# Influence of Polymer Compatibility on the Open-Circuit Voltage in Ternary Blend Bulk Heterojunction Solar Cells

Petr P. Khlyabich,[†] Andrey E. Rudenko,[†] Robert A. Street,*,[‡] and Barry C. Thompson*,[†]

[†]Department of Chemistry and Loker Hydrocarbon Research Institute, University of Southern California, Los Angeles, California 90089-1661, United States

[‡]Palo Alto Research Center, Palo Alto, California 94304, United States

S *Supporting Information*
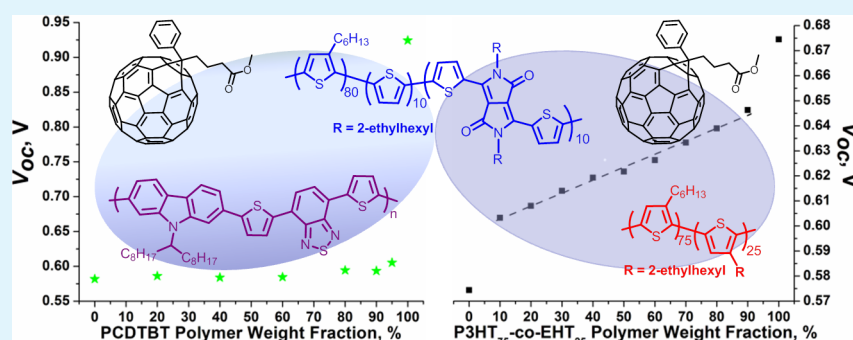
ABSTRACT: The evolution of the open-circuit voltage (V_{oc}) with composition in ternary blend bulk heterojunction (BHJ) solar cells is correlated with the miscibility of the polymers. Ternary blends based on poly[N-9′-heptadecanyl-2,7-carbazole-*alt*-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) and poly(3-hexylthiophene-thiophene-diketopyrrolopyrrole) (P3HTT-DPP-10%) with phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) acceptor were investigated. The V_{oc} is pinned to the lower value of the P3HTT-DPP-10%:$PC_{61}BM$ binary blend even up to 95% PCDTBT in the polymer fraction. This is in stark contrast to the previously investigated system based on P3HTT-DPP-10%, poly(3-hexylthiophene-*co*-3-(2-ethylhexyl)-thiophene) ($P3HT_{75}$-*co*-EHT_{25}), and $PC_{61}BM$, where the V_{oc} varied regularly across the full composition range, as explained by an organic alloy model, implying strong physical and electronic interaction between the polymers. Photocurrent spectral response (PSR) and external quantum efficiency (EQE) measurements indicate that the present system does not exhibit the hallmarks of alloy formation. Measured values of the surface energies of the polymers support miscibility of P3HTT-DPP-10% with $P3HT_{75}$-*co*-EHT_{25} but not with PCDTBT. Surface energy is proposed as a figure of merit for predicting alloy formation and compositional dependence of the V_{oc} in ternary blend solar cells and miscibility between polymers is proposed as a necessary attribute for polymer pairs that will display alloy behavior.

KEYWORDS: *solar cell, ternary blend, surface energy, organic alloy, open-circuit voltage, bulk heterojunction*

Ternary blend bulk heterojunction (BHJ) solar cells based on two donors and one acceptor (D1:D2:A)[1−7] or one donor and two acceptors (D:A1:A2)[2,6−11] provide a set of unique optoelectronic properties necessary to achieve efficiencies higher than that of binary blend solar cells and efficiency increases for three component systems were recently demonstrated.[1,3,5−7] High efficiency in ternary blend solar cells is achieved via a simultaneous increase of short-circuit current density (J_{sc}), because of broadening the absorption, and attainment of an intermediate, composition-dependent open-circuit voltage (V_{oc}).[1,2,7,8] The origin of the composition tunable V_{oc} has been ascribed to the formation of an organic alloy of the synergistic components (i.e., either the two donors or the two acceptors), proposed to result from intimate physical and electronic interaction of those components.[2,7] Observation of a continuous change in the energy of the charge-transfer (CT) state[12] with composition in ternary blends with a tunable

