Next-Generation Polymer Solar Cell Materials: Designed Control of Interfacial Variables

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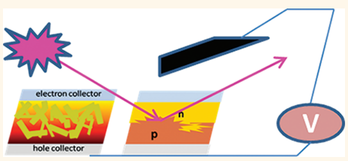
ABSTRACT Organic bulk heterojunction solar cells (BHJSCs) are the focus of a burgeoning research effort. While extensive characterization is performed in the course of many reported experimental studies, correlation of performance and physical parameters among studies done in different laboratories is low, pointing out the need to address some aspects of BHJSC active materials that have received relatively little attention. This Perspective describes how a new polymer additive series described by Lobez *et al.* in this issue of *ACS Nano*, along with some emerging morphological tools and scanning electronic nanoprobes, can help fill in some of this needed insight. A brief statistical discussion of interstudy correlations and a summary of past work on additives and interfacial studies are presented.



A bulk heterojunction solar cell (BHJSC) consists of a nanoscale phase-separated material flanked by two electrodes. One phase, the "donor", is selective for hole transport, and the other, the "acceptor", selectively transports electrons. Figure 1 illustrates the typical morphology. Ideally, the photogenerated holes and electrons are directed to opposite electrodes; interface layers and vertical gradients in the volume fractions of the two phases may aid in this selectivity. One or both phases absorb light and convert photons to excitons, which migrate until they are further converted to electron−hole pairs. In recent years, photoconversion efficiency (PCE) of the best reported BHJSCs rose from 5% to the 8% range.[1,2] Electron transporters, though generally C_{61} or C_{71} fullerenes, now include fullerene diphenylmethano and xylylene adducts, giving PCE >5%.[3,4] Hole transport polymers include more highly condensed and elaborately functionalized co-monomers[5−15] or even small-molecule donors.[16−19]

Beyond these highlighted references, there have been thousands of manuscripts published in the last several years describing material designs for improving PCEs of organic/polymer-based BHJSCs, which are envisioned as energy-capture devices well suited to flexible substrates such as canopies, tents, umbrellas, and backpacks, as well as faces of buildings. The variations are often aimed at optimizing a physical variable that is thought to influence PCE by increasing one or more of the open circuit voltage, short circuit current, and fill factor (the maximum current times voltage product obtainable). It is already established that these optimizations can involve tradeoffs, and it is especially challenging to enhance all three simultaneously.

Dang, Hirsch, and Wantz recently published a commendable survey of literature on the most popular BHJSC material combination, poly(3-hexylthiophene) donor with PCBM (C_{61}) fullerene acceptor.[20] They found reported PCEs ranging broadly around 2−4%, with several reports outside of that range. There was very little correlation of PCE with numerical characteristics of the P3HT, such as molecular weight and regioregularity. Factors that did seem to influence PCE were more qualitative and less defined processing parameters, such as solvent treatments and thermal annealing, presumably resulting in preferred morphologies, interfacial characteristics, and charge carrier mobilities.

In parallel with their study, we ourselves surveyed a series of manuscripts published during 2009−2011 that reported new polymer designs. We focused our coverage on papers that reported (a) at least one PCE ≥1% from bulk heterojunction devices and (b) two or more additional characterizations such as absorbance spectra (peak maxima and breadth), microscopic morphology (grain size and domain aspect ratio), and hole mobility and energy. As it happens, we found hardly any correlation of PCE with any

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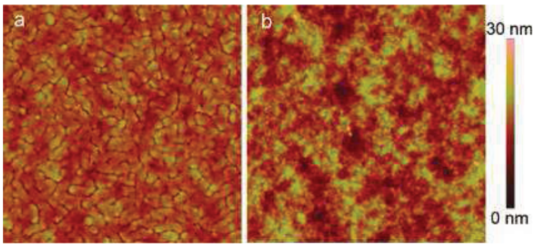

Figure 1. Atomic force microscope images (5 μm × 5 μm) of a thiophene-isoindigo copolymer mixed with a C_{71} fullerene. Reproduced from ref 6. Copyright 2011 American Chemical Society. Used with permission.

physical variable across the various studies. The only exception was hole mobility, where within each of 20 individual studies that reported PCE and hole mobility, higher mobilities led to higher efficiencies 90% of the time. However, even these selected studies, taken together, produce a statistical p value for PCE−mobility correlation of just 0.19, not considered significant (Figure 2). This does not cast doubt on the validity of any one study, but simply points out that the controlling variables in the studies are different and likely depend on subtle differences in processing steps, solvents, thermal history, and so on. The low correlation is not surprising in view of contradicting opinions that hole mobility may or may not aid exciton dissociation into separated charges.[21] The result also points out the need to consider some entirely different variables in characterizing BHJSCs and in designing new materials for them.

