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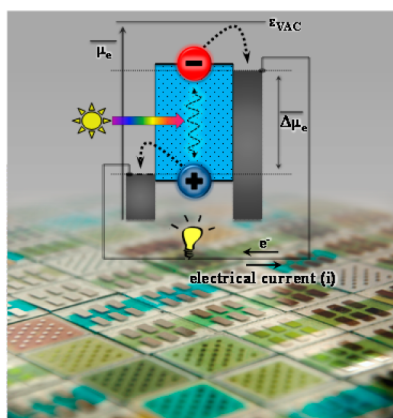
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## Organic Solar Cells—At the Interface

Organic photovoltaics (OPVs), whose active layers are polymers, small molecules, and hybrids of these material sets, have recently shown the greatest rate of improvement in power conversion efficiency relative to all other PV platforms, at least at the research cell level. Their initial embodiments with either planar- or bulk-heterojunction active layers produced power conversion efficiencies ( $\eta$ ) of 1–2%.<sup>1,2</sup> Both small molecule and polymer/small molecule bulk heterojunction OPVs have most recently demonstrated  $\eta > 10\%$ ; with at least one commercial report of ca. 12% efficiency in a tandem cell configuration.<sup>3,4</sup>

Significant challenges and opportunities remain in optimizing energy conversion in these platforms, which we comment on below in the context of the contributions of this issue of *The Journal of Physical Chemistry Letters* and other recent research reports (Figure 1). We consider here: (i) active layer materials



**Figure 1.** Schematic view of a thin-film solar cell (PV) with an organic, nanocrystalline, or organic–inorganic hybrid active layer (blue) showing the photoinduced formation of holes and electrons, and their harvesting at opposing contacts with different intrinsic work functions.  $\Delta\mu_e$  is the maximum quantity of reversible electric work that can be obtained from a single extraction–injection cycle. Challenges faced when maximizing power conversion efficiency of PV devices include the development of active layer materials that enhance photocurrent generation (the focus of this issue of *J. Phys. Chem. Lett.*), and understanding and controlling charge harvesting at both contacts, which competes with bulk and surface recombination.

for which improvements in photogeneration of charge carriers are necessary; and (ii) charge harvesting for which the careful tailoring of contact and interlayer materials can facilitate charge collection and minimize losses due to recombination.

**Active Layer Materials and the Photogeneration of Charge Carriers.** Open-circuit photovoltages ( $V_{OC}$ ) have increased significantly in OPV and related PV platforms to 0.8 V, or higher, in parallel with improved device efficiencies,<sup>5,6</sup> and in some examples, tandem OPV platforms have yielded very high operating voltages.<sup>7</sup> The percentages of incident solar photons that yield charges that are subsequently harvested at the

electrodes remains low, however, limiting the maximum voltage–current product from OPVs.

Photoexcitation in OPVs produces strongly bound Frenkel-type excitons, and thus significant free energy is lost to achieve mobile charge carriers. The dissociation of excitonic states to form individual charge carriers is hindered in low dielectric constant environments, since Coulombic interactions favor both “geminate” and “non-geminate” recombination over charge separation and collection.<sup>8</sup> Disorder on molecular length scales also helps to control the efficiencies of exciton dissociation and charge transport.<sup>9,10</sup> Several recent reports suggest, however, that modest increases in the dielectric constant of the active layer would lead to significant improvements in photocurrent generation and, with optimized extraction, enable efficiencies of 20% or possibly higher.<sup>11,12</sup>

This issue of *J. Phys. Chem. Lett.* includes four Perspectives: from Zhiqun Lin of the Georgia Institute of Technology, Nadia Camaioni of Consiglio Nazionale delle Ricerche via Gobetti, Wei You of the University of North Carolina, and Taku Hasobe of Keio University, and their co-workers, focusing specifically on routes to enhance the photogeneration of charges in organic photoactive materials, and/or to enhance absorptivity and photoelectrochemical energy conversion efficiency.