V_{oc} provides strong support for the alloy model.[2,7] The origin of variation in the CT state energy with composition is rationalized as an averaging of frontier orbital (HOMO and LUMO) energies in the alloy (D1:D2 or A1:A2), analogous to the variation of valence and conduction band energies with composition in inorganic semiconductor alloys.[13,14] As opposed to the materials-averaged CT state energies, the individual optical excitations of synergistic donors or acceptors are retained as confirmed by photocurrent spectral response (PSR), external quantum efficiency (EQE) and UV−vis measurements.[1,2,7,8] This dichotomy is likely rooted in the limited spatial extent of excitons, which is insufficient to realize materials averaging, in contrast to the significantly more
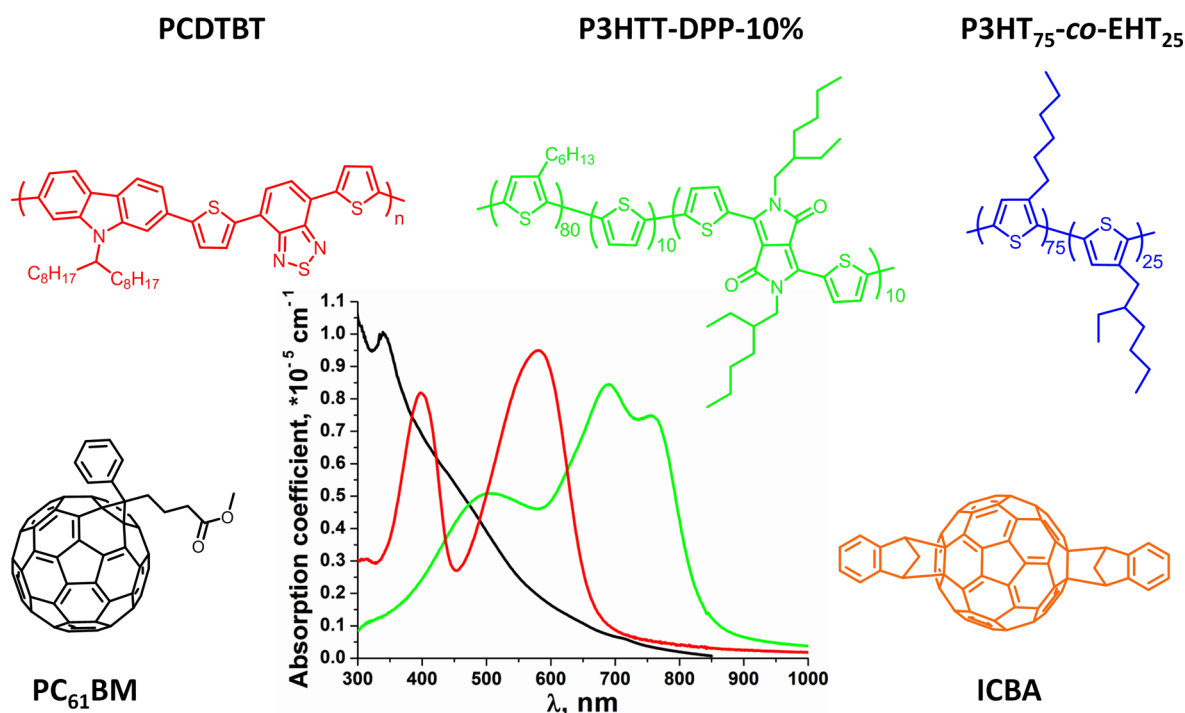
Figure 1. Structures of PCDTBT, P3HTT-DPP-10%, P3HT$_{75}$-*co*-EHT$_{25}$, PC$_{61}$BM, and ICBA. Absorption of PC$_{61}$BM (black line), PCDTBT (red line), and P3HTT-DPP-10% (green line).

delocalized CT state.[15,16] The formation of an alloy allows an intermediate V_{oc} in ternary blend solar cells and retains the ability to increase absorption breadth.

We recently were the first to demonstrate that the V_{oc} in ternary blend BHJ solar cells can vary regularly with composition across the full range between the limiting binary blends without negatively effecting the fill factor (FF).[1,8] This behavior has been observed in both the D:A1:A2 system of poly(3-hexylthiophene) (P3HT), phenyl-C$_{61}$-butyric acid methyl ester (PC$_{61}$BM), and indene-C$_{60}$ bisadduct (ICBA),[8] as well as the D1:D2:A system of poly(3-hexylthiophene-thiophene-diketopyrrolopyrrole) (P3HTT-DPP-10%)[17] and poly(3-hexylthiophene-*co*-3-(2-ethylhexyl)thiophene) (P3HT$_{75}$-*co*-EHT$_{25}$) and PC$_{61}$BM,[1,18] shown in Figure 1. In both cases, experimental evidence supports the formation of an alloy between the synergistic components.[1,2,7,8] Clearly, both previously studied pairs have strong similarities in chemical structure, supporting miscibility of the alloying components. Qualitatively, in the A1:A2 pair,[8] two monofunctional C$_{60}$-fullerenes are used, whereas the D1:D2 pair[1] is based on two random copolymers each containing 75−80% 3-hexylthiophene. As a quantitative measure of physical compatibility, surface energy is a strong predictor of miscibility in blends,[19,20] and has been used as a predictor for the location of small molecule additives in polymer−fullerene solar cells.[21,22] Thin film surface energies are found to be similar for PC$_{61}$BM (27.6 mN/m) and ICBA (24.9 mN/m), as well as P3HTT-DPP-10% (19.9 mN/m) and P3HT$_{75}$-*co*-EHT$_{25}$ (22.1 mN/m) (see the Supporting Information). Furthermore, good miscibility in the polymer pair is supported by the random-copolymer effect, commonly used to engender miscibility between polymers through the random incorporation of common comonomers.[23,24] As such, in the previous systems we have investigated, all evidence points to miscibility of the synergistic (alloying) components. Our hypothesis is that miscibility is a

necessary condition for alloy formation and an enabling parameter for composition-dependent V_{oc} in ternary blends.

Here we report a study to test the hypothesis that miscibility between synergistic components is a necessary attribute for alloy formation as a first step toward the ultimate development of a predictive model for alloy formation that will cover a broad range of structural and electronic features. Toward this end, the previously studied D1:D2:A system was modified by inclusion of poly[*N*-9′-heptadecanyl-2,7-carbazole-*alt*-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT),[25] while retaining P3HTT-DPP-10%[17] and the acceptor PC$_{61}$BM, all shown in Figure 1. The rational for choosing PCDTBT was to use a polymer that was as different from P3HTT-DPP-10% as possible, while still providing a viable pair for ternary blends (i.e., complementary absorption and distinct HOMO energies). In this way we chose to investigate an extreme case in which polymer miscibility was highly unlikely so as to serve as a nonalloying pair and provide a starting point for broader investigations of all the necessary and sufficient conditions for alloy formation and to provide an example of a nonalloying system as a basis for refining our understanding of the alloy model. Specifically, PCDTBT has a significantly higher surface energy of 29.5 mN/m relative to P3HTT-DPP-10% (19.9 mN/m) and is further differentiated as a perfectly alternating copolymer with no 3-hexylthiophene units, ruling out the random copolymer effect. Importantly, both polymers have high reported power conversion efficiencies with PC$_{61}$BM, complementary absorption profiles and different HOMO energies of 5.2 eV for P3HTT-DPP-10% and 5.4 eV for PCDTBT,[17,25] which translates to the V_{oc} of 0.582 V for P3HTT-DPP-10%:PC$_{61}$BM and 0.924 V for PCDTBT:PC$_{61}$BM.

