Beyond the Adiabatic Limit: Charge Photogeneration in Organic Photovoltaic Materials

2 AUTHORS, INCLUDING:

Ryan D. Pensack
Princeton University

25 PUBLICATIONS   **364** CITATIONS

Beyond the Adiabatic Limit: Charge Photogeneration in Organic Photovoltaic Materials

Ryan D. Pensack and John B. Asbury*

Department of Chemistry The Pennsylvania State University, University Park, Pennsylvania 16802

ABSTRACT Mounting evidence suggests that excess energy in charge-transfer (CT) excitonic states facilitates efficient charge separation in organic solar cells. Experimental and theoretical studies have revealed that this excess energy may reside in phonon modes or in electronic coordinates of organic photovoltaic materials that are directly excited by the transition from Frenkel to CT excitons. Despite their strong Coulombic attraction, electron—hole pairs in hot CT excitons are able to undergo activationless separation because the rate of separation competes with thermalization of electronic and nuclear degrees of freedom. We argue that these observations indicate strong coupling of the dynamics of electronic and nuclear coordinates in organic photovoltaic materials. Thus, a nonadiabatic description is needed to properly understand the mechanism of charge photogeneration in organic solar cells. Such a description will support continuing efforts toward the development of low-band-gap organic solar cells that efficiently generate photocurrent with minimal energy losses.
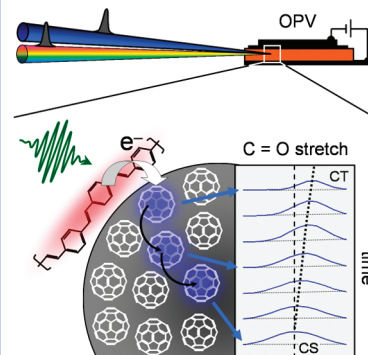
Organic Solar Cells. Organic solar cells are being explored as inexpensive alternatives to large-area solar modules because of their potential for low-cost, high-throughput production. Organic semiconductors from which these devices are made are molecular solids consisting of conjugated molecules or polymers that interact together by van der Waals forces. The comparatively weak interactions between molecules in conjunction with their low dielectric permittivity give rise to strong electron—phonon coupling that in turn cause electronic states in the materials to be highly localized. As a result, the primary electronic excited states formed by absorption of light in organic semiconductors are strongly bound electron—hole pairs called excitons.[1-3] For the most part, excitons in organic semiconductors dissociate at interfaces of electron-donating and -accepting materials.[3-6] The dynamics of excitons particularly at electron-donor/acceptor interfaces strongly influence charge photogeneration and thus the efficiency of organic solar cells.

Extensive efforts have been undertaken in the organic photovoltaic (OPV) field to develop more efficient solar cells by realizing new polymeric electron donors that absorb longer wavelengths and that have molecular orbital energy levels optimized for maximum open-circuit voltages. Numerous conjugated polymers that absorb in the near-infrared (near-IR) have been synthesized[7-16] according to the conventional wisdom that only a few tenths of an electronvolt (eV) energy difference between the lowest unoccupied molecular orbital (LUMO) of the polymer and the LUMO of the acceptor are needed to efficiently dissociate excitons into separated electrons and holes.[1] Certain champion materials have led to dramatic increases in device power conversion efficiency with state of the art values approaching 7 %.[17-19] While some champion OPV materials are able to efficiently separate charge with small free-energy differences, other materials that on the surface seem similar do not exhibit this capability.[20-23] These observations indicate that the efficiency of charge photogeneration is determined by other factors in addition to the energetics of the electron-donating and accepting states. In this Perspective, we suggest that those factors include coupling of the dynamics of electronic and nuclear degrees of freedom of charge-transfer (CT) excitons as they evolve toward charge-separated states.

> The efficiency of charge photogeneration is determined by other factors in addition to the energetics of the electron-donating and accepting states, and we suggest that those factors include coupling of the dynamics of electronic and nuclear degrees of freedom of CT excitons as they evolve toward charge-separated states.

Electron-Transfer Processes in Charge Photogeneration. In this discussion, we adopt the terminology for electronic states
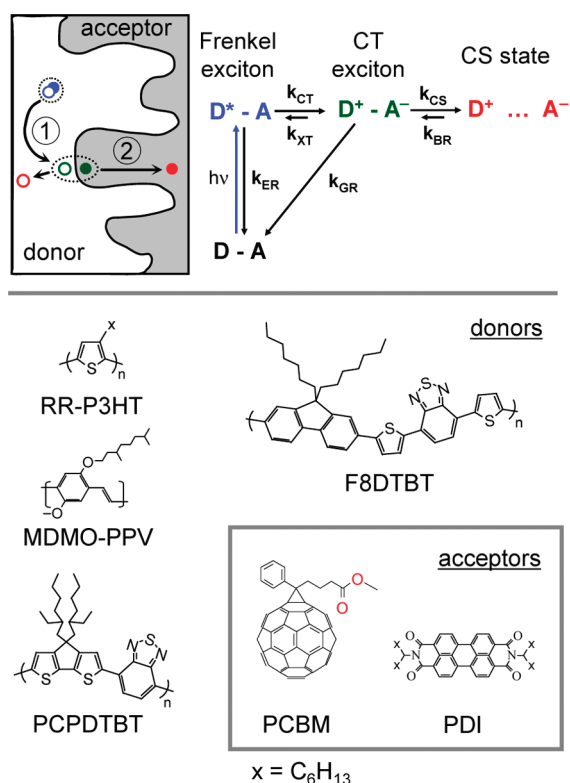
Figure 1. (top) Illustration of an organic donor/acceptor interface where charge separation occurs. Charge separation involves several intermediate states that are represented in the reaction sequence on the right. Absorption of photons ($h\nu$) produces Frenkel excitons in the organic semiconductor (D*−A) that diffuse to donor/acceptor interfaces to form CT excitons (D^+−A^-) consisting of a bound electron−hole pair. The CT excitons then dissociate into separated charge carriers ($D^+\cdots A^-$) that are able to diffuse independently of each other. (bottom) Selected structures of conjugated polymeric electron donors and small-molecule electron acceptors used in organic solar cells.

