Molecular Understanding of Organic Solar Cells: The Challenges

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CONSPECTUS

Our objective in this Account is 3-fold. First, we provide an overview of the optical and electronic processes that take place in a solid-state organic solar cell, which we define as a cell in which the semiconducting materials between the electrodes are organic, be them polymers, oligomers, or small molecules; this discussion is also meant to set the conceptual

framework in which many of the contributions to this Special Issue on Photovoltaics can be viewed. We successively turn our attention to (i) optical absorption and exciton formation, (ii) exciton migration to the donor−acceptor interface, (iii) exciton dissociation into charge carriers, resulting in the appearance of holes in the donor and electrons in the acceptor, (iv) charge-carrier mobility, and (v) charge collection at the electrodes.

For each of these processes, we also describe the theoretical challenges that need to be overcome to gain a comprehensive understanding at the molecular level. Finally, we highlight recent theoretical advances, in particular regarding the determination of the energetics and dynamics at organic−organic interfaces, and underline that the right balance needs to be found for the optimization of material parameters that often result in opposite effects on the photovoltaic performance.
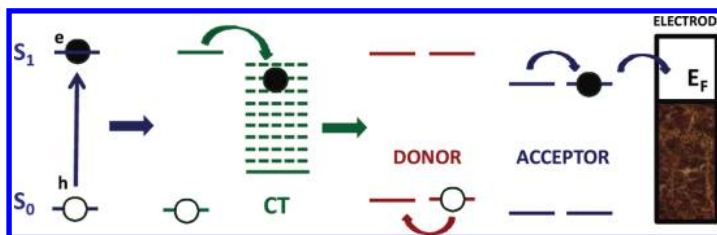
Introduction

A key feature of organic semiconductors that has impacted the design and geometry of organic photovoltaic devices for the past few decades is the excitonic character of their optical properties. This characteristic is the reason why organic solar cells[1−5] are often referred to as excitonic solar cells. While optical absorption in a conventional inorganic semiconductor results in the immediate creation of free charge carriers, it leads in an organic semiconductor to the formation of a spatially localized electron−hole pair, i.e., a Frenkel-type exciton, which is electrically neutral. The exciton binding energy is typically large, on the order of or larger than 0.5 eV. Because optical absorption in organic materials does *not* directly lead to free electron and hole carriers, to generate an electrical current, the exciton must first dissociate; this is the reason why a critical component in the architecture of organic solar cells is the design of the heterojunction between an electron-donor (D) material and an electron-acceptor (A) material.

Below, we describe the electronic and optical processes that take place during the operation of an organic solar cell, discuss recent theoretical advances, and highlight a number of theoretical challenges that still need to be met to gain a comprehensive understanding of organic solar cells at the molecular level. We successively turn our

attention to optical absorption and exciton formation, exciton migration, exciton dissociation, charge-carrier mobility, and charge collection at the electrodes.

Optical Absorption and Exciton Formation

Conjugated materials display absorption bands that are usually (i) intense, as a result of the large wave function overlap between the electronic ground state and the lowest excited state, and (ii) broad, because of the significant geometry relaxations that take place in the excited state (the width of the absorption bands can reach over 1 eV). The large extinction coefficients of organic semiconductors over a wide wavelength range can lead to a good match with a sizable portion of the solar spectrum and efficient light harvesting in layers that are relatively thin (thicknesses in the range of 100−200 nm). To maximize photon collection, increasing use is made of tandem cell geometries, in which materials with different optical band gaps are stacked on top of one another and absorb different parts of the solar spectrum; tandem cell geometries based on organic semiconductors have recently been demonstrated.[6]

π-Conjugated systems present strong electron-vibration coupling.[7] As a result, once promoted to an electronic excited state, a π-system relaxes down to the bottom of the potential energy surface of the lowest excited state, the excited state reaches its equilibrium geometry, and an exciton forms. Note that this thermalization process constitutes a significant source of power loss. This is especially detrimental when using low-bandgap polymers designed to collect photons in the near infrared.