Photovoltaic devices containing ternary blends in a conventional device configuration were fabricated in air. Binary blend solar cells with both polymers showed optimal device

performance at donor:$PC_{61}BM$ ratio of 1:1.3 under the same processing conditions. The optimized PCDTBT:$PC_{61}BM$ ratio is lower than that reported elsewhere,[25] possibly because of different processing conditions and the molecular weight of polymer used (see the Supporting Information). As a result, with ternary blends the overall polymer:fullerene ratio was kept constant at 1:1.3, whereas the ratio between P3HTT-DPP-10% and PCDTBT was varied from 1:0 to 0:1. All active layer thicknesses were 75−85 nm. Table 1 lists the average values (see the Supporting Information) of J_{sc}, V_{oc}, FF, and η obtained under simulated AM 1.5G illumination (100 mW/cm²).

Table 1. Photovoltaic Properties of P3HTT-DPP-10%:PCDTBT:$PC_{61}BM$ Ternary Blend BHJ Solar Cells at Different Polymer Ratios

P3HTT-DPP-10%:PCDTBT:$PC_{61}BM$[a]	J_{sc} (mA/cm²)[b,c]	V_{oc} (V)[d]	FF[e]	η (%)[f]
1:0:1.3	14.45	0.582	0.63	5.27
0.8:0.2:1.3	12.48	0.586	0.60	4.42
0.6:0.4:1.3	11.74	0.584	0.56	3.79
0.4:0.6:1.3	7.25	0.585	0.41	1.69
0.2:0.8:1.3	5.97	0.594	0.35	1.19
0.1:0.9:1.3	6.30	0.594	0.34	1.21
0.05:0.95:1.3	6.44	0.605	0.37	1.30
0:1:1.3	9.89	0.924	0.50	4.47

[a]All devices were spin-coated from o-dichlorobenzene and dried under N_2 for 30 min before aluminum deposition. [b]Mismatch corrected. [c]Standard deviations of less than 0.3 mA/cm² were observed in all cases averaged over eight pixels. [d]Standard deviations of less than 0.005 V were observed in all cases averaged over eight pixels. [e]Standard deviations of less than 0.02 were observed in all cases averaged over eight pixels. [f]Standard deviations of less than 0.1% were observed in all cases averaged over eight pixels.

As can be seen from Table 1 and Figure 2a, unlike the continuous change of the V_{oc} with composition that was observed in the earlier study of P3HTT-DPP-10%:P3HT$_{75}$-co-EHT$_{25}$:$PC_{61}BM$,[1] the V_{oc} for P3HTT-DPP-10%:PCDTBT:$PC_{61}BM$ ternary blends changes by only 23 mV going from 0.582 V for 1:0:1.3 to 0.605 V for 0.05:0.95:1.3. Thus, only 5% of P3HTT-DPP-10% in the overall polymer mixture pins the V_{oc} to the smallest V_{oc} value of the two limiting binary blend solar cells. These data indicate that alloy formation between polymers does not occur in the present case with two dissimilar polymer donors, as even 95% of PCDTBT in the polymer fraction has little effect on the V_{oc}. To gain further insight into this nonalloying ternary blend, we have investigated UV−vis, EQE, PSR, and GIXRD of the system and its components.

UV−vis measurements (see the Supporting Information) demonstrate that the incorporation of PCDTBT in the ternary blend leads to the continuous increase of the absorption in the visible part of the solar spectrum (peaks around 394 and 574 nm), while the absorption in the near-infrared (NIR), which comes from the P3HTT-DPP-10%, gradually decreases. Importantly, the NIR absorption of P3HTT-DPP-10% is already observable at a 0.05:0.95:1.3 ratio. Overall, the absorption profiles are described as a weighted sum of the absorptions of each component in the ternary blend. EQE measurements of the blends show strong deviation from the UV−vis data, as can be seen in Figure 2b. Incorporation of 20 or 40% of PCDTBT in the polymer component leads to a general decrease of photoresponse in the NIR, attributed to the
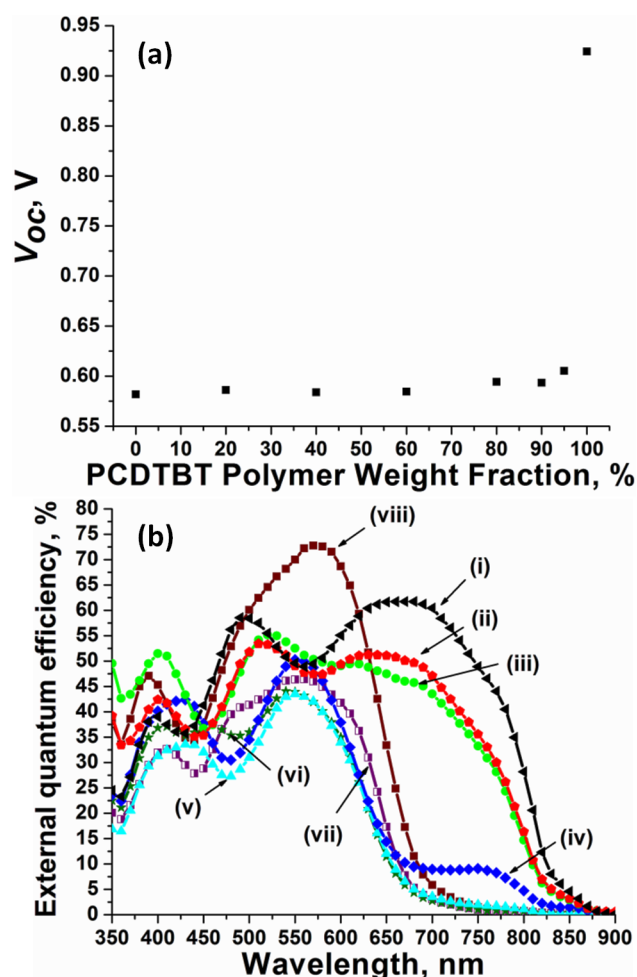

