J|A|C|S
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

pubs.acs.org/JACS

Origin of the Tunable Open-Circuit Voltage in Ternary Blend Bulk Heterojunction Organic Solar Cells

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ABSTRACT: Ternary blend bulk heterojunction organic solar cells comprising either a polythiophene donor and two fullerene acceptors or two polythiophene donors and a fullerene acceptor are shown to have unique electronic properties. Measurements of the photocurrent spectral response and the open-circuit voltage show that the HOMO and LUMO levels change continuously with composition in the respective two-component acceptor or donor pair, consistent with the formation of an organic alloy. However, optical absorption of the exciton states retains the individual molecular properties of the two materials across the blend composition. This difference is attributed to the highly localized molecular nature of the exciton and the more delocalized intermolecular nature of electrons and holes that reflect the average composition of the alloy. As established here, the combination of molecular excitations that can harvest a wide range of photon energies and electronic alloy states that can adjust the open-circuit voltage provides the underlying basis of ternary blends as a platform for highly efficient next-generation organic solar cells.

Ternary blend organic solar cells are bulk heterojunction (BHJ) devices in which typically either the donor (D) or acceptor (A) component consists of two complementary materials.[1] The blends are of the type D:A1$_x$A2$_{(1-x)}$ or D1$_x$D2$_{(1-x)}$:A, where x is varied over the composition range $0 \leq x \leq 1$. BHJ solar cells have been reported in which the acceptor is a blend of fullerenes with a poly(3-hexylthiophene) (P3HT) donor,[1a] and in which the donor is a blend of polythiophenes with a phenyl-C$_{61}$-butyric acid methyl ester (PCBM) acceptor.[1b] An unprecedented feature in both of these cases is that the open-circuit voltage (V_{oc}) changes continuously with composition x, without detriment to the fill factor (FF) of the solar cell.[1a,b] The inference is that the acceptor LUMO in the case of complementary acceptors (D:A1$_x$A2$_{(1-x)}$),[1a] and the donor HOMO in the case of complementary donors (D1$_x$D2$_{(1-x)}$:A),[1b] change energy continuously with composition in the mixture. While this is the normal behavior for an inorganic binary alloy,[2] it is less obviously expected in a molecular mixture where the separate energy levels of the two species might be preserved in the blend. Indeed, polymer blends generally have an optical absorption that is the weighted sum of the two materials rather than characteristic of a uniform material of average composition.[1b,d,e]

In a BHJ solar cell, V_{oc} is given by the energy of the interface band gap minus the quasi-Fermi energies, where the interface band gap is the energy difference between the donor HOMO and the acceptor LUMO.[3] Hence, while the obvious origin of the continuous change in V_{oc} in ternary blends is the corresponding change in the LUMO or HOMO level, it is possible that the effect reflects a change in the quasi-Fermi energies. This paper reports measurements to identify the electronic states in ternary blends and confirms the continuous change in the energy of the HOMO or LUMO of the complementary two-component material, indicative of alloy formation. However, the experiments also show that the optically excited exciton states within the two-component pairs do not reflect the average composition, but retain individual molecular characteristics. An explanation for these observations is proposed that advances a working mechanism of operation for ternary blend solar cells. The results support the potential of ternary blends to significantly enhance the efficiency of BHJ solar cells.

Here the ternary blends previously reported to show a compositional dependence of V_{oc} were further investigated.[1a,b] The system of type D:A1$_x$A2$_{(1-x)}$ consists of P3HT as D, PCBM as A1, and indene-C$_{60}$ bisadduct (ICBA) as A2.[1a] The system of type D1$_x$D2$_{(1-x)}$:A consists of the low band gap polymer poly(3-hexylthiophene-thiophene-diketopyrrolopyrrole) (P3HTT-DPP-10%)[4] as D1, poly(3-hexylthiophene-*co*-3-(2-ethylhexyl)-thiophene) (P3HT$_{75}$-*co*-EHT$_{25}$),[5] a P3HT analogue with a deep HOMO as D2, and PCBM as A.[1b] Polymers and fullerenes were prepared as previously described.[1a,b] Devices used for measurements were prepared without deviation from previous reports in a standard device architecture of ITO/PEDOT:PSS/active layer blend/Al. In each case, the composition of the complementary two-component pair was varied across the full range $0 \leq x \leq 1$ between the limiting binary blends in steps of 10% (mass basis). In the D:A1$_x$A2$_{(1-x)}$ case the overall ratio of donor to acceptor was constant at an optimal 1:1 for all compositions, while in the D1$_x$D2$_{(1-x)}$:A case the overall donor to acceptor ratio was individually optimized at each polymer:polymer ratio.