It is also useful to recall that, in general, the ground state of the π-conjugated system is singlet (spin multiplicity of zero) and denoted S_0; the lowest singlet excited state, S_1, is usually one-photon allowed (see Figure 1). In hydrocarbons with a coplanar conformation (such as pentacene), the spin−orbit coupling to triplet states (spin multiplicity of one) is vanishingly small and intersystem crossing between the singlet and triplet manifolds can be neglected; in systems with heavy atoms or far from being coplanar (for instance, metal phthalocyanines or fullerenes), this is no longer true and intersystem crossing to triplet excitons can be efficient. The lowest energy triplet exciton, T_1, typically lies a few tenths of an electrovolt below S_1. In general, the S_1 and T_1 decay times in organic semiconductors are on the order of nano- and microseconds, respectively.
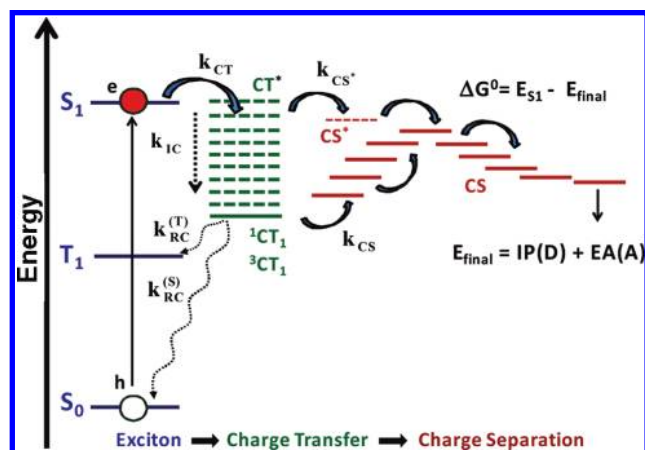
FIGURE 1. Electronic state diagram describing the photo-induced charge-carrier formation mechanism in an organic solar cell: S_0 denotes the singlet ground state of the donor or the acceptor, and S_1 denotes the first singlet excited state (excitonic state). At the D/A interface, intermolecular charge transfer leads to charge-transfer (CT) states, where the hole is on donor molecule(s) and the electron is on acceptor molecule(s). CT_1 is the lowest energy charge-transfer state. CT* represents excited ("hot") levels[28−30] of the CT/CS manifolds. The final state is a charge-separated state (CS), where the hole in the donor layer and the electron in the acceptor layer are free from one another. The k_i terms indicate various competing relaxation and electron-transfer rates. Note that in the simple molecular orbital picture, which is often used in the literature and is based on HOMO−LUMO diagrams, the S_0−S_1 transition, S_1−CT_1 transition, and E_{final} would correspond to the HOMO (D)−LUMO (D), LUMO (D)−LUMO (A), and HOMO (D)−LUMO (A) energy differences, respectively.

Exciton Migration

To generate negative- and positive-charge carriers, the excitons need to migrate to the donor−acceptor interface, where they can dissociate. Because excitons are neutral species, their motion is not influenced by an electric field and they diffuse randomly; importantly, they need to reach the heterojunction between the D and A components prior to their decay back to the ground state. Hence, the thickness of the organic layers (or phases) has to be comparable to the exciton diffusion length L ($L = (D\tau)^{1/2}$, where D is the diffusion coefficient and τ is the lifetime of the exciton). A compromise regarding the thickness of the organic layers has to be found between allowing for efficient exciton diffusion to the heterojunction (favoring thin layers) and efficient sunlight absorption (favoring thick layers).

Oligoacenes have become prototypes for studying the energetics and dynamics of charge- and energy-transfer processes in molecular crystals.[8−11] In particular, pentacene has been used in organic photovoltaic devices as a donor material in bulk heterojunctions formed by layers of pentacene and C_{60} or perylene derivatives.[12−15] While devices containing pentacene have been shown to exhibit large exciton diffusion

lengths (70 nm),[12] a coherent quantum-mechanical description of exciton transport in this class of systems is still missing.