in organic semiconductors introduced by Pope and Swenberg.[24] Evidence in the literature indicates that charge photogeneration in organic solar cells involves a number of intermediate states that are represented in Figure 1 (top).[25,26] Organic semiconductors are excitonic materials, meaning that excited electronic states formed by absorption of above-gap radiation are strongly bound electron−hole pairs residing on the same conjugated segment.[3] These excitations, known as Frenkel or singlet excitons, can form in either the electron donor (D*−A) or the acceptor (D−A*). Formally, the wave functions of Frenkel excitons extend over the entire molecular array.[27] In practice, the coherence length of an exciton is reduced by scattering from impurities, phonons, and disorder in the organic semiconductor. Disordered semiconductors such as conjugated polymers have coherence lengths that are often smaller than the lattice constant. Excitons in these materials can be viewed as localized excitations that move between neighboring molecules by a series of incoherent jumps.[24] This high degree of localization gives rise to strong electron−phonon coupling with corresponding polarization of the nuclear coordinates around the localized excitons (self-trapping). In contrast, crystalline inorganic semi-

conductors (and crystalline organic semiconductors to a lesser extent) have coherence lengths that are larger than the lattice constant with corresponding delocalized excitons. These excitons, known as Wannier excitons, exhibit much less electron−phonon coupling and have smaller polarization energies. The electron and hole in a Wannier exciton are bound by their mutual Coulombic attraction. Because of the smaller polarization energy, these excitons are well-described by hydrogenic electronic states with energy spectra that vary as $1/n^2$, where n is the principal quantum number of the state.[28]

Frenkel excitons generally must encounter junctions between electron-donating and -accepting materials in order to dissociate to form separated electron and hole states known as polarons (Figure 1, D^+−A^-, Step 1),[1−3] although there is evidence that interchain bound polaron pairs form spontaneously from Frenkel excitons in many cases.[29] A selection of electron-donating and -accepting materials is represented in Figure 1 (bottom). Intermediate states in the charge separation reaction known as CT excitons have been identified.[22,30−38] Excitons are polar species with electrons and holes located on different molecular sites that are separated by at least one lattice constant.[24] According to this definition, bound polaron pairs[39−43] would also be classified as CT excitons, although this classification might not be strictly appropriate due to the differences in spin statistics.[44,45] CT excitons have also been called exciplexes. At interfaces of electron-donating and -accepting materials, they consist of an electron on the acceptor and a hole on the donor. Several pathways exist for CT exciton formation, including intermolecular electron transfer from Frenkel excitons originating from either the electron donor or the acceptor. Additionally, Frenkel excitons can undergo excited-state energy transfer from donor to acceptor (or vise versa) followed by intermolecular electron transfer to form the D^+−A^- state. Finally, dissociation of CT excitons leads to the formation of separated electron and hole polaronic states that are able to diffuse independently of one another ($D^+\cdots A^-$, Step 2).

CT Excitons in Charge Photogeneration. Numerous reports in the literature provide evidence for the formation of CT excitons in blends of electron-donating and -accepting organic semiconductors.[22,31−38] We refer the reader to recent reviews by Bredas[25] and Durrant[26] for a more complete discussion of this topic. In particular, Loi et al. reported the appearance of a long-wavelength photoluminescence emission band in blends of F8DTBT with PCBM.[34] The emission band, assigned to CT excitons, could not be attributed to photoluminescence from the polymer or PCBM due to its long wavelength and because it only appeared when the polymer was blended with PCBM. Similarly, Inganas et al. observed electroluminescent emission from CT excitons in several polymers (MDMO-PPV, F8DTBT referred to as APFO3, and P3HT) blended with PCBM at longer wavelengths than electroluminescent emission from the pure polymers or PCBM.[35] The authors showed a linear correlation between the low-energy onset of the CT exciton emission and the open-circuit voltage of solar cells made from the same materials, suggesting that the emission originated from states closely related to the valence level of the conjugated polymer and the conduction level of PCBM.

The Coulombic attraction of electron−hole pairs must be overcome in order for CT excitons to dissociate into separated electrons and holes (Figure 1, $D^+ \cdots A^-$). The potential energy of Coulombic attraction of nearest-neighbor electron−hole pairs at donor/acceptor interfaces has been estimated on the basis of the dielectric permittivity of organic semiconductors (typical dielectric constants in the $\varepsilon \approx 3-4$ range) and the approximate separation of charge pairs (10−20 Å). These estimates fall in the range of a few tenths of an electronvolt.[20,31,46] Estimates of the corresponding free energy are lower because of the increase in entropy associated with the transition from one to two independent particles.[26] Janssen et al. experimentally examined the energy of CT excitons versus charge-separated states in a variety of blends of conjugated polymers with PCBM using a combination of optical absorption and electrochemical measurements.[47] The difference in energy between these states, which is taken to be the CT exciton binding energy, was 0.3 eV for blends of P3HT with PCBM and also for blends of MDMO-PPV with either PCBM or PDI. Zhu et al. examined the Coulombic barrier to charge separation at pentacene/vacuum interfaces and found a binding energy of more than 0.4 eV for the lowest-energy CT excitonic state.[30]

The Coulombic binding energy of electron−hole pairs in CT excitons is apparently more than an order of magnitude larger than thermal energy at room temperature (kT at 300 K = 0.025 eV) in a variety of organic semiconductors. Thus, it is unlikely that thermalized CT excitons will dissociate before decaying radiatively or nonradiatively to a triplet or ground state of the system (or endothermically re-forming Frenkel excitons).[32] In fact, the efficiency of charge separation at organic donor/acceptor junctions has been closely correlated with the energy difference between the donating and accepting states. For example, Forrest et al. used kinetic Monte Carlo simulations of charge separation at donor/acceptor interfaces in the presence of electric fields to show that the separation probability increased as the excess energy of the exciton increased.[31] The influence of the excess energy was rationalized in terms of a thermalization radius of the exciton that increased with higher excess energy, similar in spirit to Onsager's theory of geminate charge pair dissociation in the bulk.[48] Similarly, Durrant et al. examined the efficiency of charge separation in a series of polythiophene polymers blended with PCBM.[20] Decreasing the free-energy difference for charge separation in the series of blends from 0.9 to 0.6 eV resulted in 2 orders of magnitude decrease of the charge separation efficiency. The effect was interpreted in terms of decreased excess energy of CT excitons (termed bound radical pairs in ref 20) with corresponding lower probabilities of dissociation. Vardeny et al. examined the potential of CT excitons without significant excess energy to dissociate into charge-separated states.[33] Below-gap optical excitation was used to directly excite CT excitons from the ground state in blends of 2-methoxy-5-(2′-ethylhexyloxy)poly(*p*-phenylenevinylene) (MEH-PPV) with C_{60} followed by detection of photoluminescence from CT excitons. Comparison of photoluminescence excitation spectra with photocurrent action spectra revealed that CT excitons excited by below-gap radiation contributed negligibly to the photocurrent in comparison to above-gap excitation. The
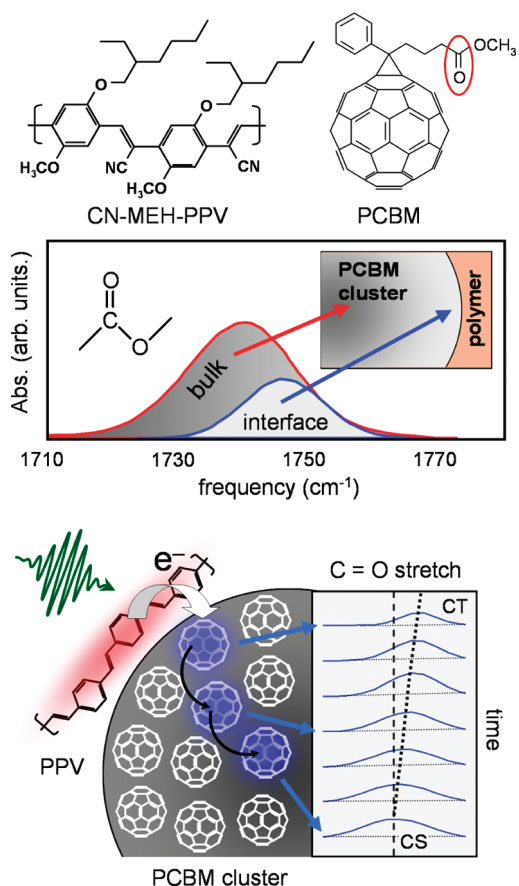
Figure 2. CT excitons can be distinguished from charge-separated states on the basis of their vibrational spectra. (top) Structure of the conjugated polymer and PCBM examined using ultrafast vibrational spectroscopy. The frequency of the carbonyl (C=O) group of PCBM is sensitive to the local morphology of the material such that a higher carbonyl frequency is observed for molecules residing near interfaces of PCBM clusters with the conjugated polymer. PCBM molecules in the interiors of the clusters possess lower-frequency carbonyl bonds. (bottom) As CT excitons dissociate, electrons move away from the interfaces and occupy PCBM molecules with lower-frequency carbonyl groups. The motion of electrons results in a time-dependent shift of the carbonyl frequency to lower values, which is observed in the transient vibrational spectra.