In the Perspective “Towards High Performance Organic–Inorganic Hybrid Solar Cells: Bringing Conjugated Polymers and Inorganic Nanocrystals in Close Contact”, He, Qiu, and Lin highlight the potential of solar cells based on hybrids of inorganic nanocrystal semiconductors and conjugated polymers (He, M.; Qiu, F.; Lin Z.-Q. Toward High Performance Organic–Inorganic Hybrid Solar Cells: Bringing Conjugated Polymers and Inorganic Nanocrystals in Close Contact. *J. Phys. Chem. Lett.* **2013**, *4*, 1788–1796). Such composite materials take advantage of the best features of both components, including: (i) high absorptivities, solution processability, and flexibility of polymers; and (ii) the high dielectric constant, high carrier mobility, and environmental stability of semiconductor nanocrystals. Achieving efficient charge generation at polymer–nanocrystal heterojunctions together with efficient charge harvesting at the electrodes, however, remains a grand challenge.

The morphology of the active layers, the interface composition, and electronic processes at nanocrystal–polymer heterojunctions are all limiting and poorly understood factors. A compromise results for the photoactive material where the polymer–nanocrystal interfacial area is optimized for efficient exciton dissociation, while maintaining contiguous charge transport pathways to the hole and electron collecting electrodes. Specific synthetic strategies are presented that vary nanocrystal capping ligands and grafting techniques to control interfacial contacts between the conductive polymers and inorganic nanocrystal semiconductors.

In “Pushing the Envelope of the Intrinsic Limitation of Organic Solar Cells”, Camaioni and Po suggest strategies to

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obtain high dielectric materials to overcome the characteristically low dielectric constant of OPV relevant materials ( $\epsilon_r \sim 3$ ) (Camaioni, N.; Po, R. Pushing the Envelope of the Intrinsic Limitation of Organic Solar Cells. *J. Phys. Chem. Lett.* **2013**, *4*, 1821–1828). This Perspective explores the introduction of polar functional groups into molecular structures, and utilizing hyper-branched, bioinspired, supramolecular structures. High dielectric materials can enhance the generation of free charge carriers and mitigate geminate and nongeminate recombination, thus enabling the use of thicker photoactive layers to enhance photon capture and photocurrent production.

In “Multi-Component Organic Solar Cells of Simple Structure”, Yang, Yan, and You mix multiple donor material components with complementary optical absorption, within a single photoactive layer, to enhance photogeneration of charge carriers, suggesting a potential pathway to overcoming the Shockley–Queisser limit,<sup>13</sup> imposed for single junction PVs (Yang, L.-Q.; Yan, L.; You, W. Organic Solar Cells beyond One Pair of Donor–Acceptor: Ternary Blends and More. *J. Phys. Chem. Lett.* **2013**, *4*, 1802–1810). OPV relevant donor materials have absorptivities of ca.  $10^5 \text{ cm}^{-1}$ , but typically only over a bandwidth of ca. 200 nm, and thus use only a small fraction of incident solar irradiance, while acceptor materials (e.g., fullerenes) typically absorb little visible light. This Perspective suggests three complementary approaches (charge transfer, energy transfer, and a parallel linkage mechanism) to enhance light absorption and create photoactive materials that facilitate the transport and collection of the photogenerated carriers.

In the Perspective “Porphyrin-Based Supramolecular Nanoarchitectures for Solar Energy Conversion”, Hasobe discusses porphyrins as building blocks for supramolecular donor–acceptor architectures, which demonstrate enhancements in photogeneration of charge carriers relative to nonorganized molecular systems (Hasobe, T. Porphyrin-Based Supramolecular Nanoarchitectures for Solar Energy Conversion. *J. Phys. Chem. Lett.* **2013**, *4*, 1771–1780). In addition to reviewing the recent advances in the field utilizing porphyrins in conjunction with fullerenes, carbon nanotubes, and nanoparticles, Hasobe presents strategies to achieve supramolecular architectures with well-defined shapes and sizes. The tunability observed for the dynamics of photoinduced electron transfer demonstrates their potential to enhance energy conversion efficiency as a component of the active layer, or as the active layer itself.