In the past, the migration of singlet excitons has often been described via a Förster resonant energy-transfer (FRET) mechanism, which involves the long-range electrostatic coupling between the excitation transition dipoles at the initial and final sites; in the case of triplet excitons, motions are considered to be restricted to adjacent sites, because they depend upon a short-range exchange (Dexter-type) mechanism relying on orbital overlap. Thus, singlet excitons can, in principle, move more quickly than triplets, but because they decay more quickly as well, the efficiency with which singlets and triplets reach the D/A interface is very much system-dependent.

An important parameter in providing a molecular description of energy transfer is the electronic coupling between interacting sites. In the traditional Förster approach, the electronic coupling is assumed to be a long-range interaction dominated by Coulombic terms and can be approximated in its simplest form by two interacting local point dipoles. However, because of the short intermolecular separations found between chromophores in a thin film, a more adequate treatment of electronic coupling requires approaches that go beyond such approximations.[16] There is also convincing evidence that charge-transfer excitations are important in oligoacenes and other molecular systems;[17,18] however, the exact nature and contributions of these charge-transfer interactions are still topics of investigation.

A challenge in dealing with π-conjugated systems is to account for the couplings between numerous π molecular orbitals that are closely spaced in energy, to describe the complex (multiconfigurational) interactions between excited states. Models have been developed that include the main effects of electron correlation; however, these models received limited applications to date.[19,20] In any event, for π-conjugated systems, molecular packing and intermolecular interactions, including Coulombic, exchange-type, and charge-transfer interactions, need to be adequately considered to examine both singlet and triplet exciton migration and the behavior of these excitonic states as they reach the D/A interface.

Exciton Dissociation at the Donor−Acceptor Interface

Upon reaching the D/A interface, excitons have to dissociate into electrons and holes. Intriguingly, at the present time, no clear picture has emerged to describe the exciton dissociation process at the molecular level. Exciton dissociation has often been described as a two-step process:[21−27] Initially, an exciton state at the D/A interface evolves into a charge-trans-fer (CT) state D^+/A^-, which then either recombines to the ground state or dissociates into free carriers via a manifold of charge-separated (CS) states (we refer to CS states as states where the electron and hole are hardly Coulombically bound or freed from one another) (see Figure 1). The energy of the final CS state, corresponding to a completely unbound electron−hole pair, is defined by the (adiabatic) ionization potential (IP) of the donor or electron affinity (EA) of the acceptor, $E_{final} = IP (D) + EA (A)$ (note that in simple HOMO−LUMO diagrams, E_{final} would be crudely approximated by the difference between the energies of the donor HOMO and acceptor LUMO). To a large extent, E_{final} defines the upper limit for the open-circuit voltage of the solar cell.

Actually, dependent upon the relative time scales of internal conversion (IC) and CS processes, two limiting scenarios for exciton dissociation can be discussed (Figure 1).

(a) $k_{IC} \gg k_{CS}$. The exciton evolves into the CT manifold, which undergoes a fast relaxation to its lowest electronic/vibrational state. Loosely speaking, the lowest D^+/A^- (CT_1) state corresponds to the situation where the hole sits on the HOMO level of a D molecule and the electron on the LUMO level of an adjacent A molecule and the charges are still strongly Coulombically bound. To dissociate, the electron and hole need to overcome the Coulomb barrier; exciton dissociation via this route is not likely to be an efficient process.

(b) $k_{IC} \ll k_{CS}$. Here, exciton dissociation can take place via excited ("hot") levels[28−30] of the CT/CS manifolds. This route is similar to the auto-ionization process[17,18] that describes intrinsic charge-carrier photogeneration from higher lying excited states in organic semiconductors. A number of experimental results point to the existence of this pathway. In particular, the formation of CT/CS states was shown to be extremely fast[22−25] (in the hundred femtosecond regime); as a result, many internal relaxation processes (such as structural relaxations along low-energy vibrational modes) are much slower than these CT/CS rates. Along the same line, experimental data obtained by means of a variety of spectroscopic techniques indicate that CT states formed via exciton dissociation (above-gap excitation) display lifetimes about 2 orders of magnitude shorter than those of CT states formed directly from the ground state (sub-gap excitation); in addition, the sub-gap CT excitations contribute less to the device photovoltaic response.[26] The implication is that, after the CT event, the charge carriers could perform a few ultrafast hops, allowing their separation before the D^+ and A^- states thermally relax and charge carriers enter the normal polaron hopping regime. The fact that these first hops could be very fast is also consistent with recent data (coming from optical spec-