implication is that excess energy from above-gap excitation plays an important role in separation of electron−hole pairs.

Although excess energy in CT excitons strongly influences the efficiency of charge separation in a variety of organic donor/acceptor blends, recent investigations of low-band-gap polymers suggest that some materials are able to efficiently separate charges with small amounts of excess energy. For example, Durrant and co-workers examined the efficiency of charge separation for the low-band-gap polymer, PCPDTBT, blended with PCBM and found that charges are generated as efficiently as the P3HT/PCBM blend but with only about a 0.2 eV free-energy difference as opposed to the 0.9 eV for P3HT/PCBM.[21] While these results are encouraging for the organic solar cell field, they present a challenge to understand why certain organic donor/acceptor materials are able to efficiently separate electrons and holes with small amounts of excess energy while other materials are not.

Dynamics of Charge Photogeneration. Recently, ultrafast vibrational spectroscopy was used to directly observe the formation and dissociation of CT excitons to form separated charge carriers in a polymer blend of CN-MEH-PPV with PCBM.[49−52] As illustrated in Figure 1 (top), both CT excitons and charge-separated states consist of a positively charged donor and a negatively charged acceptor. Many studies have shown that CT excitons cannot be distinguished from charge-separated states through their visible or near-IR spectroscopic features.[53−56] However, these species can be distinguished by their vibrational spectra in the mid-IR spectral region because the frequency of the carbonyl group of PCBM is sensitive to the local morphology of the material.[49,50] The solvent environment experienced by the carbonyl group of PCBM differs significantly if the molecule resides near a polymer/PCBM interface versus the interior of a PCBM cluster. The gradient in the solvent environment between these two regions gives rise to a shift of the vibrational frequency of the carbonyl stretch (Figure 2, top). The influence on the vibrational frequency arises from a solvatochromic[57] shift in conjunction with a vibrational Stark shift[58] (see Supporting Information). Therefore, when a CT exciton forms at a polymer/PCBM interface, the vibrational frequency of the PCBM molecule within the CT exciton is higher in comparison to that of the molecules in the interior of the PCBM clusters.[50] As CT excitons dissociate, electrons originating at donor/acceptor interfaces diffuse into the interiors of clusters where the average carbonyl stretch frequency is lower. This motion results in a time-dependent shift of the carbonyl frequency of PCBM toward lower values (Figure 2, bottom).

The ability to distinguish CT excitons from charge-separated states through their vibrational spectra permits detailed study of the dynamics of CT exciton dissociation. The dissociation dynamics can be examined through the time dependence of the ground-state carbonyl bleach spectrum of PCBM. Formation of CT excitons reduces the neutral ground-state population of PCBM molecules and decreases the corresponding absorption intensity of the carbonyl stretch vibration (termed a ground-state bleach). Ground-state bleach spectra collected at 300 K are displayed on the vertical axis in the two-dimensional (frequency−time) spectrum displayed in Figure 3 (top). The initial growth of the bleach spectrum on the picosecond time scale corresponds to the formation of CT excitons as a result of electron transfer from the polymer to PCBM.[59] As CT excitons dissociate, electrons occupy PCBM molecules with lower-frequency carbonyl stretch modes, resulting in the shift of the carbonyl bleach peak to lower frequencies with increasing time delay. The detailed assignment of the frequency shift dynamics has been explained elsewhere.[49,50] These charges continue to diffuse into the PCBM clusters and ultimately sample the equilibrium ensemble of PCBM molecules, resulting in the carbonyl bleach spectrum approaching the equilibrium center frequency (indicated by the dotted line) on the nanosecond time scale.

Temperature-dependent measurements of the dynamics of the shift of the carbonyl bleach frequency (Figure 3, bottom) reveal that the time scale for CT exciton dissociation does not depend on temperature between 200 and 350 K.[51] This observation indicates that CT exciton dissociation occurs
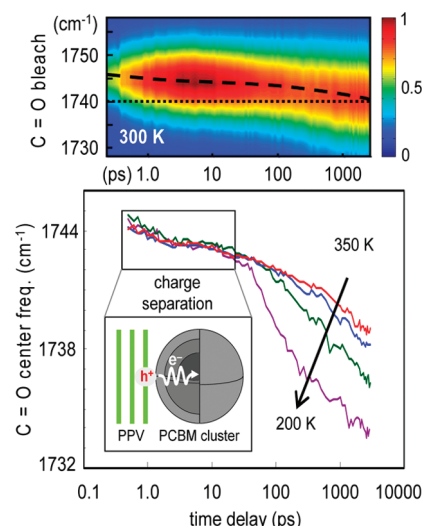
Figure 3. Measurement of the time-dependent frequency shift of the carbonyl group of PCBM provides a direct probe of CT exciton dissociation. (top) Two-dimensional frequency−time spectra of the carbonyl (C=O) bleach of PCBM measured using ultrafast vibrational spectroscopy following ultrafast excitation of the polymer blend at 560 nm. The carbonyl bleach appears at higher frequencies in comparison to the equilibrium center frequency indicated by the dotted line because CT excitons form at donor/acceptor interfaces. As electrons dissociate from CT excitons, they move into the interiors of PCBM clusters where the molecules have lower-frequency carbonyl bonds. The onset of this motion corresponds to the initial charge separation reaction. (bottom) The center frequency of the carbonyl bleach spectra plotted versus the corresponding time delay on a logarithmic scale for several temperatures (350, 300, 250, and 200 K). The frequency shift dynamics are independent of temperature within the first 30 ps because excess energy in the CT excitons enables the electron−hole pairs to overcome their Coulombic attraction to dissociate via an activationless pathway. Following CT exciton dissociation, electrons enter shallow traps, giving rise to the shift of the carbonyl frequency to lower values preferentially at lower temperature. At higher temperatures, electrons remain free to sample the equilibrium distribution of PCBM molecules on the nanosecond time scale.

