THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

pubs.acs.org/JPCC

Free Carrier Generation in Fullerene Acceptors and Its Effect on Polymer Photovoltaics

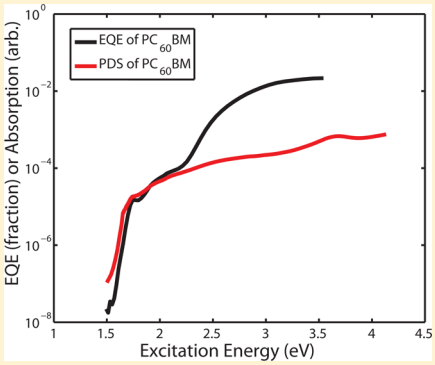
George F. Burkhard,[†] Eric T. Hoke,[†] Zach M. Beiley,[‡] and Michael D. McGehee*[,‡]

[†]Geballe Laboratory for Advanced Materials, Stanford University, Stanford, California, 94305, United States

[‡]Department of Materials Science and Engineering, Stanford University, Stanford, California, 94305, United States

Supporting Information

ABSTRACT: Early research on C_{60} led to the discovery that the absorption of photons with energy greater than 2.35 eV by bulk C_{60} produces free charge carriers at room temperature. We find that not only is this also true for many of the soluble fullerene derivatives commonly used in organic photovoltaics, but also that the presence of these free carriers has significant implications for the modeling, characterization, and performance of devices made with these materials. We demonstrate that the discrepancy between absorption and quantum efficiency spectra in P3HT:PCBM is due to recombination of such free carriers in large PCBM domains before they can be separated at a donor/acceptor interface. Since most theories assume that all free charges result from the separation of excitons at a donor/acceptor interface, the presence of free carrier generation in fullerenes can have a significant impact on the interpretation of data generated by numerous field-dependent techniques.



INTRODUCTION

In the organic photovoltaic (OPV) community, it is common to plot photocurrent as a function of field to investigate the recombination processes occurring within devices, since it is believed that the electric field intensity directly affects the rate of geminate charge separation.[1−5] Other techniques, such as time-resolved optical measurements of polaron yield,[6] and field-dependent techniques such as photo- charge extraction by linearly increasing voltage (photo-CELIV)[7,8] and time-delayed collection field (TDCF)[9] provide additional insight into the processes occurring within a device, including rates of charge generation and diffusion. When interpreting such measurements, numerical models based on Onsager−Braun theory are often used to back out physical parameters, including rates of geminate pair separation.[2] In such a model, excitons diffuse to a donor/acceptor interface and form interfacial charge transfer (CT) states, which then separate to form free charges. Separation or recombination of this geminate pair occurs via random thermal (Brownian) motion under the influence of the built-in and applied electric fields, with stronger fields resulting in higher separation rates and lower recombination rates. Because this mechanism is the only method of charge carrier production in the model, the model tacitly assumes that all photocurrent is due to the generation of charges at a type II heterojunction following photoexcitation of the active materials.

Here, we show that photocurrent is not always a result of field-assisted separation of a charge transfer state at a donor/acceptor interface. In devices with large fullerene domains, fullerenes and their derivatives spontaneously generate free carriers upon absorption of high-energy photons, which can be extracted under applied bias. This photocurrent generation due to free carriers that are generated in fullerenes has been well understood for some time,[10,11] but the implications for solar cells have not been considered until recently.[12] Because spontaneous free carrier generation happens inside fullerene domains, it is subject to its own rates of geminate separation and recombination, complicating efforts to characterize geminate recombination at the donor/acceptor interface.

