

# Direct Correlation of Charge Transfer Absorption with Molecular Donor:Acceptor Interfacial Area via Photothermal Deflection Spectroscopy

Ester Buchaca-Domingo,<sup>\*,†,‡</sup> Koen Vandewal,<sup>\*,§,||</sup> Zhuping Fei,<sup>⊥</sup> Scott E. Watkins,<sup>#</sup> Fiona H. Scholes,<sup>#</sup> James H. Bannock,<sup>⊥</sup> John C. de Mello,<sup>⊥</sup> Lee J. Richter,<sup>∇</sup> Dean M. DeLongchamp,<sup>∇</sup> Aram Amassian,<sup>‡</sup> Martin Heeney,<sup>⊥</sup> Alberto Salleo,<sup>§</sup> and Natalie Stingelin<sup>†</sup>

<sup>†</sup>Department of Materials and Centre for Plastic Electronics, Imperial College London, London SW7 2AZ, U.K.

<sup>‡</sup>Division of Physical Sciences and Engineering, Solar and Photovoltaic Engineering Research Center, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

<sup>§</sup>Department of Materials Science and Engineering, Stanford University, Stanford, California 94305, United States

<sup>||</sup>Institut für Angewandte Photophysik, TU Dresden, 01069 Dresden, Germany

<sup>⊥</sup>Department of Chemistry and Centre for Plastic Electronics, Imperial College London, London SW7 2AZ, U.K.

<sup>#</sup>CSIRO Manufacturing Flagship, Clayton, VIC 3169, Australia

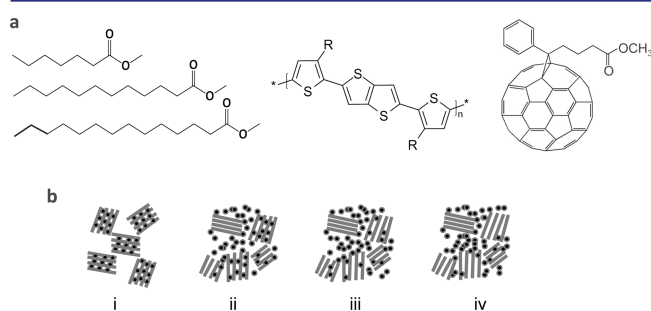
<sup>∇</sup>National Institute of Standards and Technology (NIST), Gaithersburg, Maryland 20899, United States

## Supporting Information

**ABSTRACT:** Here we show that the charge transfer (CT) absorption signal in bulk-heterojunction solar cell blends, measured by photothermal deflection spectroscopy, is directly proportional to the density of molecular donor:acceptor interfaces. Since the optical transitions from the ground state to the interfacial CT state are weakly allowed at photon energies below the optical gap of both the donor and acceptor, we can exploit the use of this sensitive linear absorption spectroscopy for such quantification. Moreover, we determine the absolute molar extinction coefficient of the CT transition for an archetypical polymer:fullerene interface. The latter is  $\sim 100$  times lower than the extinction coefficient of the donor chromophore involved, allowing us to experimentally estimate the transition dipole moment as 0.3 D and the electronic coupling between the ground and CT states to be on the order of 30 meV.

In bulk-heterojunction (BHJ) solar cells, charge carriers are generated but also recombine via interfacial charge transfer (CT) states. Since such CT states likely originate from areas where the donor and acceptor are in close proximity, there should be an optimal density of donor:acceptor interfaces that can maximize the former processes (i.e., exciton harvesting and free carrier generation) while minimizing the electron–hole recombination.<sup>1</sup> However, a clear structural picture of how to realize this is still missing, partly because it has been challenging (a) to quantify the properties of individual interfacial CT states, such as their energetics and electronic coupling to the ground state, and (b) to identify the amount of functional donor:acceptor contacts that are present in a given architecture and may lead to such interfacial CT states.