through an activationless pathway, meaning that energy to overcome the barrier to charge separation comes from the photochemical reaction rather than from the thermal bath.[52] For comparison, if electron−hole pairs were thermally promoted over an activation barrier of 0.1 eV, the time scale for charge separation at 200 K would be an order of magnitude longer than that at 350 K. The trace labeled 200 K would be horizontal in the box labeled charge separation. Instead, the time-dependent frequency follows the same time evolution at all temperatures.

> **The ability to distinguish CT excitons from charge-separated states through their vibrational spectra permits detailed study of the dynamics of CT exciton dissociation.**

Following the activationless charge separation process, electrons diffuse into the interiors of the PCBM clusters and enter shallow charge traps preferentially at lower temperature.[60] As discussed in a recent review by Zhu,[61] highly ordered regions of organic semiconductors frequently serve as intrinsic charge traps because the free energies of charge carriers are lower due to enhanced delocalization of the wave functions. In PCBM clusters, enhanced molecular order gives rise to greater dipolar coupling among neighboring carbonyl groups, which in turn reduces their frequency.[52] In particular, time-resolved vibrational spectroscopy studies of CN-MEH-PPV/PCBM polymer blends on the microsecond time scale at a temperature of 200 K reveal that electron traps in PCBM clusters have carbonyl bleach center frequencies at around 1734 cm^{-1}, considerably lower than the ensemble average at around 1740 cm^{-1}. Since the probability that an electron will remain in a shallow trap depends on the thermal energy available, this trapping process gives rise to the temperature-dependent frequency shift observed on time scales longer than 50 ps in Figure 3.[52] At higher temperatures, electrons spend comparatively less time in shallow traps. As a result, they are free to diffuse about the PCBM clusters and sample the equilibrium distribution of molecules. Correspondingly, the carbonyl bleach center frequency approaches the equilibrium frequency (1740 cm^{-1}) preferentially at higher temperature on the nanosecond time scale.

Evidence for the importance of excess energy for driving charge separation is rapidly emerging,[20,21,31−33] although the identity of the electronic and/or nuclear coordinates in which the excess energy initially resides is not clear. A few experimental and theoretical studies are beginning to probe this question, with important implications for understanding charge photogeneration in organic solar cells. In particular, Zhu and co-workers recently reported the formation of hot CT excitons at crystalline pentacene/vacuum interfaces using two-photon photoelectron spectroscopy.[30,62] The energy spectrum of CT excitons could be well-described by the $1/n^2$ dependence of hydrogenic states.[30,63] Although the lowest-energy CT exciton corresponding to a 1s hydrogenic state had a binding energy of more than 0.4 eV, hot CT excitons occupying higher-energy hydrogenic states (2s, 3s, and so forth) were observed having much smaller binding energies.

A few experimental and theoretical studies have reported evidence for direct excitation of vibrational modes of polymeric organic semiconductors during Franck−Condon transitions to Frenkel or CT excitonic states. Lanzani et al. examined vibrational modes of an MDMO-PPV film excited during optical excitation to Frenkel excitonic states using sub-10 fs laser pulses.[64] The short laser pulses mapped the ground-state vibrational wave function onto the excited state, resulting in coherent excitation of a vibrational mode of the excited state at 1085 cm^{-1}. The excited vibration was assigned to stretching motion of the conjugated backbone of the polymer, indicating that the ground- and excited-state nuclear potentials are displaced along this coordinate. Intriguingly, the authors observed that excess energy remained in "dark" vibrational modes of the polymer (modes not directly coupled to the optical transition) for periods longer than 1 ps following optical excitation. Burghardt and Bittner examined the coupling
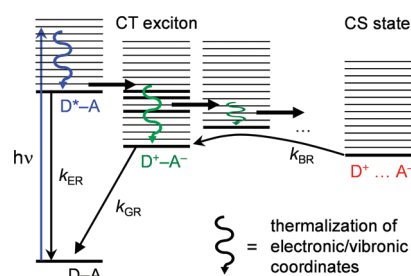
Figure 4. Electronic/vibronic state diagram describing the mechanism of charge photogeneration in organic photovoltaic materials. Following photon absorption, Frenkel excitons diffuse to donor/acceptor interfaces to form CT excitons. Since energy is conserved in the reaction, the energy difference between these thermalized states is distributed between hydrogenic electronic states of the CT excitons and vibrational modes that are coupled to the Frenkel to CT exciton transition. This excess electronic/vibronic energy can either mediate the dissociation of CT excitons to form charge-separated states via an activationless pathway (bold horizontal arrows) or dissipate into the thermal bath (wavy arrows). The competition between these two processes largely determines the efficiency of charge photogeneration in organic solar cells. Because the dynamics of the electronic and vibronic coordinates are highly coupled, diabatic descriptions of the charge separation reaction are needed to properly describe charge photogeneration in these materials.

of electronic and nuclear coordinates during the transition from Frenkel to CT excitons at heterojunctions of polyfluorene-based electron-donating and -accepting conjugated polymers using quantum dynamical computer simulations.[65,66] By coupling a linear vibronic model with a hierarchical electron−phonon model, the authors observed that high-frequency stretching modes of the conjugated backbone are highly coupled to the electronic transition. However, the transition from Frenkel excitons to CT excitons was not observed without the involvement of low-frequency ring torsional modes. Similar conclusions were drawn by Tretiak et al. using the collective electronic oscillator algorithm on PPV oligomers.[67] It is interesting to note that both experimental and theoretical examinations of electronic processes in conjugated polymers reveal pronounced dynamical coupling of electronic and nuclear degrees of freedom, suggesting that this coupling may be important in polymeric semiconductors.