EXPERIMENTAL DETAILS AND DISCUSSION

The current extracted from an OPV device at a particular bias depends on parameters including dark current, photocurrent, and photoconductivity (current injected from the electrodes whose magnitude depends on illumination of the device). To isolate the photocurrent from the other currents, external quantum efficiency (EQE) measurements were made as a function of wavelength, applied voltage, and light intensity. The measurements were performed by simultaneously illuminating the device with a mechanically chopped (~200 Hz) low-intensity (<1 $\mu W/cm^2$) monochromatic beam and a stronger white light bias of tunable intensity. This method is more accurate than merely subtracting the dark current−voltage curve from the 1 sun curve, which fails to account for series resistance in the device, changes in the injected current due to differences in the device temperature for the dark and light measurements,[13] and any photoconductive effects. More details on the experimental setup can be found in the Supporting Information.

Received: November 1, 2012
Revised: November 27, 2012
Published: November 28, 2012

dx.doi.org/10.1021/jp310821f | J. Phys. Chem. C 2012, 116, 26674−26678

We have previously made such quantum efficiency measurements on poly[3-hexylthiophene]:phenyl-C_{60} butyric methyl ester (P3HT:PCBM) solar cells and found that short-wavelength light absorbed in the PCBM generates photocurrent with ~40% of the efficiency of the longer wavelength light absorbed in the P3HT.[14] We determined that this effect was due to a problem harvesting excitons generated in large PCBM domains. Because shrinking the PCBM domain sizes resulted in recovery of the excitons (albeit at the expense of charge collection efficiency), we concluded that the excitons were recombining before they were able to diffuse to the donor/acceptor interface.

Further investigation into the bias and wavelength dependence of the EQE of these devices suggests that some of the excitons generated by high-energy (>2.35 eV, <530 nm) photons in the PCBM domains are quickly and spontaneously converted into free carriers, which can recombine geminately inside the PCBM cluster before they can be separated at the interface with the P3HT. By going to reverse bias, the internal field is increased and the rate of geminate separation of these carriers *inside the PCBM clusters* is enhanced. In contrast, low-energy photons (<2.35 eV, >530 nm) absorbed by PCBM do not generate free carriers efficiently, and a significantly weaker dependence of EQE with voltage is observed. The field dependence of free carriers generated within large PCBM domains would skew the results of an investigation of the donor/acceptor CT state separation efficiency if not properly taken into account.

Figure 1a shows external quantum efficiency spectra measured at different electrical biases for a typical P3HT:PCBM cell. As the internal field strength is increased, the quantum efficiency appears to increase predominantly in the short wavelength regions where PCBM absorbs (see Supporting Information). Changes in the EQE spectral shape with bias have been previously reported for organic heterojunction solar cells by several research groups.[15−17] Several explanations have been given, including exciton fission,[16] photomultiplication,[17] and hot charge-transfer state formation,[15] but all have suggested that the change in spectral shape is due to differences in the efficiency of charge generation by photons absorbed by the donor versus the acceptor material.

To determine if the voltage dependence of the EQE spectra for P3HT:PCBM devices can be explained by differences in current generation of light absorbed by PCBM versus light absorbed by P3HT, the EQE was measured at 350, 600, and 750 nm as a function of bias and normalized to the EQE at zero bias (Figure 1b). At both 350 and 750 nm, PCBM is the primary absorbing material (79% and 100%, respectively), while at 600 nm, P3HT absorbs nearly all (88%) of the light. The photocurrent generation at 600 nm is less voltage dependent than at the other two wavelengths where the fullerene is the primary absorber. Surprisingly, the normalized EQE at 350 nm is significantly more voltage dependent than at 750 nm, despite the fact that PCBM is being excited in both cases, and actually accounts for a larger fraction of the absorption at 750 nm than at 350 nm. These results indicate that differences in current generation for light absorbed by P3HT and PCBM cannot explain the spectral changes in the EQE. If light absorbed by PCBM were assumed to have the same voltage-dependent current generation efficiency at all wavelengths, we would actually expect a slightly weaker voltage dependence of the EQE at 350 nm (where there is some P3HT absorption) than at 750 nm where there is no P3HT absorption. This energy