The establishment of relevant structure–property interrelationships with respect to interfacial CT states will likely require that intermixed phases of the donor and acceptor are taken into account. These intermixed phases commonly result from the often considerable miscibility of fullerene derivatives within the fractions of the donor polymer that are of low molecular order—which is a rather universal behavior for binary polymer:fullerene blends.<sup>2,3</sup> Here we employ poly(2,5-bis(3-alkylthiophene-2-yl)thieno[3,2-*b*]thiophene) (pBTTT)<sup>4</sup> as the donor material and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM) as the acceptor (see Figure 1a for the chemical structures) and use suitable additives to direct the intermixing of the two components, and thus the amount of molecular interfaces, without changing the donor:acceptor composition ratio.<sup>3e</sup> This



**Figure 1.** (a) From left to right: Chemical structures of the additives (Me7, Me12, Me14 from top to bottom), pBTTT, where R = (CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>, and PC<sub>61</sub>BM. (b) Schematics that illustrate the different phase morphologies that can be obtained with these systems. From left to right: a one-phase morphology (i) is realized when no additive is used; three phases can be obtained with Me7 (ii), and predominantly two-phase systems are realized adding Me12 (iii) and Me14 (iv).<sup>3e</sup>

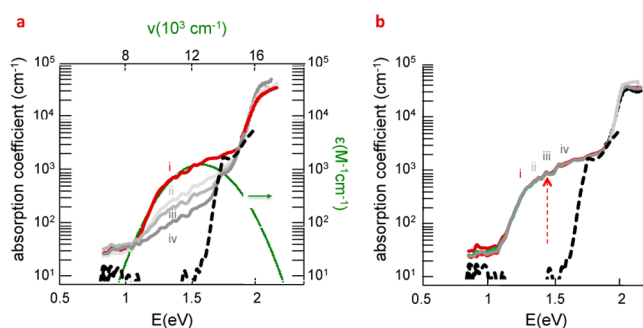
**Received:** December 12, 2014

**Published:** April 9, 2015

enables us to establish a correlation between the phase morphology and the subgap absorption strength that originates from direct CT absorption. In order to demonstrate the ability of photothermal deflection spectroscopy (PDS) to determine the relative interfacial contact area in polymer:fullerene mixed phases, we further apply this method to quantify the effect of the same additives in poly(3-hexylthiophene) (P3HT)<sup>5</sup> and PC<sub>61</sub>BM blends on their optoelectronic properties by assessing the varying amount of the intermixed amorphous phase in the different systems using photoluminescence (PL) and UV-vis spectroscopy as well as PDS.

pBTTT was selected as the initial donor polymer because it is a conjugated polymer that is able to host certain fullerene derivatives such as PC<sub>61</sub>BM in “cavities” within its molecular arrangements to form a co-crystal phase,<sup>6</sup> providing a well-defined model for donor polymer:fullerene intermixed regions. Indeed, the co-crystal represents an *ordered* intermixed phase that can be readily probed by structural techniques such as X-ray diffraction,<sup>2c,7</sup> in contrast to the intermixed amorphous solid solutions formed by, for instance, the molecularly disordered fractions in P3HT in which fullerenes such as PC<sub>61</sub>BM are miscible. Addition of methyl esters of certain fatty acids allows the manipulation of co-crystal formation,<sup>3c</sup> leading to predominantly two-phase systems composed of relatively phase-pure polymer and fullerene domains when myristic acid methyl ester (Me14) or dodecanoic acid methyl ester (Me12) are used as additives and morphologies containing three phases (phase-pure polymer and fullerene regions as well as an intermixed domain constituting the co-crystal phase) when heptanoic acid methyl ester (Me7) is employed. More recently, a structural picture of the resulting ternary systems (pBTTT:additive:PC<sub>61</sub>BM) has further been substantiated with photophysical evidence that fits our view of what phase morphologies can be achieved in pBTTT:PC<sub>61</sub>BM blends when specific fatty acid esters are added.<sup>8</sup> However, these additives, i.e., Me7, Me12, and Me14, were not intended to act as plasticizers such as processing additives like 1,8-diiodooctane (DIO), 1,8-octanedithiol (ODT) and 1,8-dichlorooctane (DCO), which are frequently applied to modify the morphology of the active layer to realize an improvement in device performance.<sup>9</sup> While trace solvent is commonly found in coat films, no significant traces of additive were detected after 2 h of film formation (further details are given in ref 3e and Figure S1 in the Supporting Information (SI)). While we cannot exclude that a minute fraction stays in the film, all of the evidence collected to date (including data presented in this work) suggests that even if trace amounts of additives are present, they do not negatively affect the behavior of the pBTTT:PC<sub>61</sub>BM blend.<sup>3e,8</sup> Schematics of the different phase morphologies achieved within pBTTT:PC<sub>61</sub>BM:fatty acid additive systems are shown in Figure 1b (for more details, see ref 3e).