Need for a Diabatic Description of Charge Photogeneration. On the basis of recent studies of exciton dynamics in organic semiconductors, we suggest the state diagram represented in Figure 4 to illustrate the charge photogeneration mechanism in OPV materials. The state diagram is similar to ideas proposed recently by Bredas[25] but includes the potential involvement of electronically excited hydrogenic states of hot CT excitons.[30,62] The diagram does not show other electronic states such as triplets that may be important in the charge photogeneration mechanism. According to this picture, Frenkel excitons form in either the donor or acceptor of an OPV material as a result of optical excitation (D*−A or D−A*). The excitons migrate to donor/acceptor interfaces by diffusion or by Forster resonant energy transfer to form CT excitons. Alternatively, Frenkel excitons may relax to form bound polaron pairs[39−43] that migrate together to donor/acceptor interfaces where the negative polaronic state transfers to the

acceptor. Electronic energy states of CT excitons are well-described by hydrogenic energy levels in crystalline organic semiconductors (bold energy levels of CT states in Figure 4). Presumably, this representation applies to more disordered organic semiconductors such as conjugated polymers, although this has not been established. The hydrogenic states are dressed by nuclear distortions (self-trapped CT excitons). As suggested by recent theoretical studies, nuclear distortions surrounding CT excitons in conjugated polymers differ from those surrounding Frenkel excitons, resulting in the excitation of vibrational modes of the polymers during the Frenkel to CT exciton transition. Consequently, excess energy in hot CT excitons is distributed to various combinations of electronic and nuclear degrees of freedom. The branching ratio between these coordinates likely depends sensitively on the molecular structure of the organic semiconductor. Similar arguments apply if polaron pairs are involved in the place of Frenkel excitons. The observation that excess energy in CT excitons facilitates activationless charge separation[51] suggests that charge photogeneration in OPV materials involves strong coupling of electronic and nuclear dynamics. This suggestion is further supported by the observation that charge separation (bold horizontal arrows in Figure 4) occurs on the picosecond time scale[52,68] and thus may compete with electronic and nuclear thermalization processes (wavy arrows). Other relaxation processes that compete with charge photogeneration include excited-state relaxation of Frenkel excitons (k_{ER}), geminate recombination of CT excitons (k_{GR}), and bimolecular recombination of separated charge carriers (k_{BR}).

Strong coupling of the dynamics along electronic and nuclear coordinates indicates that the adiabatic approximation, which is based on the assumption that the electronic wave function of the system varies slowly with respect to the nuclear coordinates, is insufficient to describe charge photogeneration in organic semiconductors. Instead, the electronic state of the system appears to evolve from charge-transfer to charge-separated character on the same time scale or faster than dissipation of energy from electronic and nuclear coordinates of CT excitons. A full description of the dynamics leading to charge photogeneration in OPV materials will need to incorporate the strong coupling of the electronic and nuclear degrees of freedom. Quantum dynamical simulations of Burghardt and Bittner,[65,66] Tretiak,[67,69,70] and Prezhdo[71−73] are recent examples of such diabatic descriptions applied to photophysics of molecular systems.

The state diagram in Figure 4 suggests two limiting cases describing possible mechanisms of charge photogeneration in organic solar cells. If CT excitons are excited electronically, then the state of the system corresponds to electron−hole pairs that are far apart and are thus already close to the dissociation limit. At high excitation levels, only small amounts of energy from excited vibrations or from the thermal bath would be required to separate the charges, giving rise to temperature-independent charge separation dynamics. The barrierless dissociation of CT excitons ceases when the excited electronic coordinates dissipate their energy to the thermal bath. On the other hand, if CT excitons are not excited electronically, then the energy exists initially in vibrational modes of the material that are excited by the Frenkel to

CT exciton transition.[65,66] In this strong electron−phonon coupling case, it is likely that vibrations are also involved in the transition to the charge-separated state. If the distributions of vibrational modes involved in the Frenkel to CT exciton and the CT exciton to charge-separated state transitions strongly overlap, then the reaction coordinate for charge separation is impulsively excited when the CT exciton forms. Thus, charge separation again occurs through an activationless process until the excess energy in the vibrational modes dissipates to the thermal bath. In both cases, the model suggests that the efficiency of charge photogeneration in OPV materials depends on the relative rates of charge separation and dissipation of electronic and vibrational energy into the thermal bath, as suggested recently by Bredas.[25]

It is instructive to point out that the proposed mechanism is simply a specific application of Onsager theory describing the probability for geminate charge pair dissociation. Onsager envisioned that geminate charge pairs would be initially generated with excess thermal energy (frequently by photoexcitation) and that thermalization of this excess energy would result in an effective separation of the charge pairs known as the thermalization radius, a.[48] The probability of geminate pair dissociation is then proportional to the exponential factor, $\exp(-r_c/a)$, where r_c is the Coulomb capture radius at which the Coulombic interaction of the charge pair is equal to thermal energy. An alternate definition of r_c adopts the random energetic disorder of the molecular solid as the energetic threshold for charge separation.[26] Thermally excited geminate charge pairs in Onsager's theory correspond to hot CT excitons. The thermalization radius of CT excitons is determined by the relative rates of charge separation and vibrational/electronic energy dissipation in the molecular solid.

The proposed mechanism of charge photogeneration suggests a framework with which to interpret recent observations of the dependence of charge photogeneration efficiency on polymer structure.[21] The strong electron−phonon coupling in organic semiconductors causes charge carriers (polarons) to move via a hoping mechanism involving electron transfer between conjugated segments.[74] Because charge separation involves movement of electrons and holes, the rate of this process depends sensitively on the intermolecular order and molecular structure of the organic semiconductor as these properties influence the electronic coupling and reorganization energy of the electron-transfer processes. Similarly, the rate of electronic and/or vibrational energy dissipation depends sensitively on molecular structure and intermolecular order because these properties determine the frequencies of inelastic electron−phonon and phonon−phonon scattering events. The observation that certain OPV materials efficiently separate charge with smaller free-energy differences may be a manifestation of the dependence of the rates of charge separation versus energy dissipation on the underlying molecular structure and intermolecular order in the material. Given that the initial events leading to charge separation primarily occur at donor/acceptor interfaces, it is likely that these properties of materials specifically at interfaces have the greatest

influence on the charge photogeneration reaction in organic solar cells.

> The observation that certain OPV materials efficiently separate charge with smaller free-energy differences may be a manifestation of the dependence of the rates of charge separation versus energy dissipation on the underlying molecular structure and intermolecular order in the material.

Biographies

Ryan D. Pensack is a graduate research assistant in the Chemistry Department at the Pennsylvania State University. His research interests include examination of the molecular nature of charge traps in organic photovoltaic materials using two-dimensional infrared spectroelectrochemical techniques and elucidation of the mechanism of charge separation in these materials.

John B. Asbury is an Assistant Professor of Chemistry at the Pennsylvania State University. He conducts research in ultrafast vibrational spectroscopy of charge carrier dynamics in organic semiconductors, spectroelectrochemical studies of defects and charge traps in disordered materials, and the influence of dielectric properties on charge carrier dynamics in organic semiconductors. For further information, see: http://research.chem.psu.edu/asburygroup/.

SUPPORTING INFORMATION AVAILABLE Vibrational spectra demonstrating the solvatochromic shift of the carbonyl group of PCBM. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author:

*To whom correspondence should be addressed. E-mail: jasbury@psu.edu.