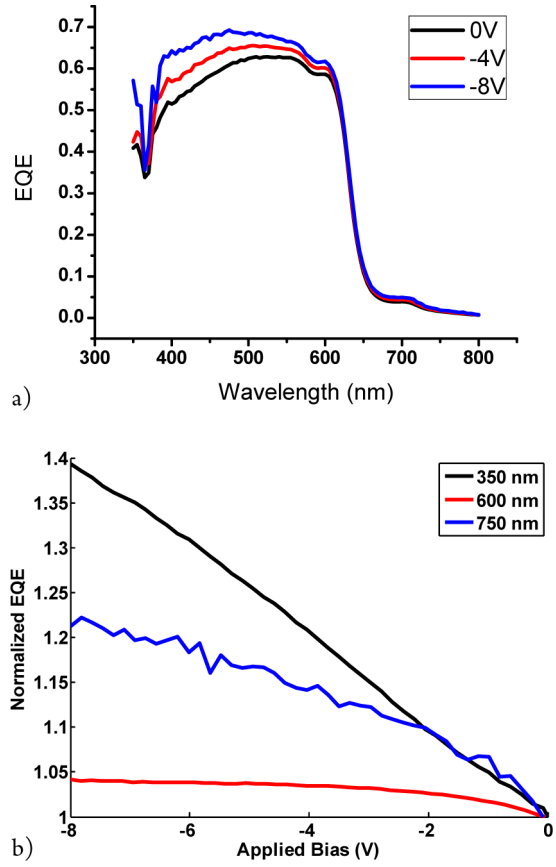


Figure 1. (a) External quantum efficiency spectra of a typical P3HT:PCBM solar cell at different applied electrical biases and under 1 sun bias illumination. (b) Raw and normalized EQE of a typical P3HT:PCBM cell at 350, 600, and 750 nm as a function of bias voltage. The normalized curves illustrate the fact that the bias dependence of the EQE is much stronger at 350 nm, than at 750 nm, despite the fact that PCBM accounts for most of the absorption at both of these wavelengths.

dependence is consistent with free carrier generation in C_{60}, since in that material more free carriers are generated at high photon energies than at low photon energies, which favor generation of neutral bound excitons.[10,11] A basic outline of this mechanism follows.

Spontaneous free carrier generation was shown to occur in C_{60} at room temperature by Kazaoui et al.[10] In C_{60}, high-energy localized excitonic states (Frenkel excitons) can transform directly into free carriers. They can also form free carriers by forming an intermolecular (between fullerene molecules) charge transfer state, which is then separated into a free electron and hole by thermal activation, since the CT energy is within k_BT of the charge-separated states.[11] An interesting result of this energy landscape is that, because free carriers are only generated by high-energy transitions or via the high-energy CT state, which lies at 2.35 eV above the ground state, there is a minimum energy for free carrier generation. Photons with energy less than 2.35 eV can only form the lowest energy singlet states, while photons with energy greater than 2.35 eV are capable of forming both long-lived singlet excitons and free carriers. We therefore expect an energy dependence of any effects resulting from free carrier generation in C_{60} due to the larger free carrier yield from photons with energy above the 2.35 eV threshold. While this effect has been confirmed by