Measurements of the photocurrent spectral response (PSR) were made to explore the electronic states of these ternary blend solar cells. The measurements are described in detail elsewhere and are made at open-circuit in the solar cells.[6] PSR measures the optical absorption of those transitions that generate mobile carriers in the solar cell, providing information about the electronic states. Previous studies have shown that the PSR spectrum at energy below the optical band gap of the separate materials arises from direct excitation at the interface from the donor HOMO to the acceptor LUMO (Figure 1a inset) and

Received: November 20, 2012
Published: January 3, 2013

dx.doi.org/10.1021/ja3112143 | *J. Am. Chem. Soc.* 2013, 135, 986−989

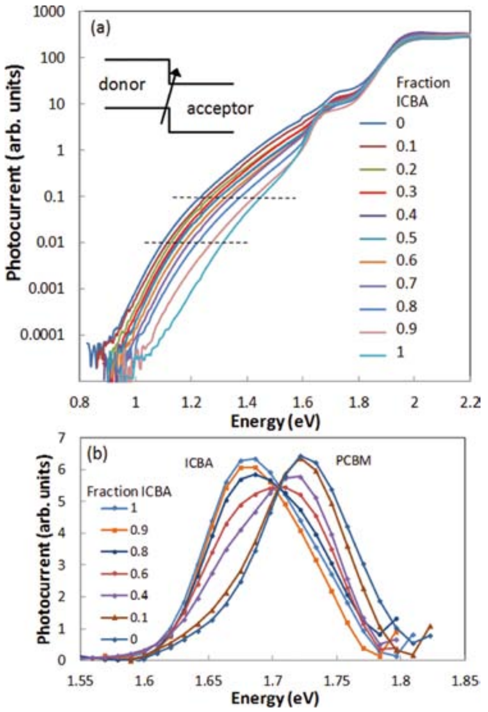

Figure 1. (a) PSR data for the P3HT:PCBM:ICBA ($D{:}A1_xA2_{(1-x)}$) ternary blend solar cells plotted as a function of ICBA fraction in PCBM:ICBA pair. The inset indicates the CT transition or interface band gap that is being measured, and the pair of dashed lines indicates the range over which the interface band gap energy is extracted. (b) Expanded plot of the peaks near 1.7 eV with the background subtracted. The peak centered above 1.7 eV corresponds to PCBM absorption, and the peak centered below 1.7 eV corresponds to ICBA.

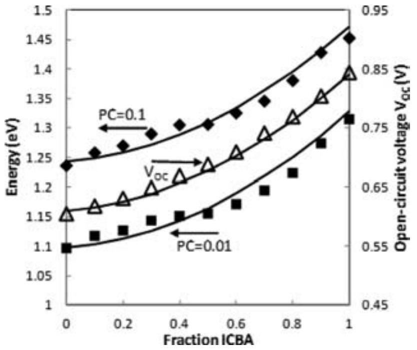

Figure 2. Plot of the estimated interface band gap energy defined by PSR at photocurrent (PC) values of 0.1 and 0.01 from Figure 1a (closed symbols) compared to the values of V_{oc} (open triangles) for P3HT:PCBM:ICBA ($D{:}A1_xA2_{(1-x)}$) ternary blend solar cells. The solid lines are the model of eq 1 with the same bowing parameter b.

measures the optical absorption of the heterojunction interface.[6,7] The excitation is usually referred to as the charge-transfer (CT) state.[8]

Figure 1a shows the PSR spectrum of the mixed acceptor system $D{:}A1_xA2_{(1-x)}$. The two fullerenes have similar optical band gaps and a 0.2 eV difference in LUMO levels.[1a,8a] The spectrum above 1.6 eV reflects bulk absorption in the donor and acceptor to create excitons that diffuse to the interface and separate. From the data below 1.6 eV in Figure 1a, it is evident that the interface CT absorption shifts in energy continuously with composition. The actual interface band gap is not clearly delineated in the PSR spectrum, but previous studies have shown that it corresponds to a photocurrent of $\sim 10^{-4}$ of the peak value, and where the shape of the PSR spectrum changes from an exponential at lower energy to a broader band at higher energy.[6] Figure 2 compares the interface absorption measured at photocurrent values of 0.1 and 0.01 (dashed lines in Figure 1a) with the change in V_{oc}. The compositional dependence is the same within experimental uncertainty. Figure 2 shows that V_{oc} is ~0.55 V smaller than the interface band gap, consistent with the expected quasi-Fermi energies.[6,9]