REFERENCES

(1) Thompson, B. C.; Frechet, J. M. J. Polymer−Fullerene Composite Solar Cells. *Angew. Chem., Int. Ed.* **2008**, *47*, 58−77.

(2) Gunes, S.; Neugebauer, H.; Sariciftci, N. S. Conjugated Polymer-Based Organic Solar Cells. *Chem. Rev.* **2007**, *107*, 1324−1338.

(3) Gregg, B. A. The Photoconversion Mechanism of Excitonic Solar Cells. *Mater. Res. Soc. Bull.* **2005**, *30*, 20−22.

(4) Forrest, S. R. The Limits to Organic Photovoltaic Cell Efficiency. *Mater. Res. Soc. Bull.* **2005**, *30*, 28−32.

(5) Yang, F.; Forrest, S. R. Photocurrent Generation in Nanostructured Organic Solar Cells. *ACS Nano* **2008**, *2*, 1022−1032.

(6) Wuerfel, P. Photovoltaic Principles and Organic Solar Cells. *Chimia* **2007**, *61*, 770−774.

(7) Soci, C.; Hwang, I.-W.; Yang, C.; Moses, D.; Zhu, Z.; Waller, D.; Gaudiana, R.; Brabec, C. J.; Heeger, A. J. Charge Carrier Photogeneration and Transport Properties of a Novel Low-Bandgap Conjugated Polymer for Organic Photovoltaics. *Proc. SPIE* **2006**, *6334*, 63340D(11).

(8) Muhlbacher, D.; Scharber, M.; Morana, M.; Zhu, Z.; Waller, D.; Gaudana, R.; Brabec, C. High Photovoltaic Performance of a Low-Bandgap Polymer. *Adv. Mater.* **2006**, *18*, 2884−2889.

(9) Lee, S. K.; Cho, N. S.; Kwak, J. H.; Lim, K. S.; Shim, H.-K.; Hwang, D.-H.; Brabec, C. J. New Low Band-Gap Alternating Polyfluorene Derivatives for Photovoltaic Cells. *Thin Solid Films* **2006**, *511*, 157−162.

(10) Thomas, C. A.; Zong, K.; Abboud, K. A.; Steel, P. J.; Reynolds, J. R. Donor-Mediated Band Gap Reduction in a Homologous Series of Conjugated Polymers. *J. Am. Chem. Soc.* **2004**, *126*, 16440−16450.

(11) Kim, Y.-G.; Thompson, B. C.; Ananthakrishan, N.; Padmanaban, G.; Ramakrishnan, S.; Reynolds, J. R. Variable Band Gap Conjugated Polymers for Optoelectronic and Redox Applications. *J. Mater. Res.* **2005**, *20*, 3188−3198.

(12) Thompson, B. C.; Kim, Y.-G.; McCarley, T. D.; Reynolds, J. R. Soluble Narrow Band Gap and Blue Propylenedioxythiophene-Cyanovinylene Polymers as Multifunctional Materials for Photovoltaic and Electrochromic Applications. *J. Am. Chem. Soc.* **2006**, *128*, 12714−12725.

(13) Campos, L. M.; Tontcheva, A.; Gunes, S.; Sonmez, G.; Neugebauer, H.; Sariciftci, N. S.; Wudl, F. Extended Photocurrent Spectrum of a Low Band Gap Polymer in a Bulk Heterojunction Solar Cell. *Chem. Mater.* **2005**, *17*, 4031−4033.

(14) Kroon, R.; Lenes, M.; Hummelen, J. C.; Blom, P. W. M.; de Boer, B. Small Bandgap Polymers for Organic Solar Cells (Polymer Material Development in the Last 5 Years). *Polym. Rev.* **2008**, *48*, 531−582.

(15) Zhang, F.; Bijleveld, J.; Perzon, E.; Tvingstedt, K.; Barrau, S.; Inganas, O.; Andersson, M. R. High Photovoltage Acheived in Low Band Gap Polymer Solar Cells by Adjusting Energy Levels of a Polymer with the LUMOs of Fullerene Derivatives. *J. Mater. Chem.* **2008**, *18*, 5468−5474.

(16) Liang, Y.; Feng, D.; Guo, J.; Szarko, J. M.; Ray, C.; Chen, L. X.; Yu, L. Regioregular Oligomer and Polymer Containing Thieno[3,4]thiophene Moiety for Efficient Organic Solar Cells. *Macromolecules* **2009**, *42*, 1091−1098.

(17) Chen, H.-Y.; Hou, J.; Zhang, S.; Liang, Y.; Yang, G.; Yang, Y.; Yu, L.; Wu, Y.; Li, G. Polymer Solar Cells with Enhanced Open-Circuit Voltage and Efficiency. *Nat. Photonics* **2009**, *3*, 649−653.

(18) Hou, J.; Chen, H.-Y.; Zhang, S.; Chen, R. I.; Yang, Y.; Wu, Y.; Li, G. Synthesis of a Low Band Gap Polymer and Its Application in Highly Efficient Polymer Solar Cells. *J. Am. Chem. Soc.* **2009**, *131*, 15586−15587.

(19) Park, S.; Roy, A.; Beaupre, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. Bulk Heterojunction Solar Cell with Internal Quantum Efficiency Approaching 100 %. *Nat. Photonics* **2009**, *3*, 297−303.

(20) Ohkita, H.; Cook, S.; Astuti, Y.; Duffy, W.; Tierney, S.; Zhang, W.; Heeney, M.; McCulloch, I.; Nelson, J.; Bradley, D. D. C.; et al. Charge Carrier Formation in Polythiophene/Fullerene Blend Films Studied by Transient Absorption Spectroscopy. *J. Am. Chem. Soc.* **2008**, *130*, 3030−3042.

(21) Clarke, T.; Ballantyne, A.; Jamieson, F.; Brabec, C.; Nelson, J.; Durrant, J. Transient Absorption Spectroscopy of Charge

Photogeneration Yields and Lifetimes in a Low Bandgap Polymer/Fullerene Film. *Chem. Commun.* **2009**, 89–91.

(22) Veldman, D.; Ipek, O.; Meskers, S. C. J.; Sweelssen, J.; Koetse, M. M.; Veenstra, S. C.; Kroon, J. M.; van Bavel, S. S.; Loos, J.; Janssen, R. A. J. Compositional and Electric Field Dependence of the Dissociation of Charge Transfer Excitons in Alternating Polyfluorene Copolymer/Fullerene Blends. *J. Am. Chem. Soc.* **2008**, *130*, 7721–7735.

(23) Mandoc, M. M.; Veurman, W.; Sweelssen, J.; Koetse, M. M.; Blom, P. W. M. Origin of the Efficiency Improvement in All-Polymer Solar Cells Upon Annealing. *Appl. Phys. Lett.* **2007**, *91*, 073518(3).