Figure 2. (a) Open-circuit voltage (V_{oc}) of the ternary blend BHJ solar cells as a function of the amount of PCDTBT in the blends. (b) External quantum efficiency of ternary blend BHJ solar cells where (i) is 1:0:1.3 (black line), (ii) is 0.8:0.2:1.3 (red line), (iii) is 0.6:0.4:1.3 (green line), (iv) is 0.4:0.6:1.3 (blue line), (v) is 0.2:0.8:1.3 (cyan line), (vi) is 0.1:0.9:1.3 (olive line), (vii) is 0.05:0.95:1.3 (purple line), and (viii) is 0:1:1.3 (wine-red line).

dilution of P3HTT-DPP-10% in the blend. Further increase of PCDTBT is characterized by a drastic decrease of the photoresponse in the NIR to 9 and 2% at 750 nm for 0.4:0.6:1.3 and 0.2:0.8:1.3, while EQE values in the visible are also reduced. The large difference between the absorption profiles and the EQE in these ternary blend solar cells implies that light can be effectively absorbed by all the components, but excitons produced in P3HTT-DPP-10% do not contribute to the photocurrent generation at large PCDTBT loadings. The large discrepancy between the UV−vis and EQE in the present ternary blends significantly differs from the case of P3HTT-DPP-10%:P3HT$_{75}$-co-EHT$_{25}$:$PC_{61}BM$,[1] where complementary absorption by all three components effectively translated to the measured photoresponse. The discrepancy in the evolution of the UV−vis and the EQE with the present nonalloying system is a further distinction from the previously studied alloying system.[1]

To more deeply probe the photoresponse and V_{oc} behavior in these ternary blends, PSR measurements were performed and the results are shown in Figure 3. PSR measures the optical absorption of those transitions that result in the generation of mobile carriers in the solar cell across a wide spectral range.[26]
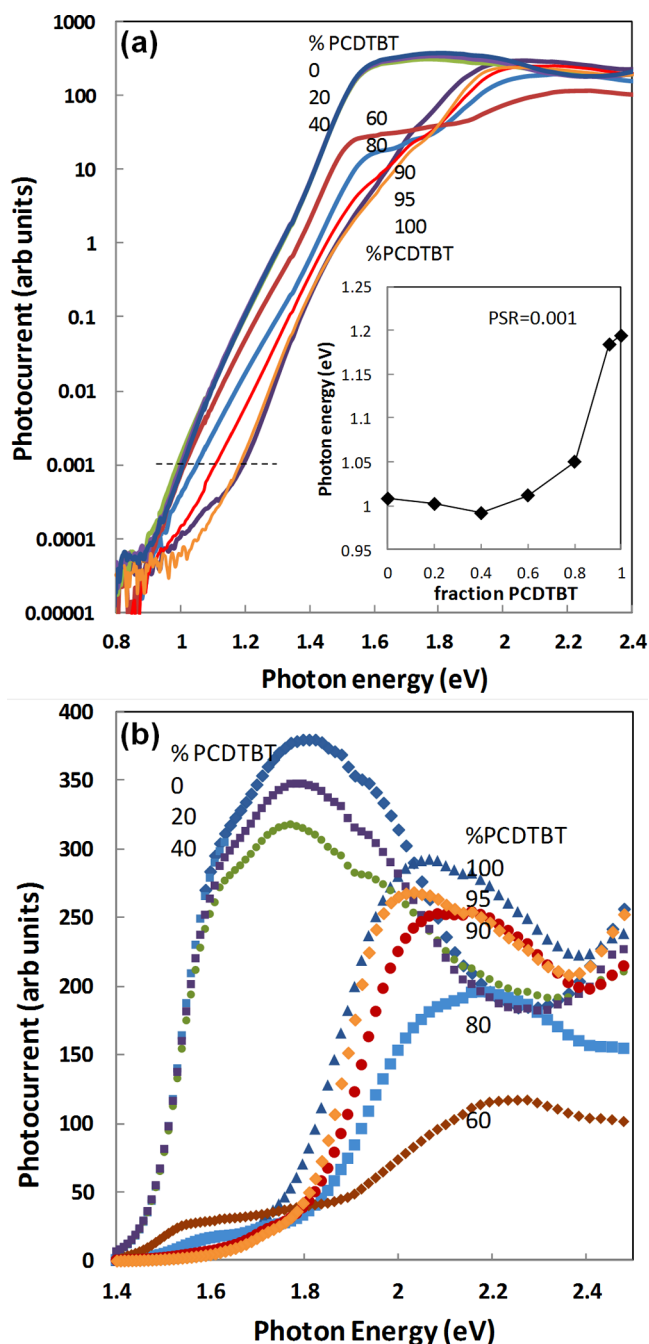
Figure 3. (a) PSR spectra of P3HTT-DPP-10%:PCDTBT:PC$_{61}$BM for different PCDTBT concentrations. (inset) Plot of the CT state energy at a fixed PSR value (dashed line) versus PCDTBT content. (b) High-energy PSR data from (a) plotted on a linear scale to show the exciton peaks.