In this issue of *ACS Nano*, Lobez *et al.* present a study that is notable for creating new material systems in which some of the less-appreciated variables can be explored.[22] Their materials lead to modulations specifically at polymer−fullerene interfaces, and the characterizations probe very specific phenomena at these interfaces, both *in situ* and in model bilayer devices. The authors rightly remind us that PCEs of bulk heterojunction solar cells must be strongly dependent on the interpenetration of hole- and electron-carrying domains, the characteristic lengths of the light-absorbing domains relative to exciton diffusion lengths, and the interfacial area between the domains, across which excitons are separated into opposite charges (and are possibly recombined, as well). The molecular packing in each domain, besides being important for charge mobility, determines the tendency for components to intermix and thus the electronic density of states of each phase. This assumes that the components are not so miscible that they do not phase separate at all, as is the case for P3HT−PCBM mixtures where P3HT is the majority component.

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The optimal balance of these morphological factors is difficult to attain, let alone stabilize, in conjugated organic photovoltaic composites. The authors cite a previous report that a rather special class of additives, the iodoalkanes, somehow enhanced BHJ morphology.[23] The mechanism of action of these additives was mysterious at the time the work was done, and their localization in the composites was somewhat unpredictable and nonselective, though a recent report indicates that such additives act by solubilizing the fullerene component and increasing its penetration and intercalation into the donor polymer.[24] A similar mechanism was also just discovered for the 4-bromoanisole additive.[25] However these additives may distribute, there is no particular model for their electronic effects, as these additives are largely nonconjugated. Reports of a limited number of other conjugated polymer additives with packing inhibited by randomized regiochemistry[26] or block copolymer architecture[27−29] are also mentioned by Lobez *et al.*[22] A polymeric aniline was helpful when added to P3HT−PCBM in small quantities, but the benefit was attributed to changed hole mobility.[30] There are additional examples of additive studies involving diiodoalkanes increasing interpenetration of domains as well as inducing other unspecified improvements.[10,31,32] Other small-molecule additives, such as 4-amino-2-trifluoromethylbenzonitrile,[33] alkylthiols and dithiols,[34,35] 1-chloronaphthalene,[36] and 1,2,3,4-tetrahydronaphthalene,[37] were also effective. With tetrahydronaphthalene, an electronic effect was also noted, as distributions of surface potentials over regions of the BHJ surface were different, depending on the additives. Lim *et al.* showed that, by terminating the P3HT donor with a small fluorinated end group, association of the donor with PCBM is inhibited and larger ordered PCBM domains are formed, with better interpenetration.[38]

The Lobez *et al.* article reports an innovative and contrasting series of additives for regioregular P3HT−PCBM solar cells that address many of the limitations of the prior examples.[22] The additives themselves are regioregular polyalkylthiophenes, so they are both electronically and morphologically compatible with the host polymer. The additive main chain lengths are short enough to facilitate locational equilibration in the composite, and because of the bulkiness of the additive functional groups (shown to prevent long-range crystallinity), their sided regiochemistry, and their appendage to relatively

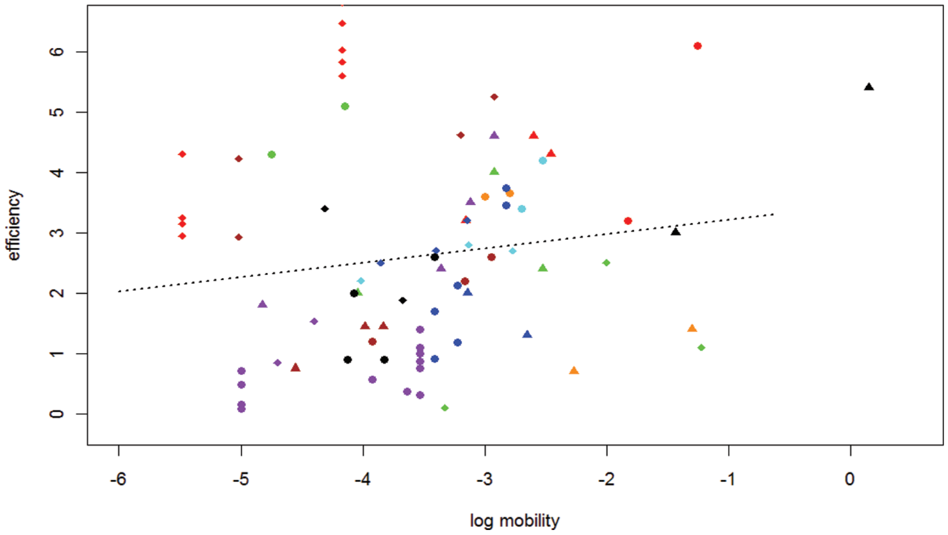

Figure 2. PCE *versus* log(hole mobility), measured either in field-effect transistors or space-charge-limited current modes, for data where two or more mobility values were reported. The points with the same color and shape come from the same study, and the correlations within each study can be observed, though there is little correlation or quantitative agreement of the correlations among all of the studies. The line is a linear regression fit. A bibliography of studies considered is in Supporting Information.