In a first set of experiments, PDS spectra were measured for pBTTT:PC<sub>61</sub>BM and the different pBTTT:additive:PC<sub>61</sub>BM systems with known degrees of intermixed phases. Absolute absorption coefficient spectra were obtained by matching the PDS spectra to absolute UV-vis absorption spectra measured in the strongly absorbing region ( $E > 1.9$  eV) on samples with known film thickness. pBTTT has an absorption onset at 1.9 eV, while PC<sub>61</sub>BM has its onset at 1.7 eV (Figure 2a). The broad but weak absorption band at photon energies below 1.5 eV originates from direct CT absorption. Tellingly, this absorption band varies in intensity when different additives are used to control the phase morphology of the pBTTT:PC<sub>61</sub>BM blends. As-cast binaries



**Figure 2.** (a) PDS data obtained on pBTTT:PC<sub>61</sub>BM samples with different contents of intermixed phases, from the highly intermixed co-crystal phase (i) to multiphase systems with decreasing amounts of intermixed phases realized with addition of fatty acids. Data for neat PC<sub>61</sub>BM (dashed line) are shown for reference. The graph also shows the molar absorption coefficient  $\epsilon$  as a function of wavenumber  $\nu$  (or photon energy  $E$ ) of a pBTTT:PC<sub>61</sub>BM charge transfer complex (green line); the molar extinction coefficient of the pBTTT:PC<sub>61</sub>BM CT complex peaks at  $\sim 1000$  M<sup>-1</sup> cm<sup>-1</sup> (see Figure S2 for more details). (b) PDS data measured on the same films after annealing at 150 °C, which drives these two- or three-phase systems to a single-phase structure consisting of the co-crystal phase.

without additives, which consist solely of the co-crystal pBTTT:PC<sub>61</sub>BM (i) and thus feature the highest amount of molecular donor:acceptor interface that is possible to reach within this system,<sup>10</sup> show the most intense CT absorption band. The CT absorption band of pBTTT:Me7:PC<sub>61</sub>BM (ii), where still a large fraction of intimately mixed co-crystal phase coexists with relatively phase-pure polymer and fullerene domains, is reduced compared with that of the pBTTT:PC<sub>61</sub>BM binary. Most notably, the blends with Me12 (iii) and Me14 (iv) show a significant decrease in their CT absorption bands that we attribute to the strong phase separation between the polymer and the fullerene that is induced by the introduction of the additive in these blend systems. In agreement with these observations is the fact that the weak optical transition of PC<sub>61</sub>BM at 1.7 eV (Figure 2; data for neat PC<sub>61</sub>BM (dashed lines) are shown for comparison) is more pronounced for the system with Me14 (iv), supporting our structural picture that these systems comprise microscopically large fullerene domains and aggregates. Also, annealing these ternary films at 150 °C, which drives these multiphase systems toward the thermodynamically stable architecture composed mainly of the co-crystal phase,<sup>3c</sup> leads to the maximum number of molecular donor:acceptor interfaces as in the pBTTT:PC<sub>61</sub>BM binary. Indeed, full recovery of the CT absorption signal is observed (Figure 2b and Table S1 in the SI). From the above it is evident that there is a direct correlation between the amount of intermixed phases and the CT absorption. This finding is interesting when put in context with our previous studies, where we demonstrated that the highest charge formation is found in the three-phase morphology realized with Me7 (ii). We had assigned this to the large donor:acceptor interfaces within the co-crystal phase in these ternaries promoting charge generation while also providing a network of relatively phase-pure regions of the donor and the acceptor that assist in maximizing long-lived carrier density and facilitate carrier extraction in the device.<sup>3c</sup>