The energy range above 1.5 eV corresponds to polymer exciton absorption and the lower energy data (at about 1×10^{-4} of the peak value) is from CT excitations from the donor HOMO to the acceptor LUMO. The addition of up to 40% of PCDTBT gives almost no change in the PSR in either energy range, showing that the effective CT state energy is unchanged by the addition of PCDTBT. At higher concentrations of PCDTBT, the P3HTT-DPP-10% exciton response at 1.5−1.8 eV decreases dramatically while the PCDTBT exciton response at 1.8−2.4 eV increases, and becomes dominant (Figure 3b). The CT response becomes broader and at about 90% of

PCDTBT moves to higher energy but is unchanged at 95% and 100% of PCDTBT. The form of the CT response is indicative of two independent absorption bands originating from the two polymers, rather than a continuously changing CT energy associated with an alloy, as we have observed in our previous study.[2,7] The inset to Figure 3a shows the PSR energy at a fixed PSR intensity, chosen to be low down the CT absorption to emphasize the separation of the absorption bands. The data show that there is almost no detectable influence of P3HTT-DPP-10% up to 5% concentration and then a rapid change in the optical absorption to an approximately constant energy associated with P3HTT-DPP-10%.

Clearly the data in the present case is distinct from that in the previous case where a continuously varying V_{oc}, CT state energy, and EQE response indicated the synergistic interaction of the two polymers through what has been termed alloy formation. Although further interpretation of the present data is provided below, it is evident that the hallmarks of alloy formation are absent here as a primary conclusion. A number of variables could be responsible for the absence of alloy formation in the present case, such as a lack of miscibility between polymers, a large difference in HOMO energies of the polymers (and the corresponding CT state energies of the limiting binary blends), as well as differences in crystallinity of the two polymers, or a combination thereof. Although a comprehensive deconvolution of these variables is not possible with the present system (or any individual system), insight into the nature of a nonalloying ternary blend can be gained through analysis and interpretation of the data presented here.

Differences in surface energy between PCDTBT (29.5 mN/m) and P3HTT-DPP-10% (19.9 mN/m) suggest that the two polymers should not be miscible. Ultimate proof will require a detailed investigation of ternary blend morphology. While the complex morphology of ternary blend solar cells has received relatively little attention, it is clear that the spatial distribution of components and their specific physical interactions do play an important role in determining device properties.[27,28] To investigate the ternary blend morphology of the present system, we performed transmission electron microscopy (TEM) and grazing-incidence X-ray diffraction (GIXRD) measurements (see the Supporting Information). Although TEM provides little information about these complex blends due to a lack of contrast between polymers, GIXRD offers some insights. Neat P3HTT-DPP-10% is found to be semicrystalline, whereas PCDTBT is amorphous. The addition of PC$_{61}$BM to P3HTT-DPP-10% does not change the intensity and position of the peak corresponding to the (100) interchain spacing, while in the case of PCDTBT:PC$_{61}$BM the polymer remains amorphous. In the ternary blend regime, the P3HTT-DPP-10% peak was observed starting from a 0.05:0.95:1.3 ratio, with intensities gradually increasing up to the 0.2:0.8:1.3 ratio and saturating later on. The polymer (100) peak position was unaffected by the three-component ratio. In the previous study of P3HTT-DPP-10%:P3HT$_{75}$-co-EHT$_{25}$:PC$_{61}$BM ternary blends, both polymers were semicrystalline and two peaks were observed in GIXRD.[1] Importantly, GIXRD peaks of the polymers in the previous system were found to shift with composition, in contrast to the current study.[1] As such, in the previous system that demonstrated alloy behavior, the polymers were subject to a strong physical interaction that influenced their solid-state structure. In the present, nonalloying system, such interaction is not observed. Coupling this data with surface energy data and the intrinsic absence of the random copolymer effect strongly

supports the absence of miscibility between PCDTBT and P3HTT-DPP-10% in this nonalloying system. The impact of having one amorphous and one semicrystalline polymer on alloy formation and the relative importance of this contrasting property relative to differences in surface energy is unknown at this time.

Within the context of an immiscible polymer blend, a framework for interpreting the solar cell data can be developed. Considering the UV–vis spectra (see the Supporting Information) and the EQE data in Figure 2b, the inability to harvest excitons generated in P3HTT-DPP-10% at higher PCDTBT loadings implies that P3HTT-DPP-10% is remote from the $PC_{61}BM$ interface, consistent with the more similar surface energies of PCDTBT (29.5 mN/m) and $PC_{61}BM$ (27.6 mN/m). Consider that with even 20% of P3HTT-DPP-10% in the blend, no photoresponse is observed from the polymer as seen in Figure 2b. In effect, we propose that P3HTT-DPP-10% is an exciton trap in this incompatible or nonalloy system, contributing to the low FF and dramatically reduced J_{sc} in ternary blends with high PCDTBT content as seen in Table 1. It also follows that the higher lying HOMO of P3HTT-DPP-10% acts as a hole trap and dominates hole transport, pinning the V_{oc} to the lower limiting value even up to 95% of PCDTBT in the blend (Figure 2a). Both interpretations are consistent with a pair of polymers that are not subject to strong physical and electronic interaction engendered by miscibility and point to miscibility as a necessary, even if not sufficient, attribute of polymer pairs that are capable of alloy formation.