The data confirm that V_{oc} accurately measures the change in the interface band gap (E_{GI}) and that E_{GI} changes continuously with the composition of two-component acceptor. The composition dependence of the band gap for an alloy is often described by a quadratic dependence on composition, using an extension of Vegard's law,[2a,10]

$$E_{GI}(x) = (1-x)E_{G1} + xE_{G2} - bx(1-x) \quad (1)$$

where b is known as the bowing factor and E_{G1} and E_{G2} are the band gaps of the two materials. Figure 2 shows that this model fits the data well. The same bowing factor ($b = 0.18$) and value of $E_{G2} - E_{G1}$ (= 0.23 eV) are used to fit the three sets of data, and the fit value of $E_{G2} - E_{G1}$ is close to the measured difference in LUMO levels of the two fullerenes.

Figure 1b shows the changes in the fullerene absorption peak near 1.7 eV as a function of composition in the ternary blends. The data are obtained by subtracting a smooth background from the PSR spectrum between 1.55 and 1.85 eV and are scaled vertically to give approximately the same integrated absorption strength for each composition. The absorption peaks differ by ~0.045 eV with ICBA at lower energy. It is evident from the data and confirmed by modeling that the intermediate compositions have an absorption that is the weighted sum of the two peaks of the pure materials, rather than a single peak at an average energy. Hence the alloy model of eq 1 does not apply to the optical excitation of the bulk acceptor material.

Figures 3 and 4 show analogous data for the solar cells with mixed polymer donors, $D1_xD2_{(1-x)}{:}A$. The two polymers have slightly different HOMO levels (5.2 eV for P3HTT-DPP-10% and 5.4 eV for P3HT$_{75}$-*co*-EHT$_{25}$) but widely differing optical band gaps (1.5 and 1.9 eV, respectively).[2b,4,5] In this system V_{oc} is also found to change continuously with donor composition, but the change is smaller than for the mixed acceptor case. Figure 4 shows that the composition dependence of the interface band gap energy corresponding to two values of the photocurrent in Figure 3a is consistent with the changes in V_{oc}. The lines are a linear fit ($b = 0$). The composition end points deviate from the fit, particularly at $x = 1$; this is discussed below.

Figure 3b shows the spectral response data plotted on a linear vertical scale to focus on the high-energy optical excitations of the polymers. The spectra clearly display the optical excitations of the two polymers since their onset differs by almost 0.5 eV. The low-energy peaks marked E1 and E2 correspond to P3HTT-DPP-10%, while the higher energy peaks are a combination of P3HTT-DPP-10% and P3HT$_{75}$-*co*-EHT$_{25}$ (as well as PCBM). Inspection shows that these peaks change intensity with composition but do not change in energy. This observation is confirmed by fitting the spectra to a sum of Gaussian bands, shown by the solid lines in Figure 3b, where each fit uses the same peak energies. Evidently, the composition dependence of the high-energy absorption spectrum again has a different behavior from the continuously changing interface band gap. In both the mixed polymer and mixed fullerene systems, the high-energy