short lengths of P3HT, the chains should preferentially migrate to domain boundaries but still present a compatible side to the bulk P3HT, thus acting as surfactants. No attempt was made *a priori* to predict electronic effects of functional groups, so a range of electron donors and acceptors were selected. More subtly, a range of functional group shapes were also covered, again to seek special interactions that might be repulsive with ordinary P3HT or attractive with PCBM.

The summary result is that nearly all of the additives influence solar cell performance parameters even when present at 0.25%. Since P3HT crystallization is maintained even at a 10% additive level, it is reasonable to expect that a very low level of additive has an amplified effect because it is a much higher volume fraction of a small but performance-limiting volume of the device, most likely the near-boundary regions. For the cases where PCE was higher, this was more because of improved current output than from increased open circuit voltage. It has been argued that morphological changes alone could not increase open circuit voltage because of recombination canceling some of the voltage built up from efficient charge dissociation.[39] Intriguingly, though the number of charge carriers collected by Lobez *et al.* was higher, consistent with more interface area for photocharge generation and longer continuous pathways for migration to electrodes, the rate of charge recombination was actually lower. Thus, even though open circuit voltages in bulk heterojunctions were not necessarily increased by the additives, other favorable interfacial voltages may have been set up.

One of the unique contributions of this paper, therefore, was to observe a signature of these voltages. This was done by making layered, rather than heterojunction, devices. In these cases, open circuit voltages were increased as additive functional group dipole moments were increased. While the interface dipole might not be a simple projection of a molecular dipole on a surface, this is the first time to our knowledge that a role of internal interface dipoles conferred by additives by any mechanism has been considered in BHJ solar cell performance, independently of the effects of the additives on morphologies.

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A wide range of structural characterization techniques have been employed to probe the morphology of BHJs and other organic solar cell (OSC) structures of relevance for solar energy collection. Many of these have been recently reviewed by Brady *et al.*[40] Of particular potential relevance for the work described by Lobez *et al.*[22] is depth profiling by neutron reflectometry, where surprising compositional nonuniformities in BHJs have been noted[41] and intermixing in layered P3HT/PCBM structures fabricated using nominally orthogonal solvents has been reported.[42,43] In the layered structures of Lobez *et al.*, the PCBM was vapor deposited, which should reduce intermixing compared to spin-coating, but an important follow-up question to their interesting results is to determine the detailed structure of the interfaces in their P3HT/additive/PCBM layers. Given the similarity of their additives to P3HT, neutron scattering will likely not be able to resolve the structure and degree of intermixing at the P3HT/additive boundary, but a recently introduced method that increases X-ray scattering contrast by "heavy atom labeling"[43] may hold considerable promise for such measurements.

A powerful method for measuring the interfacial potentials in BHJs and other OSCs involves scanning probe microscopy (SPM). Depending on the mode of scanning, SPM can reveal information ranging from morphology to spatially resolved electric fields to nanoscale dynamics. In particular, Kelvin probe force microscopy (KPFM) can measure the local surface potential both under dark and illuminated conditions, allowing the visualization of the photoinduced charge generation in BHJs.[44−48] David Ginger's group has used time-resolved electrostatic force microscopy in addition to KPFM to link local dynamics with device behavior in BHJs in a series of papers,[49−51] while Lee *et al.* used KPFM to map the internal potential distribution in a cleaved BHJ solar cell turned on its side.[52] While the layered structures of Lobez *et al.*[22] firmly establish a link between internal interfacial dipoles and the solar cell performance, a combination of scanning probe methods would offer additional opportunities to gather data leading toward a firmer understanding of the physical mechanisms that govern this relationship. We anticipate that further investigation of nanoscopic electronic effects at the internal BHJ interfaces, along with continued attention to morphological factors, will be fruitful in advancing the BHJ solar cell field.

More broadly, organic photovoltaics have been on a steady path of improvements in PCE, and a manufacturing base has also been developed. The many new materials being designed and synthesized offer additional processing options and means for further technological enhancements. Standardization of processes and evaluation methods will be helpful in the introduction of materials beyond the typical sets on which much of the research to date has been reported. New materials, along with analytical methods discussed in this Perspective, will aid in the preservation of the highest PCEs as the device areas and manufacturing throughput are scaled up.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: Bibliography of references used in the statistical investigation. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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