The PSR data are also consistent with the proposed lack of polymer miscibility. The CT state does not change continuously, as was observed with miscible polymers,[1] but instead is dominated by the P3HTT-DPP-10% HOMO level over a large segment of the composition range. While some aspects of the PSR data appear different from the V_{oc} data, on closer analysis they are also consistent with a model of two immiscible polymers. For example, the CT transition energy in the PSR data is unchanged for P3HTT-DPP-10% concentrations in the range of 0 to 5% (inset Figure 3a), but in this composition region V_{oc} drops by ~0.3 V from the PCDTBT:$PC_{61}BM$ value of 0.924 to 0.605 V. The CT absorption energy at this composition of 5% P3HTT-DPP-10% therefore reflects the PCDTBT HOMO level, whereas the hole transport energy is evidently determined by the P3HTT-DPP-10% HOMO level, as the V_{oc} determining factor. The proposed explanation is that the polymers are not miscible and P3HTT-DPP-10% is preferentially located away from fullerene interface (consistent with the relative surface energies of the three components) and thus does not have significant CT absorption in this composition range. The P3HTT-DPP-10% forms deep states with respect to the PCDTBT HOMO level, which suppresses the hole quasi-Fermi energy and consequently reduces V_{oc}.[29] These states likely act as recombination centers, accounting for the low J_{sc} and FF. The discussion of EQE data in Figure 2b reaches the same conclusion concerning the remoteness of P3HTT-DPP-10% from the fullerene interface at high PCDTBT loadings. Evidently, in the range of 0–40% PCDTBT, P3HTT-DPP-10% as the major polymer component is present at the fullerene interface and thus exhibits complete control over the CT state energy as seen in Figure 3a via favorable population of the lower energy CT state. The presumed presence of P3HTT-DPP-10% at the interface when it is the major polymer component also evidently allows the harvesting of low-energy excitons generated via photo-

excitation of P3HTT-DPP-10% (Figure 2b). When the composition undergoes inversion and PCDTBT becomes the major polymer component, there is a clear change in both the EQE (Figure 2b) and the PSR data (Figure 3) consistent with dominance of a PCDTBT at the fullerene interface. When PCDTBT is the major component the long wavelength EQE response of P3HTT-DPP-10% is suppressed and the CT state energy shifts away from the lower energy value toward the limiting value of PCDTBT:$PC_{61}BM$ blend. As such, the data support a picture of two immiscible (and noninteracting polymers) that do not function synergistically as in the case of a miscible and alloying system.

Additional support for the immiscible nature of the polymer pair and the role of P3HTT-DPP-10% comes from mobilities measured by the space-charge limited current (SCLC) technique (see the Supporting Information).[30] The hole mobilities for the ternary blends were found to be similar, between 1.18×10^{-3} and 2.90×10^{-3} cm^2/(Vs), although subject to a steady increase as the P3HTT-DPP-10% content was increased. This increase emphasizes that hole transport is dominated by P3HTT-DPP-10%, which has a higher intrinsic hole mobility of 2.55×10^{-4} cm^2/(Vs) compared to 7.9×10^{-5} cm^2/(Vs) for PCDTBT. Also diagnostic is the influence of composition on the electron mobility. When comparing the limiting binary blends, the electron mobility of P3HTT-DPP-10%:$PC_{61}BM$ is significantly higher than for PCDTBT:$PC_{61}BM$ at 3.44×10^{-3} cm^2/(Vs) relative to 4.45×10^{-5} cm^2/(Vs). Previous studies on PCDTBT:$PC_{61}BM$ blends agree with our data and also indicate a very high ratio of hole mobility to electron mobility for this blend.[31] It is unclear why the PCDTBT:$PC_{61}BM$ blend works so well in a solar cell with such imbalanced hole and electron mobility, but it is likely a consequence of fullerene intercalation in the polymer.[32] As the P3HTT-DPP-10% content increases in the ternary blends, modest increases in electron mobility in the 5−10% composition range are followed by a steep increase starting at 20% P3HTT-DPP-10%. This indicates that P3HTT-DPP-10% begins to interact more strongly with $PC_{61}BM$ when its content increases. This is consistent with both EQE (Figure 2b) and PSR (Figure 3b) data in which the long-wavelength photoresponse from P3HTT-DPP-10% is first observed when content exceeds 20% of the polymer fraction and is indicative of the presence of P3HTT-DPP-10% at the fullerene interface.

The data presented here strongly supports the idea that polymer miscibility plays an important role in the device performance of ternary blends. We propose that surface energies of the components can serve as a predictor of differences in miscibility as one necessary factor that either enables or prevents organic alloy formation. Similar surface energies in case of P3HTT-DPP-10% (19.9 mN/m) and P3HT$_{75}$-co-EHT$_{25}$ (22.1 mN/m) or $PC_{61}BM$ (27.6 mN/m) and ICBA (24.9 mN/m) facilitate mixing between synergistic components, allowing the formation of an organic alloy and leading to intermediate V_{oc}, high J_{sc}, and high FF. Significant differences in the surface energies, as found for P3HTT-DPP-10% (19.9 mN/m) and PCDTBT (29.5 mN/m), likely prevent polymer mixing and alloy formation, resulting in solar cells that suffer from low J_{sc}, V_{oc}, and FF. Future efforts are underway to more deeply interrogate the morphology of these systems and to establish a clear correlation between surface energy, miscibility, and solar cell performance. Other reported ternary blend systems support the hypothesis that polymers with highly

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similar chemical structures and likely good miscibility can exhibit tunable V_{oc} and high efficiency in solar cells.[5,9−11]