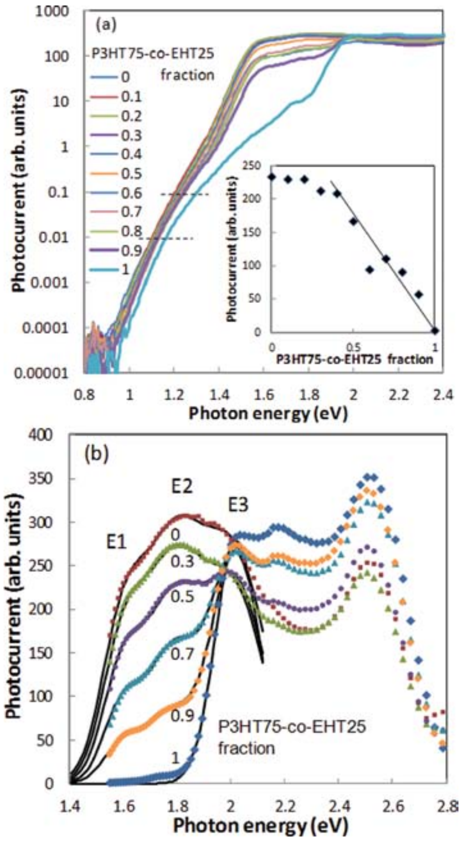

Figure 3. (a) PSR data for the P3HTT-DPP-10%:P3HT$_{75}$-*co*-EHT$_{25}$:PCBM ($D1_xD2_{(1-x)}$:A) ternary blend solar cells plotted as a function of P3HT$_{75}$-*co*-EHT$_{25}$ fraction in the polymer donor pair. The pair of dashed lines indicates the range over which the interface band gap energy is extracted. The inset shows the photocurrent signal at 1.6 eV as a function of P3HT$_{75}$-*co*-EHT$_{25}$ fraction in the polymer donor pair. (b) High-energy PSR data from (a) plotted on a linear scale to show the exciton peaks from the donor mixture. Solid lines are fits to the E1, E2, and E3 peaks. The P3HT$_{75}$-*co*-EHT$_{25}$ fraction is indicated.

transitions retain the properties of the individual materials of the mixture, while the interface band gap exhibits the properties of an average composition of the two-component donor or acceptor.

We propose that these contrasting properties arise from the nature of the electronic excitations. The high-energy transitions are excitonic in character, comprising a set of peaks that are narrow enough to include distinguishable phonon side bands (e.g., E2 is a side band of E1). The complete overlap of the electron and hole wavefunctions and the strong Coulomb interaction of the exciton lead to a highly localized state confined within a single molecule (or segment of a polymer chain)[11] and not subject to variation based on blending of components, as in an alloy. Hence the exciton states are characteristic of the individual components rather than the average material composition. On the other hand, the interface band gap is an excitation comprising a hole in the donor material and an electron in the acceptor. Due to the phase-separated BHJ structure, the electron and hole are physically apart from each other, with a much smaller Coulomb interaction, and consequently are more delocalized.[11] The delocalized wavefunction extends over more than a single molecule and thus is determined by the average composition of the donor and acceptor phases at the interface rather than by a single molecule of either type. Therefore the CT state energy (and thus V_{oc}) is observed to vary as the composition of either the donor or acceptor is changed. The variation in CT energy is regular and described well by an alloy model, as developed here.

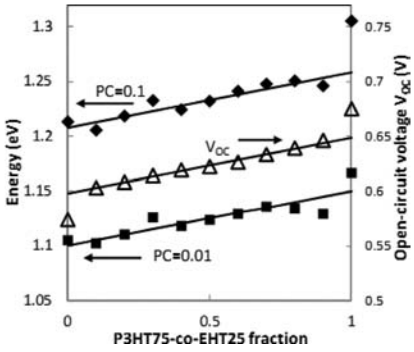

Figure 4. Plot of the estimated interface band gap energy defined by PSR at photocurrent (PC) values of 0.1 and 0.01 from Figure 3a (closed symbols) compared to the values of V_{oc} (open triangles), as a function of P3HT$_{75}$-*co*-EHT$_{25}$ fraction for the mixed donor system. Solid lines are linear fits to the data with the same slope ($b = 0$).

As such, the data presented here are consistent with a model in which the two-component material in a ternary blend forms an alloy with HOMO and LUMO energies based on average composition. Alloy formation implies that the components are subject to intimate and uniform electronic interaction and that delocalization of states is extensive. Consistent with this model, the polymer donors in $D1_xD2_{(1-x)}$:A are of similar structure and are both semirystalline, as determined by X-ray analysis;[1b,4,5] hence the hole wavefunction is expected to be substantially delocalized. The crystallinity of the fullerene acceptors in D:$A1_xA2_{(1-x)}$ is undetermined (although PCBM is well known to form crystallites in polymer blends),[12] but delocalization of the electron wavefunction is evidently sufficient to lead to an electron energy determined by the average composition. The delocalization and weak electron−hole interaction of the interface CT excitation are consistent with the absence of obvious excitonic peaks in the low-energy region of the spectral response, and the measured interface band gap is consistent with the values of V_{oc}, which relate to one-electron energies.