(24) Pope, M.; Swenberg, C. E. *Electronic Processes in Organic Crystals and Polymers*; Oxford University Press: New York, 1999.

(25) Bredas, J.-L.; Norton, J. E.; Cornil, J.; Coropceanu, V. Molecular Understanding of Organic Solar Cells: The Challenges. *Acc. Chem. Res.* **2009**, *42*, 1691–1699.

(26) Clarke, T. M.; Durrant, J. R. Charge Photogeneration in Organic Solar Cells. *Chem. Rev.* **2010**, *110*, doi: 10.1021/cr900271s.

(27) Frenkel, J. On the Transformation of Light into Heat in Solids. I. *Phys. Rev.* **1931**, *37*, 17–44.

(28) Wannier, G. H. The Structure of Electronic Excitation Levels in Insulating Crystals. *Phys. Rev.* **1937**, *52*, 191–197.

(29) Rothberg, L. Photophysics of Conjugated Polymers. In *Semiconducting Polymers*; Hadziioannou, G., Malliaras, G. G., Eds.; Wiley-VCH: Weinheim, Germany, 2007; Vol. 1; pp 179–204.

(30) Muntwiler, M.; Yang, Q.; Tisdale, W. A.; Zhu, X.-Y. Coulomb Barrier for Charge Separation at an Organic Semiconductor Interface. *Phys. Rev. Lett.* **2008**, *101*, 196403(4).

(31) Peumans, P.; Forrest, S. R. Separation of Geminate Charge-Pairs at Donor−Acceptor Interfaces in Disordered Solids. *Chem. Phys. Lett.* **2004**, *398*, 27–31.

(32) Morteani, A. C.; Sreearunothai, P.; Herz, L. M.; Friend, R. H.; Silva, C. Exciton Regeneration at Polymeric Semiconductor Heterojunctions. *Phys. Rev. Lett.* **2004**, *92*, 247402(4).

(33) Drori, T.; Sheng, C.-X.; Ndobe, A.; Singh, S.; Holt, J.; Vardeny, Z. V. Below-Gap Excitation of π-Conjugated Polymer− Fullerene Blends: Implications for Bulk Organic Heterojunction Solar Cells. *Phys. Rev. Lett.* **2008**, *101*, 037401(4).

(34) Loi, M. A.; Toffanin, S.; Muccini, M.; Forster, M.; Scherf, U.; Scharber, M. Charge Transfer Excitons in Bulk Heterojunctions of a polyfluorene Copolymer and a Fullerene Derivative. *Adv. Funct. Mater.* **2007**, *17*, 2111–2116.

(35) Tvingstedt, K.; Vandewal, K.; Gadisa, A.; Zhang, F.; Manca, J.; Inganas, O. Electroluminescence from Charge Transfer States in Polymer Solar Cells. *J. Am. Chem. Soc.* **2009**, *131*, 11819–11824.

(36) Vandewal, K.; Gadisa, A.; Oosterbaan, W. D.; Bertho, S.; Banishoeib, F.; van Severen, I.; Lutsen, L.; Cleij, T. J.; Vanderzande, D.; Manca, J. V. The Relation Between Open-Circuit Voltage and the Onset of Photocurrent Generation by Charge-Transfer Absorption in Polymer:Fullerene Bulk Heterojunction Solar Cells. *Adv. Funct. Mater.* **2008**, *18*, 2064–2070.

(37) Hallermann, M.; Haneder, S.; Da Como, E. Charge-Transfer States in Conjugated Polymer/Fullerene Blends: Below-Gap Weakly Bound Excitons for Polymer Photovoltaics. *Appl. Phys. Lett.* **2008**, *93*, 053307(3).

(38) Goris, L.; Poruba, A.; Hodakova, L.; Vanecek, M.; Haenen, K.; Nesladek, M.; Wagner, P.; Vanderzande, D.; De Schepper, L.; Manca, J. V. Observation of the Subgap Optical Absorption in Polymer−Fullerene Blend Solar Cells. *Appl. Phys. Lett.* **2006**, *88*, 052113(3).

(39) Hsu, J. W. P.; Yan, M.; Jedju, T. M.; Rothberg, L. J. Assignment of the Picosecond Photoinduced Absorption in Phenylene Vinylene Polymers. *Phys. Rev. B* **1994**, *49*, 712–715.

(40) Rothberg, L. J.; Yan, M.; Papadimitrakopoulos, F.; Galvin, M. E.; Kwock, E. W.; Miller, T. M. Photophysics of Phenylene-vinylene Polymers. *Synth. Met.* **1996**, *80*, 41–58.

(41) Cuppoletti, C. M.; Rothberg, L. J. Persistent Photoluminescence in Conjugated Polymers. *Synth. Met.* **2003**, *139*, 867–871.

(42) Schweitzer, B.; Arkhipov, V. I.; Bassler, H. Field-Induced Delayed Photoluminescence in a Conjugated Polymer. *Chem. Phys. Lett.* **1999**, *304*, 365–370.

(43) Hertel, D.; Romanovskii, Y. V.; Schweitzer, B.; Scherf, U.; Bassler, H. The Origin of the Delayed Emission in Films of a Ladder-Type Poly(para-phenylene). *Synth. Met.* **2001**, *116*, 139–143.

(44) Vardeny, Z. V.; Wei, X. Studies of Photoexcitations in Conducting Polymers by the Absorption-Detected Magnetic Resonance Technique. *Synth. Met.* **1993**, *54*, 99–111.

(45) Swanson, L. S.; Lane, P. A.; Shinar, J. Polarons and Triplet Polaronic Excitons in Poly(Paraphenylenevinylene) (PPV) and Substituted PPV: An Optically Detected Magnetic Resonance Study. *Phys. Rev. B* **1991**, *44*, 10617–10621.

(46) Gregg, B. A.; Chen, S.-G.; Cormier, R. A. Coulomb Forces and Doping in Organic Semiconductors. *Chem. Mater.* **2004**, *16*, 4586–4599.

(47) Veldman, D.; Meskers, S. C. J.; Janssen, R. A. J. The Energy of Charge-Transfer States in Electron Donor−Acceptor Blends: Insight into the Energy Losses in Organic Solar Cells. *Adv. Funct. Mater.* **2009**, *19*, 1939–1948.

(48) Onsager, L. Initial Recombination of Ions. *Phys. Rev.* **1938**, *54*, 554–557.

(49) Barbour, L. W.; Hegadorn, M.; Asbury, J. B. Watching Electrons Move in Real Time: Ultrafast Infrared Spectroscopy of a Polymer Blend Photovoltaic Material. *J. Am. Chem. Soc.* **2007**, *129*, 15884–15894.

(50) Pensack, R. D.; Banyas, K. M.; Barbour, L. W.; Hegadorn, M.; Asbury, J. B. Ultrafast Vibrational Spectroscopy of Charge Carrier Dynamics in Organic Photovoltaic Materials. *Phys. Chem. Chem. Phys.* **2009**, *11*, 2575–2591.