troscopy in the near-visible and THz regimes combined with measurements of electrical transients in the microsecond regime), suggesting that the charge mobility at the early stage of charge separation is very high and decreases with time by several orders of magnitude.[30] A theoretical challenge here will be to develop a coherent quantum-mechanical description of these ultrafast CT and CS processes at D/A interfaces.

We also need to bear in mind that many other factors can complicate the description of the D/A interfacial processes. Suppose that the exciton reaching the interface has formed in the donor. First, instead of direct electron transfer from D to A, there could occur energy transfer leading to the formation of an exciton on A, followed by hole transfer from A to D; this process has been demonstrated in the case of oligophenylene−fullerene dyads.[31] While the final state is the same as for the direct electron-transfer process, the rates involved in the energy- and hole-transfer processes can be markedly different. Second, even when singlet excitons are exclusively formed in D, triplet excitons can appear at the interface. For instance, in bis-dicyanovinyl-oligothiophenes/fullerene blends, it has been observed that, for certain thiophene oligomer lengths, excitons can efficiently transfer to C_{60}, where the large intersystem crossing leads to the formation of triplet excitons, which then hop back to the donor; such processes do not result in charge separation and constitute a loss mechanism.[32] Clearly, the situation is much more complex than what the simple HOMO−LUMO diagrams often found in the literature would lead one to believe. In addition, charge separation can also be influenced by gradients in charge-carrier densities near the heterojunction or local morphology variations.

Thus, it is critical to develop theoretical methodologies that can take into account these competing mechanisms and provide a reliable quantum-mechanical description of (i) the geometric and electronic structure of the relevant states at the D/A heterojunction and (ii) the (ultrafast) CT and CS processes. We now turn to a more specific discussion of some of these issues.

(i) Nature of the Electronic Ground State at the D/A Heterojunction. The electronic ground states of D/A interfaces (and the simplified HOMO/LUMO diagrams used in the literature) have generally been described by considering the D and A components in their isolated form. However, doing so neglects the specific electronic interactions at the D/A interface that are related to electronic polarization effects (expected to be different at the interface from the D or A bulk) and possible charge transfers from D to A

molecules.[33] Such interactions lead to the formation of an interface dipole at the D/A heterojunction and translate into a vacuum level shift in ultraviolet photoelectron spectra.[34] To date, organic/organic interfaces have received much less theoretical attention than metal/organic interfaces.[35] Recently, we investigated a model complex formed by the strong donor tetrathiafulvalene (TTF) and the strong acceptor tetracyanoquinodimethane (TCNQ) (see Figure 2); the goal was to shed light on the origin of interface dipoles at D/A interfaces and quantify their impact. The interface between TTF and TCNQ layers displays a very significant vacuum level shift, on the order of 0.6 eV, as measured by UPS.[36] Figure 2 shows the evolution of the calculated interface dipole as a function of the intermolecular separation in a cofacial complex. At short intermolecular distances, both charge-transfer and polarization effects contribute to the dipole moment; interestingly, for an intermolecular distance of 5 Å, the dipole moment remains significant ($\sim$0.4 D) even though there is no longer any net charge transfer between the two molecules, which illustrates the importance of the electronic polarization effects. Figure 2 also shows the evolution of the dipole moment upon translation of one molecule along its long axis for a cofacial complex at a fixed intermolecular distance of 3.5 Å. At such a short distance, the dipole has a significant charge-transfer contribution and follows the evolution of the net charges on TTF or TCNQ (Figure 2). Interestingly, upon lateral displacement of one molecule of the complex, a strong correlation is observed between the magnitude of the dipole and the calculated shifts in HOMO and LUMO energies. These energy shifts can reach a few tenths of an electrovolt and correspond to a destabilization [stabilization] of the frontier electronic levels of TCNQ [TTF] because of the appearance of a partial negative [positive] charge.

