Organic Photovoltaics: Focus on Its Strengths

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Organic photovoltaics are far more inexpensive, and compared with silicon solar panels are increasingly favorable and thus represent a moving target.

There is a perception among scientists that the creation of knowledge is important for its own sake, regardless of its future application. There are those in the community who have told me that whether organic solar cells ever see the light of day is unimportant. They say, rightly, that we have learned a great deal about charge transport in disordered media, synthesis of \( \pi \)-conjugated molecules, X-ray analysis of semicrystalline polymers, solution-phase dynamics of comb-like molecules, and fabrication of thin-film devices by roll-to-roll manufacturing. Given these outcomes, they argue, the actual production of energy on the gigawatt scale using organic solar cells is incidental, and may never have been the goal in the first place. This analysis seems revisionist.

For me and other researchers whose first language was organic synthesis, learning about the existence of organic solar cells produced a deep sense of excitement. The organic solar cell seemed to be the most direct way in which one’s training in synthesis and structural determination could contribute to the global energy challenge. Tragically, however, that which makes organic solar cells interesting from an academic standpoint also makes them challenging to deploy. For example, complex molecular structures are susceptible to manifold pathways of degradation. Moreover, the nanoscale structures of interpenetrating networks of electron-donating and electron-accepting materials—crucial for charge separation and transport—are interesting to elucidate but difficult to arrange (and to keep stable). These intrinsic challenges are compounded by an extrinsic one: benchmarks of cost-per-watt established by silicon are increasingly favorable and thus represent a moving target.

In what it portends for the future of life on Earth, the decline in the price of silicon is, of course, to be celebrated. In any technological transformation, however, there are winners and losers. A researcher selects his or her topic not only by the expected societal impact but also by that which leverages his or her education and experience. Reduced funding in the United States and Europe for organic solar cells thus suggests a future in which hundreds of researchers no longer have the financial resources to work on the topic that best suits their intellectual resources. This scenario may force a large number of highly creative individuals to leave the energy sciences entirely. If one’s interest is in electrochemistry or energy in general, there are myriad technologies under development to explore. To the organic chemist, however, there is something somewhat boring about polycrystalline solids such as perovskites, whose unit cells contain only a few atoms. Is there a use case for organic solar cells that will retain the enthusiasm of its research community and continue to extract value from the huge volume of existing knowledge?

One strategy for leveraging existing expertise and research in organic solar cells is to recommit to aspects of organics that would be difficult or impossible to replicate using inorganic technologies. The characteristics of...
solution processing, extreme light weight,\(^1\) and tunable color\(^2\) are now shared by perovskites and thus are no longer unique to organics. There are, however, at least two broad areas in which organic cells can still be said to have superiority: environmental benignity and mechanical robustness. This set of characteristics is not exclusive, and the future of organic solar cells may depend on the community identifying others. For example, semitransparency, although also possible to achieve in perovskites, may be more straightforward with organics in applications such as smart windows.\(^3\)

The first area of near-certain superiority for organic solar cells is in their potential for the reduction of e-waste, i.e., disposability, recyclability, and degradability.\(^4\) This advantage is salient when compared with perovskite modules based on methylammonium lead iodide, which would be damaging if released into the environment. (Tin-based perovskites are more environmentally friendly than their lead-containing counterparts, but are less efficient.) Organic solar cells also have an exceptionally short energy payback time, over which the energy produced cancels out the energy of manufacturing and deployment.\(^5\) Designing substrates, electrodes, and absorbers with low embodied energies and that can be degraded into benign products is purview of green chemistry, and indeed this subject has already begun to receive the attention of the community working in organic solar cells.\(^6\)

The second area in which organic—especially polymeric—electronic devices have unequivocal advantages is in extreme mechanical deformability. Indeed, flexibility, stretchability, and mechanical robustness underpin many of the advantages of organic solar cells. A minimum level of deformability is even required for roll-to-roll manufacturing, perhaps the least expensive method to fabricate these modules. In addition, a robust response against cyclic thermal and mechanical loading in the outdoor environment—due to diurnal and seasonal expansion and contraction, and especially due to the forces of wind, rain, snow, and hail—is a prerequisite for modules with long lifetimes. Extreme forms of deformability are required for portable and off-grid applications, as might be required for military, intelligence, and disaster relief. The deformability of organic solar cells cannot be assumed, however. Despite the carbon framework common to all organic semiconductors, these materials are not always “plastic,” in the sense of deformable. The molecular structures and processing conditions have a strong influence on the microstructures adopted by solid films when cast, and thus on the mechanical properties.\(^7\)

Given the importance of the mechanical properties of organic semiconductors, it is surprising that the mechanical response of these materials has historically taken a back seat to concern over optoelectronic performance. Moreover, field-effect mobilities of semiconducting polymers are typically measured on silicon, and power conversion efficiencies of solar cells are typically measured on glass. These rigid substrates obscure the wide range of mechanical properties possessed by thin films of these materials. Recent work on flexible substrates, however, suggests that—without judicious selection of materials and processing conditions—these devices can fail with cohesive fracture energies of the organic semiconductors among the lowest of all electronic materials.\(^8\) Despite the challenges related to the thermomechanical reliability of organic solar cells, that of perovskites is expected to be worse, as the cohesion of the active layer cannot be increased using the tools of polymer engineering.