(51) Pensack, R. D.; Asbury, J. B. Barrierless Free Carrier Formation in an Organic Photovoltaic Material Measured with Ultrafast Vibrational Spectroscopy. *J. Am. Chem. Soc.* **2009**, *131*, 15986–15987.

(52) Pensack, R. D.; Banyas, K. M.; Asbury, J. B. Vibrational Energy Mediates Charge Separation in Organic Photovoltaic Materials. *IEEE J. Sel. Top. Quantum Electron.* **2010**, in press.

(53) Gulbinas, V.; Hertel, D.; Yartsev, A.; Sundstrom, V. Charge Carrier Photogeneration and Recombination in Ladder-Type Poly(para-phenylene): Interplay Between Impurities and External Electric Field. *Phys. Rev. B* **2007**, *76*, 235203(7).

(54) Muller, J. G.; Lupton, J. M.; Feldmann, J.; Lemmer, U.; Scharber, M. C.; Sariciftci, N. S.; Brabec, C. J.; Scherf, U. Ultrafast Dynamics of Charge Carrier Photogeneration and Geminate Recombination in Conjugated Polymer:Fullerene Solar Cells. *Phys. Rev. B* **2005**, *72*, 195208(10).

(55) Westenhoff, S.; Howard, I. A.; Hodgkiss, J. M.; Kirov, K. R.; Bronstein, H. A.; Williams, C. K.; Greenham, N. C.; Friend, R. H. Charge Recombination in Organic Photovoltaic Devices with High Open-Circuit Voltages. *J. Am. Chem. Soc.* **2008**, *130*, 13653–13658.

(56) Piris, J.; Dykstra, T. E.; Bakulin, A. A.; van Loosdrecht, P. H. M.; Knulst, W.; Trinh, M. T.; Schins, J. M.; Siebbeles, L. D. A. Photogeneration and Ultrafast Dynamics of Excitons and Charges in P3HT/PCBM Blends. *J. Phys. Chem. C* **2009**, *113*, 14500–14506.

(57) Cho, M. Vibrational Solvatochromism and Electrochromism: Coarse-Grained Models and Their Relationships. *J. Chem. Phys.* **2009**, *130*, 094505(15).

(58) Park, E. S.; Boxer, S. G. Origins of the Sensitivity of Molecular Vibrations to Electric Fields: Carbonyl and Nitrosyl Stretches in Model Compounds and Proteins. *J. Phys. Chem. B* **2002,** *106*, 5800–5806.

(59) Barbour, L. W.; Pensack, R. D.; Hegadorn, M.; Arzhantsev, S.; Asbury, J. B. Excitation Transport and Charge Separation in an Organic Photovoltaic Material: Watching Excitations Diffuse to Interfaces. *J. Phys. Chem. C* **2008,** *112*, 3926–3934.

(60) Pensack, R. D.; Banyas, K. M.; Asbury, J. B. Charge Trapping in Organic Photovoltaic Materials Examined with Time Resolved Vibrational Spectroscopy. *J. Phys. Chem. C* **2010,** *114*, 5344–5350.

(61) Kaake, L. G.; Barbara, P. F.; Zhu, X.-Y. Intrinsic Charge Trapping in Organic and Polymeric Semiconductors: A Physical Chemistry Perspective. *J. Phys. Chem. Lett.* **2010,** *1*, 628–635.

(62) Zhu, X.-Y.; Kahn, A. Electronic Structure and Dynamics at Organic Donor/Acceptor Interfaces. *MRS Bull.* **2010**, *35*, ASAP.

(63) Bounds, P. J.; Siebrand, W. Charge-Transfer Excitons in Anthracene Crystals and Their Role in Optical Charge Carrier Generation. *Chem. Phys. Lett.* **1980,** *75*, 414–418.

(64) Lanzani, G.; Cerullo, G.; Brabec, C.; Sariciftci, N. S. Time Domain Investigation of the Intrachain Dynamics of a Prototypical Light-Emitting Conjugated Polymer. *Phys. Rev. Lett.* **2003,** *90*, 047402(4).

(65) Tamura, H.; Ramon, J. G. S.; Bittner, E. R.; Burghardt, I. Phonon-Driven Exciton Dissociation at Donor—Acceptor Polymer Heterojunctions: Direct versus Bridge-Mediated Vibronic Coupling Pathways. *J. Phys. Chem. B* **2008,** *112*, 495–506.

(66) Tamura, H.; Bittner, E. R.; Burghardt, I. Exciton Dissociation at Donor—Acceptor Polymer Heterojunctions: Quantum Non-adiabatic Dynamics and Effective-Mode Analysis. *J. Chem. Phys.* **2007,** *126*, 021103(5).

(67) Tretiak, S.; Saxena, A.; Martin, R. L.; Bishop, A. R. Conformational Dynamics of Photoexcited Conjugated Molecules. *Phys. Rev. Lett.* **2002,** *89*, 097402(4).

(68) Hwang, I.-W.; Moses, D.; Heeger, A. J. Photoinduced Carrier Generation in P3HT/PCBM Bulk Heterojunction Materials. *J. Phys. Chem. C* **2008,** *112*, 4350–4354.

(69) Kilina, S.; Tretiak, S. Excitonic and Vibrational Properties of Single-Walled Semiconducting Carbon Nanotubes. *Adv. Funct. Mater.* **2007,** *17*, 3405–3420.

(70) Fernandez-Alberti, S.; Kleiman, V. D.; Tretiak, S.; Roitberg, A. E. Nonadiabatic Molecular Dynamics Simulations of the Energy Transfer Between Building Blocks in a Phenylene Ethynylene Dendrimer. *J. Phys. Chem. A* **2009,** *113*, 7535–7542.

(71) Duncan, W. R.; Prezhdo, O. V. Temperature Independence of the Photoinduced Electron Injection in Dye-Sensitized TiO_2 Rationalized by Ab Initio Time-Domain Density Functional Theory. *J. Am. Chem. Soc.* **2008,** *130*, 9756–9762.

(72) Prezhdo, O. V.; Duncan, W. R.; Prezhdo, V. V. Dynamics of the Photoexcited Electron at the Chromophore—Semiconductor Interface. *Acc. Chem. Res.* **2008,** *41*, 339–348.

(73) Prezhdo, O. V. Photoinduced Dynamics in Semiconductor Quantum Dots: Insights from Time-Domain Ab Initio Studies. *Acc. Chem. Res.* **2009,** *2009*, 2005–2016.

(74) Hutchison, G. R.; Ratner, M. A.; Marks, T. J. Hopping Transport in Conductive Heterocyclic Oligomers: Reorganization Energies and Substituent Effects. *J. Am. Chem. Soc.* **2005,** *127*, 2339–2350.