These results carry important implications for organic solar cells. On the one hand, the appearance of an interface dipole tends to reduce the driving force for exciton dissociation. On the other hand, the interface dipole contributes to an increase in the HOMO (D)/LUMO (A) energy gap; the consequence is to reduce the thermal generation of charge carriers at the interface and, thus, to reduce the reverse saturation current in the dark, a feature that impacts favorably the open-circuit voltage (V_{oc}).[37] Note also that these results underline that the actual HOMO (D)/LUMO (A) energy gap can be significantly different from the one inferred from measurements performed on the isolated compounds; they also suggest that, because the magnitude of the dipole is a function of the interfacial
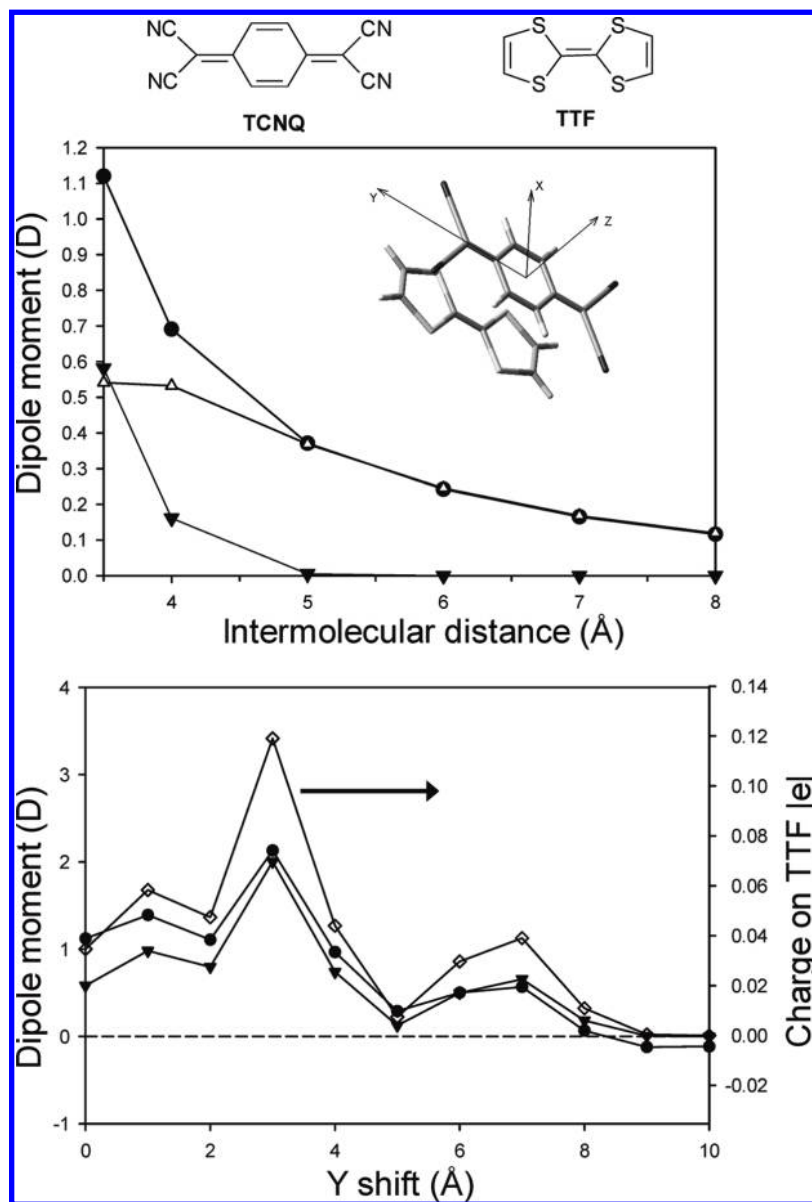
FIGURE 2. (Top) Evolution of the total dipole moment normal to the molecular planes (●) and the charge-transfer contribution (▼) in a cofacial TTF/TCNQ complex with $Y = 0$ Å, as a function of the intermolecular distance along the z axis. The curve with △ shows the resulting polarization component of the dipole. (Bottom) Evolution of the total dipole moment normal to the molecular planes (●) and the charge-transfer contribution (▼) in the complex as a function of the lateral shift between the molecular centers (with the intermolecular distance fixed at 3.5 Å); the total Mulliken charge on the TTF molecule is also shown (◇). All calculations were performed at the DFT/BH and HLYP 6-31G(d) level. This figure was adapted from ref 33.