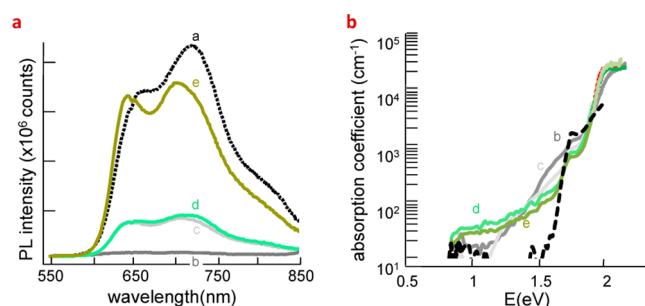
Having established a structural correlation with the CT absorption of donor:fullerene blends, we then exploited our model systems to determine the molar extinction coefficient, transition dipole moment and coupling matrix element of the

pBTTT:PC<sub>61</sub>BM CT complex. For this, we first calculated the molar density of pBTTT:fullerene contacts in such architectures to be 0.84 M (see the SI for details) using the structural details reported by McGehee and co-workers, who recently determined the unit cell of the pBTTT:PC<sub>71</sub>BM co-crystal,<sup>11</sup> which structurally is very similar to the pBTTT:PC<sub>61</sub>BM binary.<sup>10</sup> Using the molar density and the absorption coefficient as well as the fact that the binary containing no additives (blend *i*) exclusively consists of the co-crystal phase, we can obtain a molar extinction coefficient for a single pBTTT:fullerene CT complex in the spectral region of CT absorption ( $1 \text{ eV} < E < 1.6 \text{ eV}$ ). The result is shown in Figure 2a (also see Figure S2 for further details). The molar extinction coefficient of the pBTTT:PC<sub>61</sub>BM CT complex peaks at  $\sim 1000 \text{ M}^{-1} \text{ cm}^{-1}$ , which is about 100 times lower than the peak molar extinction coefficient of  $10^5 \text{ M}^{-1} \text{ cm}^{-1}$  at 2 eV for the pBTTT chromophore involved in the complex (with an equal amount of fullerene and pBTTT chromophores in a unit cell). In the next step, we determined important quantum-mechanical parameters related to a single pBTTT:PC<sub>61</sub>BM CT complex. These parameters are becoming increasingly popular to determine properties of the donor:acceptor interface in organic solar cells. For example, the electronic coupling determines the rate of (back) electron transfer from the CT state to the ground state and the fraction of charge transferred in the ground state. Even though quantum-chemical calculations of these parameters have been performed for model donor:C<sub>60</sub> interfaces,<sup>12</sup> an experimental determination of the transition dipole moment *M* and the electronic coupling matrix element *V* on a model polymer:fullerene system for organic photovoltaic applications seems not to have been performed to date. We obtained values of 27 meV and 0.3 D for *V* and *M*, respectively (see the SI for details). The coupling *V* of the CT state to the ground state is less than the coupling (or transfer integral) between two pBTTT chains ( $\sim 100\text{--}200 \text{ meV}$ ).<sup>13</sup> Hence, it is not surprising that CT states dissociate into free carriers when relatively phase-pure domains of either component are in the vicinity of this interface. It should be noted in this context that a transition dipole moment of 0.3 D is about 1 order of magnitude smaller than typical transition dipole moments of singlet transitions of organic molecules, but indeed visible in sensitive absorption measurements.<sup>14</sup>

We now turn to PDS as a means to compare the density of donor:acceptor contacts in our systems. Table S1 summarizes the PDS data showing the percentages of co-crystal phase obtained in the binaries and ternaries studied here. It shows that the amount of molecular interfaces is reduced from close to 100% in the 1:1 pBTTT:PC<sub>61</sub>BM binary (*i*) with 0.84 M donor–acceptor contacts to only  $\sim 15\%$  in pBTTT:Me14:PC<sub>61</sub>BM ternaries (*iv*) composed of predominately phase-pure domains of pBTTT and PC<sub>61</sub>BM. These values are in very good agreement with estimates we produced previously based on grazing-incidence wide-angle X-ray scattering (GIWAXS), scanning transmission X-ray microscopy (STXM), and PL decay measurements,<sup>3e</sup> which had demonstrated the ability of asymmetrical additives to manipulate the co-crystal phase into structures comprising two to three phases. However, the percentages obtained from STXM and PDS should be compared with caution. Both techniques cannot distinguish whether the fullerene is intercalated or not, and compared with STXM, PDS will additionally probe polymer:PC<sub>61</sub>BM cluster interfaces.