dx.doi.org/10.1021/jp310821f | J. Phys. Chem. C 2012, 116, 26674−26678

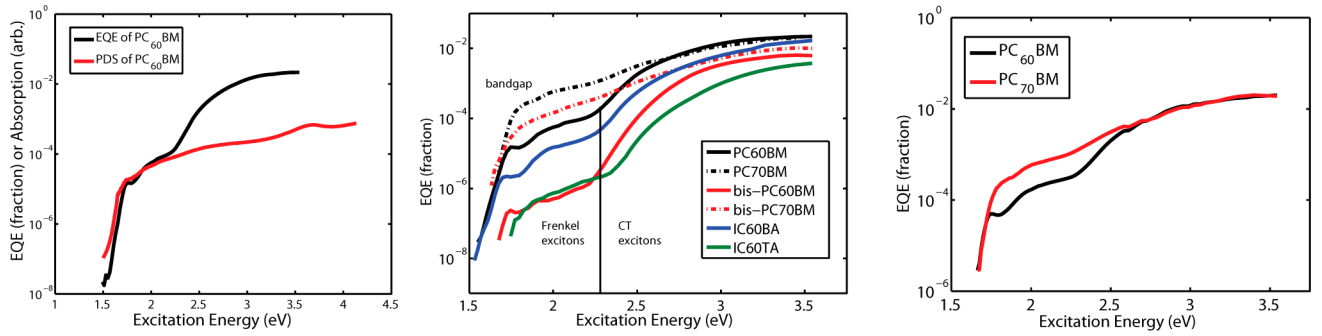


Figure 2. (a) PCBM absorption as measured by photothermal deflection spectroscopy (PDS) and EQE of a PCBM-only device. EQE and absorption share the same spectral shape below 2.35 eV, where EQE is due only to the generation of excitons. Above 2.35 eV, free carriers are generated more efficiently, resulting in a dramatic increase in EQE. (b) EQE of commonly used soluble fullerene adducts. The vertical line is placed at 2.35 eV, showing the delineation between Frenkel excitons and CT excitons in adducts based on C_{60}. Adducts based on C_{70} generate free carriers starting above 1.85 eV and therefore show stronger EQE response all the way to that energy. (c) Comparison of EQE spectra from $PC_{60}BM$- and $PC_{70}BM$-only devices.

measuring the quantum efficiency of C_{60}-only devices as a function of photon energy, no such studies have been performed, to our knowledge, on any of its soluble adducts that are commonly used in polymer:fullerene bulk heterojunction solar cells.

To confirm that free carriers are also generated in $PC_{60}BM$ and other fullerene adducts, we performed very sensitive EQE and absorption measurements on fullerene-only devices or films. Absorption measurements were performed using photothermal deflection spectroscopy (PDS) as described previously.[18,19] Fullerene-only devices were made using a structure ITO/PEDOT:PSS/fullerene/Ca/Al which is analogous to the P3HT:PCBM solar cells. Sensitive EQE measurements were performed using a lock-in amplifier as described in the Supporting Information. Figure 2a shows the absorption coefficient and EQE of $PC_{60}BM$ on a logarithmic scale. Absorption and EQE are correlated below 2.35 eV, with photocurrent most likely due to the dissociation of Frenkel excitons at the selective contacts. Above 2.35 eV, however, the EQE and absorption diverge, with a dramatic increase in the photocurrent quantum efficiency. This enhancement in photocurrent occurs at ~2.35 eV and confirms that $PC_{60}BM$ behaves in a similar fashion as C_{60}. Figure 2b shows EQEs of devices made from a number of other C_{60} adducts, including bis-$PC_{60}BM$ and bis- and tris-indene C_{60} adducts ($IC_{60}BA$ and $IC_{60}TA$, respectively), which all exhibit similar behavior. The EQEs shown in Figure 2a–c are all from devices with fullerene-only active layers, and thus the EQEs are very small due to Langevin recombination in the bulk. However, this does not imply that free carriers generated in fullerene domains could not result in significant current generation in a bulk heterojunction solar cell, where electrons and holes migrate through the device in separate materials.

Kazaoui et al. also performed similar measurements on C_{70}, which showed similar behavior, except that the intermolecular CT state occurred at 1.85 eV, which is almost equal to the bandgap energy. Thus, C_{70} exhibits a mix of Frenkel and CT excitons at all wavelengths and has been shown to generate free carriers across its entire absorption spectrum. For completeness, we performed the same measurements on $PC_{70}BM$ and bis-$PC_{70}BM$, and contrast them to the behavior of $PC_{60}BM$ (Figure 2b,c). We conclude that $PC_{70}BM$ and bis-$PC_{70}BM$ behave like C_{70}; we observe free carrier generation across all photon energies greater than 1.85 eV.