packing configuration, the situation can vary markedly in D/A bilayer interfaces versus bulk heterojunctions.

(ii) Nature of the CT/CS States at the D/A Heterojunction. Whether exciton dissociation involves hot polaron pairs, coupling to higher lying CT states, interfacial dipoles, and/or charge concentration gradients, it is essential to gain an understanding of the potential energy surfaces for the CT and CS states at the D/A interface. The importance of Coulomb and polarization effects in crystalline and amorphous organic structures is well-known.[17] Polarization effects around single

charge carriers in oligoacene crystals, illustrated in Figure 3a, have recently been investigated using various theoretical approaches, including hybrid quantum mechanics/molecular mechanics and polarizable force-field methods[38] or valence bond-type methods.[39] Because the Coulomb and polarization interactions can have contributions that are significantly different for adjacent charges in a CT state and well-separated charges in a CS state, it is necessary to gain an accurate description of these electronic effects at organic−organic interfaces. For example, the electronic polarization energy around
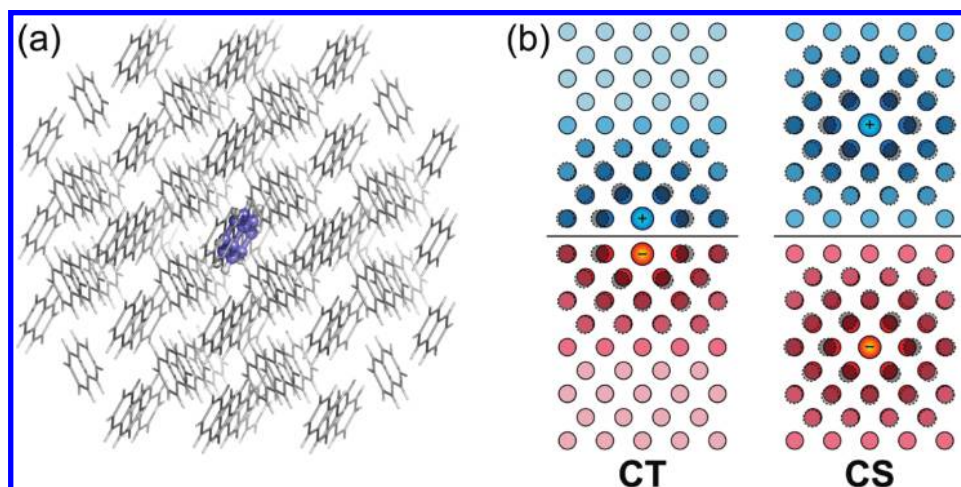
FIGURE 3. (a) Spherical cluster of naphthalene molecules in the crystalline phase, illustrating the polarization effect of a single charge carrier surrounded by a lattice of naphthalene molecules. (b) Schematic representation of the charge-transfer (CT) state at a donor−acceptor organic−organic interface, where the electronic structure of the lattice, depicted as dotted lines, is perturbed by asymmetric Coulomb and polarization interactions. In the charge-separated (CS) state, the individual charges are significantly far from the interface and only experience polarization effects from within their respective donor or acceptor materials.

an exciton in an oligoacene crystal is on the order of a few tenths of an electrovolt, whereas this value can be a full electrovolt for CT states and several electrovolts for CS states.[17] These contrasting cases are shown schematically in Figure 3b, where the CT state subsequently formed from an exciton involves adjacent charges that experience asymmetric electronic effects from the donor and acceptor materials. As the CS state evolves, the individual charges experience the polarization effects of their respective donor or acceptor materials. The challenge for theory will be to assess how much the potential energy differences of interfacial charges are dependent upon the specific system, the relative movements of the separated charges, and the screening effects of the bulk materials and electrodes.