Since optical techniques such as PDS (or alternative sensitive external quantum efficiency measurements when photovoltaic devices are available) can be used for fast quantification of

molecular donor:acceptor interfacial area without the need for synchrotron-irradiation-based techniques, we tested the generality of our strategy by applying it to the ubiquitous P3HT:PC<sub>61</sub>BM system.<sup>15</sup> We varied the amount of molecular donor:acceptor interfaces by again using methyl ester fatty acids as processing additives. Qualitatively, the effect of these additives on the intrachain order of P3HT could be followed analyzing the UV–vis spectra of the resulting binary and ternary systems.<sup>9b</sup> For 1:1 (by weight) P3HT:PC<sub>61</sub>BM blends with between 0.5 and 2.5 molar equiv of Me7 and Me14 per P3HT monomer unit, the 0–0 absorption transition of P3HT increased, indicative of an increase in P3HT aggregation (see Figure S3);<sup>16</sup> thus, a higher fraction of phase-pure P3HT domains is obtained where the polymer can aggregate better, leading to the observed stronger 0–0 absorption feature. This observation indicates that the polymer and fullerene may phase-separate more strongly upon addition of these fatty acids, in agreement with the increase in PL intensity: decreased PL quenching was obtained for these blends compared with the additive-free P3HT:PC<sub>61</sub>BM binary, especially when high amounts of the long-chain additive Me14 were used (Figure 3a). Finally, the most intense CT absorption



**Figure 3.** (left) PL spectra of (a) neat P3HT, (b) neat P3HT:PC<sub>61</sub>BM, and (c–e) P3HT:additive:PC<sub>61</sub>BM blends. The emission of P3HT is enhanced when 0.5 molar equiv of (c) Me7 or (d) Me14 per P3HT monomer unit is introduced into the binary. The PL intensity further increases when a higher amount of Me14 (2.5 molar equiv) was used (e). (right) PDS data obtained for (b) P3HT:PC<sub>61</sub>BM and (c–e) P3HT:additive:PC<sub>61</sub>BM ternaries; data for PC<sub>61</sub>BM (dashed line) are shown for reference.

band, visible as a broad shoulder at photon energies above 1.5 eV (Figure 3b), was again observed for the system with the highest intermixing, i.e., the additive-free P3HT:PC<sub>61</sub>BM binary. In fact, similar to the pBTTT:PC<sub>61</sub>BM systems, we found the CT absorption to decrease when the fullerene and the P3HT strongly phase-separate, again induced by the addition of the fatty acids: we observed a reduction of almost 75% of the interfacial area when we introduced high amounts of Me14 into the P3HT:PC<sub>61</sub>BM blend, as summarized in Table S1.

From the above it is thus evident that a direct correlation between the CT absorption band intensities and the presence of highly intermixed phases within polymer:fullerene blends exists. Using model systems in which we manipulated the fraction of these intermixed regions by adding fatty acids, we have demonstrated that PDS can be applied as a fast and reliable method to correlate the phase morphology of polymer:fullerene blend films with their optoelectronic features. This novel methodology not only can be used as a tool to obtain additional information on relevant BHJ systems, but also can provide *experimentally* determined parameters such as the electronic coupling between the ground and CT states. The latter could to date be calculated only applying quantum-chemical methods and

it is indeed a crucial parameter in order to determine the electron transfer rates, which are directly related to the device performance. Our work thus will allow future screening of other relevant BHJ systems, including high-performance blends containing high-performance donor polymers. It will also give insight into how to optimize these complex architectures with respect to the amount of intermixed phase that is needed to maximize charge generation without reaching a regime that is dominated by charge recombination.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Experimental details, additional figures, and calculations as mentioned in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Authors

\*e.buchaca-domingo@imperial.ac.uk

\*koen.vandewal@iapp.de

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by a Global Collaborative Research Grant by KAUST (Award CRG-1-2012-THO-015). In addition, E.B.-D. was supported by a SABIC Fellowship and N.S. by an ERC Starting Independent Research Fellowship under Grant Agreement 279587, and J.H.B. holds an Industrial Fellowship with the Royal Commission for the Exhibition of 1851. E.B.-D. is also grateful to the RSC for their support with an RSC International Author Journals Grant.