While we have observed that free carriers generated in PCBM play an important role in the bias dependence of photocurrent in P3HT:PCBM solar cells, others have observed similar effects in other ordered systems, including bilayer CuPc:C_{60} devices.[12] As we noted in our original investigation, this effect does not appear to occur in disordered (amorphous) systems with small PCBM domains. We have investigated blends of poly[2-methoxy-5-(2′-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV), poly[[9-(1-octylnonyl)-9*H*-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT), and poly[di(2-ethylhexyloxy)-benzo[1,2-*b*:4,5-*b*′]dithiophene-*co*-octylthieno[3,4-*c*]pyrrole-4,6-dione] (PBDTTPD) with $PC_{60}BM$ and $PC_{70}BM$, and none of these systems show this dependence of the photocurrent on electrical bias. We speculate that the reason bias-dependent EQE has been observed in systems like P3HT:PCBM and CuPc:C_{60} but not in others is due to the large fullerene domains in these devices. Because recombination is very efficient when both charges are in the same material, systems with large fullerene domains show a high rate of recombination of free carriers, which can be reduced by applying a strong electrical bias. In amorphous polymer:fullerene systems the fullerene domains are much smaller. This ostensibly allows the hole generated in the fullerene to migrate to the polymer before it recombines with the electron. Thus, in the case of small domains, photocurrent generation from free carriers may not be experimentally distinguishable from photocurrent generation from exciton dissociation at the heterojunction interface. We therefore suspect that free carrier generation happens in the fullerenes used in these systems as well, but applied electrical bias plays no role, since those carriers can already be separated before they recombine. Additionally, while fullerenes are particularly efficient at generating free carriers (due to the close proximity of the intermolecular CT state with the lowest lying charge-separated ionic states), spontaneous free carrier generation has been shown to be general and can happen in polymers and other organic semiconductors.[20−23]

In an effort to eliminate all other explanations for an apparent field dependence of exciton harvesting that occurs in PCBM only, we considered the possibility that PCBM excitons might recombine with trapped charges via an Auger-like process mediated by Förster energy transfer from the exciton to the trapped polaron.[24] In this situation, the electric field would change the occupation of energetic charge traps by raising or

dx.doi.org/10.1021/jp310821f | *J. Phys. Chem. C* 2012, 116, 26674−26678

lowering the quasi-Fermi levels in the device. The change in the density of trapped charges would effectively shorten or lengthen the distance an exciton can diffuse before recombining with the charge, lowering or raising the exciton harvesting efficiency. We ruled out this possibility by examining the dependence of the EQE spectrum on illumination intensity. At thermal equilibrium and relatively low carrier densities, the electric field affects the quasi-Fermi levels equally and inversely to an equivalent change in the generation rate

$$n_t \propto \frac{G}{V_{bi} - V}$$

where n_t, G, V_{bi}, and V represent the trap occupancy, generation rate, built-in voltage, and applied bias, respectively (see Supporting Information for a more detailed analysis).[25] Therefore, we expect that if the exciton loss is due to Auger recombination with trapped charges, decreasing the illumination intensity should affect the EQE spectrum in a similar way as applying a strong reverse electrical bias.

Figure 3a shows EQE spectra at various illumination intensities, and Figure 3b shows differential EQE as a function

