	90

Unit cell information for terthiophene

Conclusions

- Reliable terthiophene crystals most efficiently produced in a toluene/pentane vapor diffusion setup.
- Reliable sexithiophene crystals are most efficiently produced by zone sublimation.
- Though the powder diffraction data from sublimation-grown terthiophene did not match as well as the others, the single crystal XRD data showed that the sample possessed the same unit cell and packing morphology as the sample grown by vapor diffusion
- Vapor diffusion for terthiophene and zone sublimation for sexithiophene produce reliable crystals for characterization and analysis for inclusion in a library alongside data from Raman microscopy.