*Contact and Interlayer Materials and the Competition between Charge Transport, Collection, and Losses Due to Recombination.* The rate at which electrical work is extracted (i.e., power) from PV platforms is defined by the product of the operating voltage and photocurrent. Optimizing this power requires the highest-possible fill-factor (FF), whose value reflects the competition between charge harvesting and bulk or surface recombination, near  $V_{OC}$ .<sup>8,14–19</sup> For OPV and related thin-film PV platforms, with optimized active layers, the external efficiency, measured at short-circuit conditions where internal fields are high, often approaches 85% and in some cases higher. This efficiency is substantially lower if measured near  $V_{OC}$  or the maximum power point,  $V_{Pmax}$ , suggesting that charge extraction limits efficiency more than charge creation. Increasing attention is thus focused on understanding and controlling the interfacial factors that influence the efficiency of charge extraction.<sup>15–19</sup>

The metal–insulator–metal model (MIM) is typically used to describe the importance of high work function differences between the hole-harvesting and electron-harvesting contacts,

in order to achieve the internal fields needed to sweep charge carriers selectively toward the desired contacts, and to achieve high  $V_{OC}$ .<sup>20</sup> It is increasingly apparent, however, that interfacing metal, metal oxide, and/or conducting polymer-based contacts (or interlayers) with organic or nanocrystalline active layers can result in complex interphases quite different in composition and energetics than either of the isolated surfaces. These interfacial composition and energetic differences strongly influence the efficiency of charge extraction for emerging solar cell platforms.<sup>17,19,21,22</sup>

Work function differences between anode and cathode contacts alone are not sufficient to ensure the hole or electrons harvesting is selective at opposing contacts, and so additional steps must be taken to create this selectivity.<sup>23</sup> A variety of “interlayer” materials have been developed to assist in selective charge harvesting and enhance OPV performance.<sup>19</sup> For electron extraction, thin-film metal oxide interlayers (ZnO and  $\text{TiO}_2$ ) are often used. Their work functions and conduction band energies match well with the transport LUMO energies of electron acceptors (e.g., fullerenes), and their large bandgaps ensure hole blocking—provided they are missing midgap states that are sites for surface recombination. Recent discoveries that simple aliphatic amine polyethylenimine polymers can be deposited as thin layers on these metal oxides, and a variety of other metal, metal oxide, and conducting polymer contacts, to further lower the work function of the electron extracting contact have produced exciting results and energized material design for new thin film PV platforms.<sup>24</sup>

Applying these same principles to selective hole-extraction has been challenging. Most interlayer materials, such as the conducting polymer PEDOT:PSS, can be used to increase contact work function but are not particularly selective to hole harvesting. High work function n-type metal oxides hole transport materials (e.g.,  $\text{MoO}_3$  and  $\text{WO}_3$ ) also enhance the efficiency of hole extraction by increasing effective work function, but without imparting selectivity.<sup>19</sup> Significantly, interlayer films created from solution-processed  $\text{NiO}_x$  layers, when properly processed, provide both a high work function contact and, because of the high band gap of this oxide, apparent electron rejection, providing for high hole-harvesting efficiencies.<sup>17,18</sup>

The remaining challenges to be considered for efficient charge extraction in these new PV platforms are focused on (i) quantifying the dynamics of charge extraction,<sup>25,26</sup> as a function of contact/active layer or interlayer/active layer interfacial composition and energetics, (ii) the design of interfaces for charge extraction that are appropriately passivated so as to minimize dark injection of charge, a process that limits power conversion efficiency,<sup>27</sup> and (iii) understanding and controlling the effect of compositional and energetic heterogeneity in the contact.<sup>28,29</sup> Just the process of forming the electrical contact with the organic or nanocrystalline active layers can affect interfacial composition, ordering, and energetic dispersion of transport orbital energies, and can in some instances introduce new states for dark charge injection.<sup>30–32</sup> Strategies have been developed in silicon-based PV platforms to passivate surfaces in contact with extraction electrodes to minimize surface recombination and midgap state formation, with increasing success.<sup>33,34</sup> Similar levels of effort will be required for the new generations of organic and nanocrystalline PV platforms.

While the general development of PV platforms based on organic and semiconductor nanocrystalline active layers has been rapid and exciting, significant challenges remain. Our

understanding of active layer design is evolving, and it is clear that electrical contacts to these emerging active layers will have to be understood and tailored at atomic and molecular length scales, and matched to specific active layer materials, to ensure that the efficiencies of both charge formation and harvesting are optimized in formats that are readily scaled to large areas, while retaining the low material and processing costs inherent to these thin-film energy conversion platforms.

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