In summary, we prepared ternary blend solar cells based on two polymers with highly different surface energies. Unlike the previously studied P3HTT-DPP-10%:P3HT$_{75}$-co-EHT$_{25}$:PC$_{61}$BM system,[1] where both polymers have similar surface energies and very similar chemical structures, P3HTT-DPP-10%:PCDTBT:PC$_{61}$BM ternary blend solar cells did not form an organic alloy, as supported by PSR measurements. The V_{oc} was pinned to the smallest V_{oc} of the corresponding binary blends even at P3HTT-DPP-10% content as low as 5% of the polymer component. Furthermore, J_{sc}, FF, and efficiency of ternary blend solar cells at high PCDTBT loadings were found to be lower than the corresponding binary blend solar cells. We speculate that the lack of miscibility between the polymers facilitates preferential location of the P3HTT-DPP-10% away from the PC$_{61}$BM interface at high PCDTBT contents and does not allow CT state averaging or effective hole transport. As a result, we propose the use of the surface energy of the components in the blend as a figure of merit to predict the formation of an organic alloy and the behavior of the V_{oc} in ternary blend solar cells. Similar surface energies should facilitate polymer mixing and formation of an organic alloy, while large difference in the surface energies should favor demixing, preventing alloying of the polymers and causing significant decrease in the solar cell performance. As such, miscibility among synergistic components is proposed as a necessary attribute for alloy formation. However, it is not clear if miscibility is sufficient for alloy formation and future work is focused on the deconvolution of additional variables that may influence alloy formation such as HOMO energy and relative crystallinity of the components thorough the design and evaluation of new polymer pairs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Procedures, NMR, surface energy, CV, GIXRD, UV−vis, TEM, mobility, and J−V data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: barrycth@usc.edu.
*E-mail: street@parc.com.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Khlyabich, P. P.; Burkhart, B.; Thompson, B. C. Compositional Dependence of the Open-Circuit Voltage in Ternary Blend Bulk Heterojunction Solar Cells Based on Two Donor Polymers. *J. Am. Chem. Soc.* **2012**, *134*, 9074−9077.

(2) Street, R. A.; Davies, D.; Khlyabich, P. P.; Burkhart, B.; Thompson, B. C. Origin of the Tunable Open-Circuit Voltage in Ternary Blend Bulk Heterojunction Organic Solar Cells. *J. Am. Chem. Soc.* **2013**, *135*, 986−989.

(3) Koppe, M.; Egelhaaf, H.-J.; Clodic, E.; Morana, M.; Lüer, L.; Troeger, A.; Sgobba, V.; Guldi, D. M.; Ameri, T.; Brabec, C. J. Charge Carrier Dynamics in a Ternary Bulk Heterojunction System Consisting of P3HT, Fullerene, and a Low Bandgap Polymer. *Adv. Energy Mater.* **2013**, *3*, 949−958.

(4) Cha, H.; Chung, D. S.; Bae, S. Y.; Lee, M.-J.; An, T. K.; Hwang, J.; Kim, K. H.; Kim, Y.-H.; Choi, D. H.; Park, C. E. Complementary Absorbing Star-Shaped Small Molecules for the Preparation of Ternary Cascade Energy Structures in Organic Photovoltaic Cells. *Adv. Funct. Mater.* **2013**, *23*, 1556−1565.

(5) Yang, L.; Zhou, H.; Price, S. C.; You, W. Parallel-Like Bulk Heterojunction Polymer Solar Cells. *J. Am. Chem. Soc.* **2012**, *134*, 5432−5435.

(6) Ameri, T.; Khoram, P.; Min, J.; Brabec, C. J. Organic Ternary Solar Cells: A Review. *Adv. Mater.* **2013**, *25*, 4245−4266.

(7) Khlyabich, P. P.; Burkhart, B.; Rudenko, A. E.; Thompson, B. C. Optimization and Simplification of Polymer−Fullerene Solar Cells Through Polymer and Active Layer Design. *Polymer* **2013**, *54*, 5267−5298.

(8) Khlyabich, P. P.; Burkhart, B.; Thompson, B. C. Efficient Ternary Blend Bulk Heterojunction Solar Cells with Tunable Open-Circuit Voltage. *J. Am. Chem. Soc.* **2011**, *133*, 14534−14537.

(9) Li, H.; Zhang, Z.-G.; Li, Y.; Wang, J. Tunable Open-Circuit Voltage in Ternary Organic Solar Cells. *Appl. Phys. Lett.* **2012**, *101*, 163302.

(10) Chen, L.; Yao, K.; Chen, Y. Can Morphology Tailoring Based on Functionalized Fullerene Nanostructures Improve the Performance of Organic Solar Cells? *J. Mater. Chem.* **2012**, *22*, 18768−18771.

(11) Kang, H.; Kim, K.-H.; Kang, T. E.; Cho, C.-H.; Park, S.; Yoon, S. C.; Kim, B. J. Effect of Fullerene Tris-Adducts on the Photovoltaic Performance of P3HT:Fullerene Ternary Blends. *ACS Appl. Mater. Interfaces* **2013**, *5*, 4401−4408.

(12) Vandewal, K.; Tvingstedt, K.; Inganäs, O. Charge Transfer States in Organic Donor−Acceptor Solar Cells In *Quantum Efficiency in Complex Systems, Part II From Molecular Aggregates to Organic Solar Cells*; Semiconductors and Semimetals Series; Wiley: New York, 2011; Vol. *85*, pp 261−295.

(13) Moses, P. G.; Van de Walle, C. G. Band Bowing and Band Alignment in InGaN Alloys. *Appl. Phys. Lett.* **2010**, *96*, 021908.

(14) Rockett, A. *The Materials Science of Semiconductors*; Springer: New York, 2008.