(iii) Electronic Coupling between the Exciton and CT States at the D/A Heterojunction. The electronic coupling between the molecular (exciton) and CT/CS states is a major parameter that controls the dynamics of the charge separation and charge recombination (CR) processes at D/A interfaces.[40−42] While much theoretical work remains to be done, here, we illustrate this issue by considering a pentacene/C_{60} complex. In principle, several CT states can contribute to exciton dissociation. This is especially the case in this complex because the LUMO level of C_{60} is triply degenerate. Upon addition of one electron, the lack of symmetry of the local environment and Jahn−Teller effects concur to lift the orbital degeneracy and result in at least three closely lying C_{60} anion states that can all participate in charge separation. To analyze the electronic coupling among the lowest molecule-based (local) singlet and triplet states and the lowest CT states, we
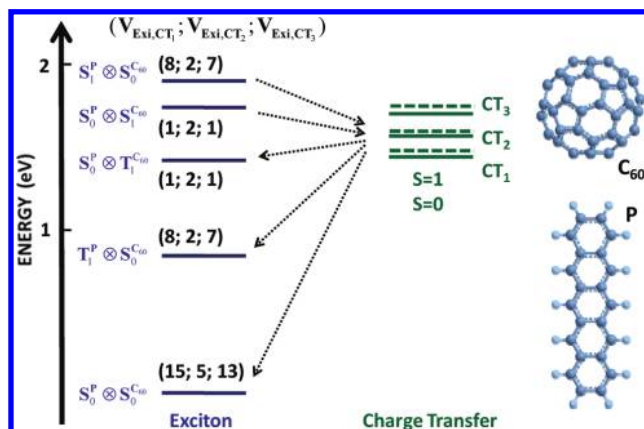
FIGURE 4. Electronic couplings ($V_{Exi,CTi}$, in cm^{-1}) calculated at the INDO level between the lowest singlet and triplet states of pentacene (P) and C_{60} and the lowest three CT states of the P/C_{60} complex for a perpendicular configuration with a distance of 4 Å between the nearest carbon atoms of the two molecules. Both S_1 and T_1 states of C_{60} are orbitally degenerate; therefore, an averaged value over all state components is only shown above. Calculations performed by Dr. Y. Yi at Georgia Tech.

recently developed a computational approach[42] based on the construction of local excited states and CT states as antisymmeterized products of the isolated donor and acceptor wave functions. The electronic couplings derived from such calculations [using the intermediate neglect of differential overlap (INDO) Hamiltonian] for a perpendicular configuration of the pentacene/C_{60} complex are shown in Figure 4. The results point out that (i) the lowest singlet CT states are most strongly coupled to the pentacene S_1 state and the D/A ground state and (ii) the electronic couplings between the pentacene S_1 state and the lowest CT state and between the pentacene T_1 state and the lowest triplet CT state are nearly equal. Because

the molecular triplet states can be energetically very close to the lowest CT state, it can provide an efficient pathway for the deactivation of the CT state. As expected, the electronic couplings are very sensitive to packing configurations; for a cofacial configuration of the pentacene/C_{60} complex, they are up to 2 orders of magnitude larger than the values shown in Figure 4.

The examples discussed above underline that a complete quantum-mechanical description of the electronic processes occurring in solar cells relies on the availability and reliability of a diverse set of theoretical approaches and computational techniques. Further progress in our understanding depends upon improving existing approaches and developing new methodologies.