## ■ REFERENCES

- (1) Vandewal, K.; Himmelberger, S.; Salleo, A. *Macromolecules* **2013**, *46*, 6379.
- (2) (a) Tumbleston, J. R.; Stuart, A. C.; Gann, E.; You, W.; Ade, H. *Adv. Funct. Mater.* **2013**, *23*, 3463. (b) Collins, B. A.; Li, Z.; Tumbleston, J. R.; Gann, E.; McNeill, C. R.; Ade, H. *Adv. Energy Mater.* **2013**, *3*, 65. (c) Collins, B. A.; Li, Z.; McNeill, C. R.; Ade, H. *Macromolecules* **2011**, *44*, 9747. (d) Treat, N. D.; Varotto, A.; Takacs, C. J.; Batara, N.; Al-Hashimi, M.; Heeney, M. J.; Heeger, A. J.; Wudl, F.; Hawker, C. J.; Chabiny, M. L. *J. Am. Chem. Soc.* **2012**, *134*, 15869.
- (3) (a) Watts, B.; Belcher, W. J.; Thomsen, L.; Ade, H.; Dastoor, P. C. *Macromolecules* **2009**, *42*, 8392. (b) Collins, B. A.; Gann, E.; Guignard, L.; He, X.; McNeill, C. R.; Ade, H. *J. Phys. Chem. Lett.* **2010**, *1*, 3160. (c) Treat, N. D.; Brady, M. A.; Smith, G.; Toney, M. F.; Kramer, E. J.; Hawker, C. J.; Chabiny, M. L. *Adv. Energy Mater.* **2011**, *1*, 1. (d) Pfannmüller, M.; Flügge, H.; Benner, G.; Wacker, I.; Sommer, C.; Hanselmann, M.; Schmale, S.; Schmidt, H.; Hamprecht, F. A.; Rabe, T.; Kowalsky, W.; Schröder, R. R. *Nano Lett.* **2011**, *11*, 3099. (e) Buchaca-Domingo, E.; Ferguson, A. J.; Jamieson, F. C.; McCarthy-Ward, T.; Shoaee, S.; Tumbleston, J. R.; Reid, O. G.; Yu, L.; Madec, M. B.; Pfannmüller, M.; Hermerschmidt, F.; Schröder, R. R.; Watkins, S. E.; Kopidakis, N.; Portale, G.; Amassian, A.; Heeney, M.; Ade, H.; Rumbles, G.; Durrant, J.; Stingelin, N. *Mater. Horiz.* **2014**, *1*, 270.
- (4) (a) McCulloch, I.; Heeney, M.; Bailey, C.; Genevicius, K.; MacDonald, I.; Shkunov, M.; Sparrowe, D.; Tierney, S.; Wagner, R.; Zhang, W.; Chabiny, M. L.; Kline, R. J.; McGehee, M. D.; Toney, M. F. *Nat. Mater.* **2006**, *5*, 328. (b) Rivnay, J.; Mannsfeld, S. C. B.; Miller, C. E.; Salleo, A.; Toney, M. F. *Chem. Rev.* **2012**, *112*, 5488.
- (5) (a) Chang, J. F.; Clark, J.; Zhao, N.; Sirringhaus, H.; Breiby, D. W.; Andreasen, J. W.; Nielsen, M. M.; Giles, M.; Heeney, M.; McCulloch, I. *Phys. Rev. B* **2006**, *74*, No. 115318. (b) Zhang, R.; Li, B.; Iovu, M. C.; Jeffries-El, M.; Sauv e, G.; Cooper, J.; Jia, S.; Tristram-Nagle, S.; Smilgies, D. M.; Lambeth, D. N.; McCullough, R. D.; Kowalewski, T. *J. Am. Chem. Soc.* **2006**, *128*, 3480.