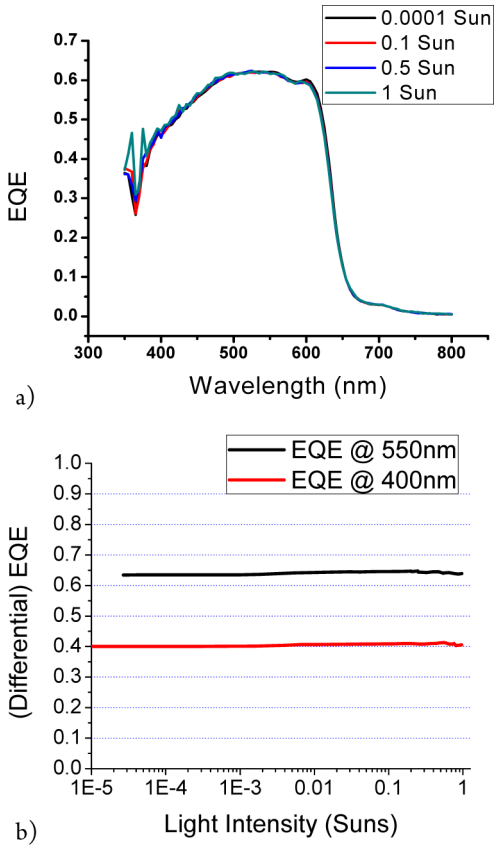


Figure 3. (a) EQE spectra of a P3HT:PCBM device at increasing light intensity. (b) Differential EQE as a function of light intensity in P3HT:PCBM at 400 and 550 nm. There is no appreciable dependence of EQE on light intensity, indicating that trapped charges do not play a role.

of illumination intensity at 550 nm, where absorption is due primarily to the P3HT and at 400 nm, where PCBM is responsible for approximately half of the absorption. These data indicate that there is almost no light intensity dependence of the EQE spectra at the range of light intensities measured (10^{-5} to 1 sun). The very small light intensity dependence visible in Figure 3b occurs equally at both wavelengths and is attributable to the slight dependence of carrier mobility on steady-state charge density and the onset of Langevin (bimolecular) recombination at higher light intensities. Because the EQE spectra are independent of light intensity, we can rule out Auger recombination with trapped charges as a possible explanation for the dependence of EQE on bias. It is important to note that while others have shown that interfacial traps play an important role in charge transport and recombination in P3HT:PCBM cells,[26,27] our observations indicate that the presence of such traps does not affect the free carriers generated in the PCBM phase until after they are separated at the donor/acceptor interface.

CONCLUSION

We have shown that free carriers are generated spontaneously at room temperature in the soluble fullerene molecules most commonly used in bulk heterojunction organic solar cells, and that these carriers contribute appreciably to the photocurrent in devices with large fullerene domains. Because the generation of these carriers is a function of the electric field intensity in the device, studies of other field-dependent processes should take this effect into account. Namely, studies of geminate recombination rates, which typically fit current–voltage curves to an Onsager–Braun model, would be complicated by this effect. We suggest that measuring quantum efficiency as a function of wavelength, electrical bias, and illumination intensity would greatly enhance such studies, as these measurements provide much more information than current–voltage curves can on their own. A way to minimize the impact of free carrier generation on other field-dependent studies is to excite the device using monochromatic light at a wavelength where the non-fullerene component provides a majority of the absorption.

ASSOCIATED CONTENT

Supporting Information

A description and discussion of experimental methods including EQE measurements as well as the extinction coefficients for P3HT and PCBM; a derivation of the dependence of trap occupancy on generation rate and applied bias. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail mmcgehee@stanford.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Center for Advanced Molecular Photovoltaics (Award KUS-C1-015-21), made by King Abdullah University of Science and Technology (KAUST). E.T.H. was supported by the National Science Foundation GRFP and the Fannie and John Hertz Foundation. We thank Rodrigo Noriega and Alberto Salleo for help with the PDS measurements and Koen Vandewal for his insights.

REFERENCES

(1) Pasveer, W. F.; Cottaar, J.; Tanase, C.; Coehoorn, R.; Bobbert, P. A.; Blom, P. W. M.; de Leeuw, D. M.; Michels, M. A. J. *Phys. Rev. Lett.* **2005**, *94*, 206601.

(2) Mihailetchi, V. D.; Koster, L. J. A.; Hummelen, J. C.; Blom, P. W. M. *Phys. Rev. Lett.* **2004**, *93*, 216601−216604.

(3) Petersen, A.; Ojala, A.; Kirchartz, T.; Wagner, T. A.; Urthner, F. W.; Rau, U. *Phys. Rev. B* **2012**, *85*, 245208.

(4) Nelson, J. *Mater. Today* **2011**, *14*, 462−470.

(5) Clarke, T. M.; Durrant, J. R. *Chem. Rev.* **2010**, *110*, 6736−6767.