Our observations supporting the formation of an organic alloy in ternary blends are unprecedented in BHJ solar cells and differ from previous results as discussed below. Recent studies have measured the PSR spectra of a BHJ solar cell with a fullerene mixture of PC$_{84}$BM and PC$_{70}$BM, which have LUMO levels that differ by ~0.2 eV.[13] At concentrations of 1−10%, PC$_{84}$BM acts as a localized trap having a separate absorption band below the interface transitions associated with PC$_{70}$BM, rather than as an alloy material with an average composition. A transition from a localized state characteristic of a dopant to alloy behavior is expected as the concentration increases, following the inorganic alloy analogy. The electron wavefunction is determined by the average material only when the concentration of the dilute phase of the mixture is sufficiently high. It appears that >10% concentration is sufficient to show alloy properties, since the dopant state behavior is not evident in Figure 1 for the material with 10% PCBM. The large drop in energy between P3HT$_{75}$-*co*-EHT$_{25}$ fractions of 1 and 0.9 in Figure 4, and the slightly different shape of the $x = 0.9$ data in Figure 1, might be due to the transition from dopant to alloy. The corresponding transition from pure P3HTT-DPP-10%:PCBM to 10% P3HT$_{75}$-*co*-EHT$_{25}$ is not expected to show the same doping effect because P3HT$_{75}$-

co-EHT$_{25}$ has the larger band gap and thus leads to states within the band rather than within the band gap.

While the alloy nature of ternary blends is clearly manifest in the variation of V_{oc} with composition, the molecular nature of the excitonic properties is equally apparent. The Figure 3a inset shows that the photocurrent at 1.6 eV, associated with the low band gap polymer P3HTT-DPP-10%, is proportional to the polymer concentration even at low concentrations down to 10%. This implies that an exciton created in this dilute component reaches the interface and splits into an electron−hole pair with the same efficiency as it does at high concentrations. The P3HTT-DPP-10% exciton energy is much less than for the P3HT$_{75}$-*co*-EHT$_{25}$ material, and so the transport of the exciton cannot be through the latter material. Either the exciton can diffuse easily through the dilute component even when its concentration is below the usual percolation threshold, or the transition to the interface is by a direct energy-transfer process that does not involve diffusion. Further studies are needed to understand this process. However, it is clear that photons can be harvested effectively by both components in the alloy.

The property of these ternary blends having molecular optical excitations together with material-averaged one-electron states offers interesting ways to improve the efficiency of BHJ solar cells. Specifically for multidonor systems $D1_xD2_{(1-x)}$:A, suitably paired donors can harvest light over a much broader range than either individual component, offering a way to increase short-circuit current density (J_{sc}), and a V_{oc} larger than that achievable for the donor with higher HOMO can be achieved, providing a route to a higher $J_{sc}V_{oc}$ product (and efficiency) in ternary blends than possible in binary blends.[1a,b] Further, a substantial contribution to the efficiency loss of an organic solar cell arises from the band offset needed to separate the electron−hole pair.[14] It is generally found that if the exciton energy is too close to the interface band gap, then efficient exciton separation does not occur, even though it is energetically favorable.[9a,15] The problem is often attributed to a small band offset between the donor and acceptor LUMOs.[8a] However, if the same material is mixed with a higher energy donor, two benefits occur: (1) The second donor provides high-energy optical transitions to more fully cover the solar energy spectrum, as discussed previously.[1b,d,e,] (2) The addition of the high-energy material pushes the one-electron LUMO states of the donor mixture higher in energy by the alloying effect. The band offset at the interface is therefore increased and the exciton is more efficiently split, even though the exciton energies are unchanged. Thus, a suitably designed ternary blend has the potential for much higher solar cell efficiency than binary blends.

The results presented here support the previously observed tunability of V_{oc} in ternary blend BHJ solar cells and describe how this phenomenon occurs by invoking an alloy model for the two-part component, either the acceptor in $D{:}A1_xA2_{(1-x)}$ or the donor in $D1_xD2_{(1-x)}$:A. In this model, optical excitation within the alloy is molecular in nature due to the highly localized nature of the exciton. As such, two donors within a distinct band gap can be used in complementary fashion to harvest light over a broad range and target high J_{sc}. Most importantly, the donor−acceptor interface and corresponding interface band gap (CT state), which determines V_{oc}, display a material-averaged electronic structure due to the more delocalized nature of the one-electron states, resulting in a V_{oc} that reflects the average composition of the interface. In the case of a $D1_xD2_{(1-x)}$:A system, this allows a higher V_{oc} in the ternary blend than possible in the binary blend of the lower band gap (higher HOMO) polymer and the acceptor, as we have previously reported,[1b] leading to higher efficiencies. In a broader sense, an implication of the alloy model is that two complementary components should be mixed for effective electronic interaction. Further studies are needed to understand the role of morphology in these ternary blends.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This material is based upon work supported as part of the Center for Energy Nanoscience, an Energy Frontier Research Center funded by U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award No. DE-SC0001013, specifically for partial support of P.P.K., B.B., and B.C.T.

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