(15) Kaake, L. G.; Jasieniak, J. J.; Bakus, R. C.; Welch, G. C.; Moses, D.; Bazan, G. C.; Heeger, A. J. Photoinduced Charge Generation in a Molecular Bulk Heterojunction Material. *J. Am. Chem. Soc.* **2012**, *134*, 19828−19838.

(16) Bakulin, A. A.; Rao, A.; Pavelyev, V. G.; van Loosdrecht, P. H. M.; Pshenichnikov, M. S.; Niedzialek, D.; Cornil, J.; Beljonne, D.; Friend, R. H. The Role of Driving Energy and Delocalized States for Charge Separation in Organic Semiconductors. *Science* **2012**, *335*, 1340−1344.

(17) Khlyabich, P. P.; Burkhart, B.; Ng, C. F.; Thompson, B. C. Efficient Solar Cells from Semi-Random P3HT Analogues Incorporating Diketopyrrolopyrrole. *Macromolecules* **2011**, *44*, 5079−5084.

(18) Burkhart, B.; Khlyabich, P. P.; Thompson, B. C. Influence of the Ethylhexyl Side-Chain Content on the Open-Circuit Voltage in rr-Poly(3-hexylthiophene-co-3-(2-ethylhexyl)thiophene) Copolymers. *Macromolecules* **2012**, *45*, 3740−3748.

(19) Sun, Y.; Chien, S.-C.; Yip, H.-L.; Chen, K.-S.; Zhang, Y.; Davies, J. A.; Chen, F.-C.; Lin, B.; Jen, A. K.-Y. Improved Thin Film Morphology and Bulk-Heterojunction Solar Cell Performance

9918

dx.doi.org/10.1021/am502122a | *ACS Appl. Mater. Interfaces* 2014, 6, 9913−9919

Through Systematic Tuning of the Surface Energy of Conjugated Polymers. *J. Mater. Chem.* **2012**, *22*, 5587−5595.

(20) Huang, J.-H.; Hsiao, Y.-S.; Richard, E.; Chen, C.-C.; Chen, P.; Li, G.; Chu, C.-W.; Yang, Y. The Investigation of Donor-Acceptor Compatibility in Bulk-Heterojunction Polymer Systems. *Appl. Phys. Lett.* **2013**, *103*, 043304.

(21) Honda, S.; Ohkita, H.; Benten, H.; Ito, S. Selective Dye Loading at the Heterojunction in Polymer/Fullerene Solar Cells. *Adv. Energy Mater.* **2011**, *1*, 588−598.

(22) Xu, H.; Ohkita, H.; Hirata, T.; Benten, H.; Ito, S. Near-IR Dye Sensitization of Polymer Blend Solar Cells. *Polymer* **2014**, *55*, 2856−2860.

(23) De Wit, J.; van Ekenstein, G. A.; Polushkin, E.; Korhonen, J.; Ruokolainen, J.; ten Brinke, G. Random Copolymer Effect in Self-Assembled Hydrogen-Bonded P(S-co-4VP)(PDP) Side-Chain Polymers. *Macromolecules* **2009**, *42*, 2009−2014.

(24) Sperling, L. H. *Introduction to Physical Polymer Science*, 4th ed.; Wiley: New York, 2006.

(25) Beaupré, S.; Leclerc, M. PCDTBT: En Route for Low Cost Plastic Solar Cells. *J. Mater. Chem. A* **2013**, *1*, 11097−11105.

(26) Street, R. A.; Song, K. W.; Northrup, J. E.; Cowan, S. Photoconductivity Measurements of the Electronic Structure of Organic Solar Cells. *Phys. Rev. B* **2011**, *83*, 165207.

(27) Li, N.; Machui, F.; Waller, D.; Koppe, M.; Brabec, C. J. Determination of Phase Diagrams of Binary and Ternary Organic Semiconductor Blends for Organic Photovoltaic Devices. *Sol. Energy Mater. Sol. Cells* **2011**, *95*, 3465−3471.

(28) Machui, F.; Rathgeber, S.; Li, N.; Ameri, T.; Brabec, C. J. Influence of a Ternary Donor Material on the Morphology of a P3HT:PCBM Blend for Organic Photovoltaic Devices. *J. Mater. Chem.* **2012**, *22*, 15570−15577.

(29) Cowan, S. R.; Leong, W. L.; Banerji, N.; Dennler, G.; Heeger, A. J. Identifying a Threshold Impurity Level for Organic Solar Cells: Enhanced First-Order Recombination via Well-Defined $PC_{84}BM$ Traps in Organic Bulk Heterojunction Solar Cells. *Adv. Funct. Mater.* **2011**, *21*, 3083−3092.

(30) Kokil, A.; Yang, K.; Kumar, J. Techniques for Characterization of Charge Carrier Mobility in Organic Semiconductors. *J. Polym. Sci., Part B: Polym. Phys.* **2012**, *50*, 1130−1144.

(31) Faist, M. A.; Shoaee, S.; Tuladhar, S.; Dibb, G. F. A.; Foster, S.; Gong, W.; Kirchartz, T.; Bradley, D. D. C.; Durrant, J. R.; Nelson, J. Understanding the Reduced Efficiencies of Organic Solar Cells Employing Fullerene Multiadducts as Acceptors. *Adv. Energy Mater.* **2013**, *3*, 744−752.

(32) Beiley, Z. M.; Hoke, E. T.; Noriega, R.; Dacuña, J.; Burkhard, G. F.; Bartelt, J. A.; Salleo, A.; Toney, M. F.; McGehee, M. D. Morphology-Dependent Trap Formation in High Performance Polymer Bulk Heterojunction Solar Cells. *Adv. Energy Mater.* **2011**, *1*, 954−962.