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Understanding the Reduced Efficiencies of Organic Solar Cells Employing Fullerene Multiadducts as Acceptors

Mark A. Faist, Safa Shoaee, Sachetan Tuladhar, George FA. Dibb, Samuel Foster, Wei Gong, Thomas Kirchartz, Donal DC. Bradley, James R. Durrant, and Jenny Nelson*

The use of fullerenes with two or more adducts as acceptors has been recently shown to enhance the performance of bulk-heterojunction solar cells using poly(3-hexylthiophene) (P3HT) as the donor. The enhancement is caused by a substantial increase in the open-circuit voltage due to a rise in the fullerene lowest unoccupied molecular orbital (LUMO) level when going from mono-adducts to multiadducts. While the increase in the open-circuit voltage is obtained with many different polymers, most polymers other than P3HT show a substantially reduced photocurrent when blended with fullerene multiadducts like *bis*-PCBM (*bis* adduct of Phenyl- C_{61} -butyric acid methyl ester) or the indene C_{60} *bis*-adduct ICBA. Here we investigate the reasons for this decrease in photocurrent. We find that it can be attributed partly to a loss in charge generation efficiency that may be related to the LUMO-LUMO and HOMO-HOMO (highest occupied molecular orbital) offsets at the donor-acceptor heterojunction, and partly to reduced charge carrier collection efficiencies. We show that the P3HT exhibits efficient collection due to high hole and electron mobilities with mono- and multiadduct fullerenes. In contrast the less crystalline polymer Poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl (PCDTBT) shows inefficient charge carrier collection, assigned to low hole mobility in the polymer and low electron mobility when blended with multiadduct fullerenes.

1. Introduction

In the field of organic solar cells, the power conversion efficiency (PCE) has progressed very quickly in recent years, with certified efficiencies of single-junction cells now reaching

9%.^[1] Most of this progress, however, is due to the development of novel donor polymers. The fullerene derivative PCBM (Phenyl- C_{61} -butyric acid methyl ester), first synthesized in 1995,^[2] is still the most widely used acceptor material. Possible alternative acceptors are the higher adducts of fullerene derivatives, such as the *bis*-adducts of indene- C_{60} fullerene (ICBA (indene- C_{60} -*bis*-adduct) and PCBM (*bis*-PCBM) which offer an increased open-circuit voltage due to the higher lying LUMO energy, which in turn results from the strain induced in the C_{60} cage by the attachment of multiple substituents. Blends of P3HT (poly(3-hexylthiophene)) and ICBA (first developed by Laird et al. in 2006^[3]) led to a certified device efficiency of 5.4%, a record for organic solar cells at that time.^[4] Blends of P3HT and *bis*-PCBM were shown to improve PCE as well when compared to P3HT:PCBM blends.^[5] More recently, the P3HT:ICBA system was further optimized, reaching PCEs of 6.5%.^[6,7]

Despite the successes of fullerene multiadducts in blends with P3HT, these acceptor materials have usually shown

a disappointing performance when blended with other donor polymers.^[8,9] Figure 1 shows the power conversion efficiency of a variety of polymers with the fullerene multiadducts *bis*-PCBM, ICBA and ICTA (indene- C_{60} -*tris*-adduct, relative to the efficiency of the polymer when blended with PCBM. While the multiadducts show increased performance in blends with P3HT and poly[(4,4'-bis(3-(2-ethyl-hexyl)dithieno[3,2-b':3',4'-d]silole)-2,6-diyl-alt-(2,5-bis(3-(2-ethyl-hexyl)thiophen-2-yl)thiazolo[5,4-d]thiazole)] (PSEHTT), the power conversion efficiency is greatly reduced in blends with all other polymers. In all cases the poor efficiency is accompanied by inefficient photocurrent generation.