Charge-Carrier Mobility

Once the charges have separated, they move toward their respective electrodes with an efficiency depending upon their mobilities. In crystalline inorganic semiconductors, the three-dimensional character and rigidity of the lattice ensure wide valence and conduction bands and large charge-carrier mobilities (typically on the order of several $10^2 - 10^3$ cm^2 V^{-1} s^{-1}). In contrast, in organic semiconductors, the weakness of the electronic couplings (because of their intermolecular character), the large electron-vibration couplings (leading to marked geometry relaxations), and the disorder effects all conspire to produce more modest carrier mobilities because of charge-carrier localization and formation of polarons; transport then relies on polarons hopping from site to site. As a result, the charge-carrier mobilities strongly depend upon morphology and can vary over several orders of magnitude when going from highly disordered amorphous films (typically, $10^{-6}-10^{-3}$ cm^2 V^{-1} s^{-1}) to highly ordered materials (>1 cm^2 V^{-1} s^{-1}).

While significant progress has been achieved in our understanding of the factors influencing charge-carrier mobilities in organic semiconductors, much still needs to be done. Two areas are in particular need of better descriptions. The first is related to the determination of the molecular and morphological structure of the organic layers. Given that crystal-structure predictions continue to represent a challenging task, our ability to depict structural defects at the nanoscale (disorder, for instance, because of variations in local molecular packing) and mesoscale (disorder, for instance, because of grain boundaries) remains at a primitive stage. However, these defects critically impact the charge mobilities. The second aspect is related to the fact that π-conjugated materials usually find themselves in a complex charge-transport regime, where electronic coupling between adjacent molecules and electron-vibration (phonon) coupling are both significant and of the same order of magnitude. The description at the molecular level of the coupling between the charge carriers and the intermolecular vibrations still requires more work.[43] Finally, the development of reliable temperature-dependent polaronic models for this complex regime would be of major importance.

Charge Collection at Electrodes

The nature of the electrode/organic layer interfaces is complex. The efficiency of the charge collection process cannot be simply determined from the difference between the workfunction of the isolated electrode and the donor IP or acceptor EA. The deposition of organic layers on electrodes (or vice versa) leads to interfacial charge-density redistributions, geometry modifications, and/or chemical reactions that strongly affect the alignment of the organic frontier electronic levels versus the electrode Fermi level.[35] Here, as well, our understanding of the intricate details of these hybrid interfaces and their impact on the charge collection/injection rates remains primitive. We note that surface modification of the electrodes via deposition of self-assembled monolayers is an efficient way to enhance the quality of the electrical contact as well as, in particular, when dealing with conducting oxide electrodes, to promote compatibilization between the (hydrophilic) oxide surface and (hydrophobic) organic layer.

Conclusion

As a concluding note, we stress that the optimization of organic solar cells is a fine balancing act. It requires finding the optimal compromise among a combination of materials characteristics that can work in opposite directions. For instance, we highlighted that the presence of an interfacial dipole at the D/A interface can reduce the driving force for exciton dissociation but help in improving the open-circuit voltage. Also, optimization of the D/A interface can increase the electronic coupling between the excitonic and CT/CS states, thereby enhancing the photocurrent (that needs to be maximized) but, at the same time, can also increase the coupling between the CT states and the D/A ground state, leading to a larger reverse saturation current in the dark (which needs to be minimized to secure a higher V_{oc}). Many efforts have been recently directed toward the design and synthesis of low-bandgap copolymers incorporating alternating donor and acceptor units, used as new D materials to harvest the low-energy photon part of the solar spectrum.[44−46] Increasing the strength of the acceptor unit shifts the LUMO level down, while the HOMO energy is less affected; the LUMO becomes more local-

ized on the acceptor unit, while the HOMO remains well-delocalized for hole transport. However, a lower energy S_1 state has an unfavorable impact on the driving force for charge separation; in addition, the localized nature of the LUMO in the copolymer can cause a decrease in wave function overlap between the frontier molecular orbitals and, thus, in oscillator strength of the S_0-S_1 transition.

Clearly, designing materials for organic photovoltaics involves careful balances and a comprehensive understanding of all of the processes described in this Account.

BIOGRAPHICAL INFORMATION

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