The mechanical response of conventional polymers and engineering plastics is the subject of a large body of literature that spans half a century.\(^9\) While much of this literature is directly applicable to the design of semiconducting polymers—e.g., high molecular weight is nearly always conducive to mechanical reliability (Figures 1A and 1B)—these materials have structural characteristics that set them apart from their non-conjugated counterparts. (For example, the flat shape and rigidity of a \(\pi\)-conjugated polymer, along with alkyl side chains required for solubility, are not found in conventional plastics.) In addition, when increasing the robustness of these

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**Figure 1. Mechanical Properties of Semiconducting Polymers and Organic Solar Cells**

(A) Molecular weight increases the resilience and toughness of regioregular poly(3-hexylthiophene) (P3HT). Reproduced with permission from Rodríguez et al.\(^{10}\) Copyright 2017, American Chemical Society.

(B) Coarse-grained molecular dynamics simulation showing the stress concentration on semiconducting polymers under strain (courtesy of Samuel Root).

(C) Organic solar cells survive thousands of cycles of cyclic bending and torsion.
polymers, sufficient absorption and charge transport must be retained. Indeed, the very characteristics required for charge transport—rigid π-conjugated backbones and aggregated microstructures—are those that would seem to increase the stiffness and brittleness when polymer chains condense to form solid films.

Efforts to increase the mechanical stability of organic semiconductors and whole solar cells have required expertise in many areas, namely organic synthesis, molecular and continuum modeling, device fabrication, and testing in simulated real-world conditions. While there is not yet a “recipe” for producing organic semiconductors that can resist any deformation, this research illustrates the critical importance of molecular weight, the side chain, and the position of the glass transition relative to the operating temperature. High molecular weight increases the density of entanglements between chains. The principal effect of increasing the length and branching of the alkyl side chain is to increase the deformability, largely by decreasing the glass transition temperature. The effect of the rigidity of the main chain is not straightforward: its effect on the mechanical properties seems to arise from its influence on the microstructure when cast from solution. Blending semiconducting polymers with derivatives of buckminsterfullerene (used as an electron-transporting material) nearly always increases the \( T_g \), these vitrified films are stiffer and more brittle than the polymeric components alone. Blends with the greatest mechanical deformability seem to be those in which both the electron-transporting and hole-transporting materials are polymers. Achieving a close match between the modulus of the active materials with that of the substrate decreases the strain energy release rate of propagating fracture, and is associated with greater robustness of whole modules. Furthermore, good adhesion and encapsulation between layers in a device stack serve to distribute strain energy and prevent the concentration of stress, which would otherwise lead to cracking and ultimately failure of the devices. Perhaps surprisingly, solution-processed small molecules—which lack chain entanglements—have modes of mechanical deformation that do not involve fracture and can thus be used in flexible (and even stretchable) applications.

With this knowledge, it has been possible to demonstrate solar cells with unprecedented levels of deformability. For example, organic solar cells can be stretched biaxially over hemispherical surfaces without generating cracks or wrinkles. This work led to an “all-rubber” solar cell, in which the substrate, encapsulant, anode, cathode, and semiconducting polymer (although not the fullerene) were elastomeric, along with the first skin-wearable solar cell with extraordinary robustness against cyclic loading. A group at KAIST demonstrated a stretchable all-polymer solar cell with efficiency close to the state of the art for a non-stretchable device fabricated on a rigid substrate. While these laboratory-scale demonstrations are interesting, such concepts can also be applied to thin-film modules manufactured in ways amenable to the grid scale. Organic solar modules produced by Risa DTU were found to survive many thousands of cycles of bending and torsion (Figure 1C). This work suggests that some routes of mechanical failure can be mitigated at the level of packaging.

Three decades of work on organic solar cells has produced an enormous body of knowledge. A noteworthy byproduct of this research has been the training of many thousands of scientists and engineers, along with analytical techniques that can be applied to other problems within chemistry, materials science, and electrical engineering. But what of the organic solar cell, per se? Given competition from incumbent silicon and upstart perovskite technologies, it is possible that the dream of organic solar cells producing many gigawatts of clean energy may never come to fruition. If, however, the research community emphasizes aspects of organics that cannot be replicated in other materials, there is an immense opportunity to leverage the research done so far into something approaching this aspiration. Fundamental work on synthesis, charge transport, microstructure, and device design should be done with at least one eye on a clean energy future. Organic solar cells are most likely to contribute to this future if we keep in mind the strengths—literally and figuratively—of organic and polymeric structures.

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