(6) Credgington, D.; Jamieson, F. C.; Walker, B.; Nguyen, T.-Q.; Durrant, J. R. *Adv. Mater.* **2012**, *24*, 2135−2141.

(7) Juška, G.; Arlauskas, K.; Viliūnas, M.; Kočka, J. *Phys. Rev. Lett.* **2000**, *84*, 4946−4949.

(8) Lorrmann, J.; Badada, B. H.; Inganas, O.; Dyakonov, V.; Deibel, C. *J. Appl. Phys.* **2010**, *108*, 113705−113708.

(9) Kniepert, J.; Schubert, M.; Blakesley, J. C.; Neher, D. *J. Phys. Chem. Lett.* **2011**, *2*, 700−705.

(10) Kazaoui, S.; Minami, N.; Tanabe, Y.; Byrne, H. J.; Eilmes, A.; Petelenz, P. *Phys. Rev. B* **1998**, *58*, 7689−7700.

(11) Pope, M. Swenberg, C. E. *Electronic Processes in Organic Crystals*, 2nd ed.; Oxford University Press: New York, 1999.

(12) Jeong, W.-I.; Lee, Y. E.; Shim, H.-S.; Kim, T.-M.; Kim, S.-Y.; Kim, J.-J. *Adv. Funct. Mater.* **2012**, *22*, 3089−3094.

(13) Limpinsel, M.; Wagenpfahl, A.; Mingebach, M.; Deibel, C.; Dyakonov, V. *Phys. Rev. B* **2010**, *81*, 085203.

(14) Burkhard, G. F.; Hoke, E. T.; McGehee, M. D. *Nano Lett.* **2009**, *9*, 4037.

(15) Brenner, T. J. K.; Li, Z.; McNeill, C. R. *J. Phys. Chem. C* **2011**, *115*, 22075−22083.

(16) Lee, J.; Jadhav, P.; Baldo, M. A. *Appl. Phys. Lett.* **2009**, *95*, 033301−033303.

(17) Huang, J.; Yang, Y. *Appl. Phys. Lett.* **2007**, *91*, 203505−203503.

(18) Goris, L.; Haenen, K.; Nesladek, M.; Wagner, P.; Vanderzande, D.; De Schepper, L.; D'Haen, J.; Lutsen, L.; Manca, J. *J. Mater. Sci.* **2005**, *40*, 1413−1418.

(19) Ko, S.; Hoke, E. T.; Pandey, L.; Hong, S.; Mondal, R.; Risko, C.; Yi, Y.; Noriega, R.; McGehee, M. D.; Brédas, J.-L.; Salleo, A.; Bao, Z. *J. Am. Chem. Soc.* **2012**, *134*, 5222−5232.

(20) Vandewal, K.; Ma, Z.; Bergqvist, J.; Tang, Z.; Wang, E.; Henriksson, P.; Tvingstedt, K.; Andersson, M. R.; Zhang, F.; Inganäs, O. *Adv. Funct. Mater.* **2012**, *22*, 3480−3490.

(21) Castro, G.; Hornig, J. F. *J. Chem. Phys.* **1965**, *42*, 1459−1460.

(22) Jortner, J. *Phys. Rev. Lett.* **1968**, *20*, 244−247.

(23) Karl, N. *Adv. Solid State Phys.* **1974**, *14*, 261−290.

(24) Bolinger, J. C.; Traub, M. C.; Adachi, T.; Barbara, P. F. *Science* **2011**, *331*, 565−567.

(25) Taylor, G.; Simmons, J. *J. Non-Cryst. Solids* **1972**, *8*, 940−946.

(26) MacKenzie, R. C. I.; Shuttle, C. G.; Chabinyc, M. L.; Nelson, J. *Adv. Energy Mater.* **2012**, *2*, 662−669.

(27) Kirchartz, T.; Pieters, B. E.; Kirkpatrick, J.; Rau, U.; Nelson, J. *Phys. Rev. B* **2011**, *83*, 115209.