- (6) (a) Cates, N. C.; Gysel, R.; Beiley, Z.; Miller, C. E.; Toney, M. F.; Heeney, M.; McCulloch, I.; McGehee, M. D. *Nano Lett.* **2009**, *9*, 4153. (b) Miller, N. C.; Cho, E.; Gysel, R.; Risko, C.; Coropceanu, V.; Miller, C. E.; Sweetnam, S.; Sellinger, A.; Heeney, M.; McCulloch, I.; Br edas, J.-L.; Toney, M. F.; McGehee, M. D. *Adv. Energy Mater.* **2012**, *2*, 1208.
- (7) (a) He, X.; Collins, B. A.; Watts, B.; Ade, H.; McNeill, C. R. *Small* **2012**, *8*, 1920. (b) Hitchcock, A. P.; Tylliszczak, T.; Koprinarov, I.; Stover, H.; Li, W. H.; Heng, T. M.; Murti, K.; Gerroir, P.; Dutcher, J. R.; Dalnoki-Veress, K.; Ade, H. W. *AIP Conf. Proc.* **2000**, *507*, 231.
- (8) Scarongella, M.; De Jonghe-Risse, J.; Buchaca-Domingo, E.; Causa, M.; Fei, Z.; Heeney, M.; Stingelin, N.; Banerji, N. *J. Am. Chem. Soc.* **2015**, *137*, 2908.
- (9) (a) Gu, Y.; Wang, C.; Russell, T. P. *Adv. Energy Mater.* **2012**, *2*, 683. (b) Shin, N.; Richter, L. J.; Herzing, A. A.; Kline, R. J.; DeLongchamp, D. M. *Adv. Energy Mater.* **2013**, *3*, 938.
- (10) (a) Jamieson, F. C.; Buchaca-Domingo, E.; McCarthy-Ward, T.; Heeney, M.; Stingelin, N.; Durrant, J. R. *Chem. Sci.* **2012**, *3*, 485. (b) Rance, W. L.; Ferguson, A. J.; McCarthy-Ward, T.; Heeney, M.; Ginley, D. S.; Olson, D. C.; Rumbles, G.; Kopidakis, N. *ACS Nano* **2011**, *5*, 5635.
- (11) Miller, N. C.; Cho, E.; Junk, M. J. N.; Gysel, R.; Risko, C.; Kim, D.; Sweetnam, S.; Miller, C. E.; Richter, L. J.; Kline, R. J.; Heeney, M.; McCulloch, I.; Amassian, A.; Acevedo-Feliz, D.; Knox, C.; Hansen, M. R.; Dudenko, D.; Chmelka, B. F.; Toney, M. F.; Br edas, J.-L.; McGehee, M. D. *Adv. Mater.* **2012**, *24*, 6071.
- (12) (a) Yi, Y.; Coropceanu, V.; Br edas, J.-L. *J. Mater. Chem.* **2011**, *21*, 1479. (b) Liu, T.; Troisi, A. *J. Phys. Chem. C* **2011**, *115*, 2406.
- (13) (a) Rivnay, J.; Noriega, R.; Northrup, J. E.; Kline, R. J.; Toney, M. F.; Salleo, A. *Phys. Rev. B* **2011**, *83*, No. 121306.
- (14) Turro, N. J.; Ramamurthy, V.; Scaiano, J. C. *Principles of Molecular Photochemistry: An Introduction*; University Science Books: Sausalito, CA, 2009.
- (15) Goris, L.; Poruba, A.; Hod akova, L.; Van cek, M.; Haenen, K.; Nesl adek, M.; Wagner, P.; Vanderzande, D.; De Schepper, L.; Manca, J. V. *Appl. Phys. Lett.* **2006**, *88*, No. 052113.
- (16) (a) Clark, J.; Silva, C.; Friend, R. H.; Spanno, F. C. *Phys. Rev. Lett.* **2007**, *98*, No. 206406. (b) Reid, O. G.; Nekuda-Malik, J. A.; Latini, G.; Dayal, S.; Kopidakis, N.; Silva, C.; Stingelin, N.; Rumbles, G. *J. Polym. Sci., Part B: Polym. Phys.* **2012**, *50*, 27.