Efficient photocurrent generation in an organic donor:acceptor solar cell requires both (1) efficient *generation* of charge pairs at the donor:acceptor interface (avoiding losses to so-called geminate recombination) and (2) efficient *collection* of the separated charges at the electrodes (avoiding losses due to non-geminate recombination). Charge pair generation is influenced by the free energy driving force at the interface, i.e. by the difference in energies between the excitonic and charge separated excited states.^[13] This quantity is often approximated as

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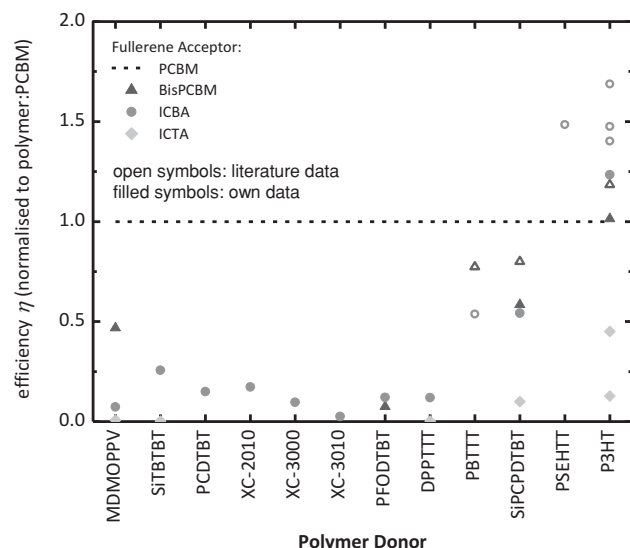


Figure 1. Power conversion efficiencies of polymer:fullerene blends with fullerene multiadduct acceptors *bis*-PCBM (triangles), ICBA (circles) and ICTA (diamonds), normalized to data for the same polymers with PCBM as acceptor (dashed horizontal line). The plot includes data from proprietary Plextronics polymers (XC-2010, XC-3000, XC-3010, see supporting information for device data) and published device data (open symbols) for poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT),^[8,10] P3HT,^[5–7] Poly((4,4'-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole)-2,6-diyl-alt-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5'-diyl) (SiPCPDTBT),^[11] and PSEHTT.^[12]

the difference in LUMO energies of the donor and acceptor and a range of values from zero up to 0.8 eV have been proposed for the threshold enabling charge separation.^[14–18] This driving force will also be influenced by the density of states,^[19] by the local (nano)morphology^[20–22] and in some cases by the excitation energy^[23,24] and by the local electrostatic field.^[25,26] Charge collection is influenced by (nano)morphology close to the donor-acceptor interface,^[27] by the degree of ordering (and hence mobility) in the electron and hole transporting phases,^[20,21,28–30] by the degree of phase segregation in the binary blend^[8,31] and the carrier mobility in the respective phases.^[32] Fine intermixing of the components can disrupt local molecular ordering, restrict charge transport pathways, especially in the fullerene phase, and increase recombination.^[8,33,34]

Whilst previous studies have found disappointing performance by fullerene multiadducts,^[8,11,35–37] as yet no comprehensive study has been carried out to explain the performance of polymer:multiadduct devices in terms of charge pair generation and collection. Especially the influence of the polymer ordering tendency on charge collection in these systems has to our knowledge not yet been discussed at all.

In this paper, we study the effect of fullerene multiadducts on device performance in terms of charge generation and charge collection. Using transient absorption spectroscopy, electroluminescence and current/voltage measurements, we study the behavior of three different fullerene multiadducts (*bis*-PCBM, ICBA and ICTA) in blends made from three widely studied and representative polymers. Using differential pulse voltammetry (DPV),^[38] the fullerene multiadducts have been demonstrated

to have successively higher lying LUMO energies than PCBM. Of the three polymers, namely P3HT, SiPCPDTBT (poly[(4,4-bis(2-ethylhexyl)dithieno[3,2-b:2,3-d]silole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl]) and PCDTBT (Poly[(9-(1-octylnonyl)-9H-carbazole-2,7-diyl)-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl]), the latter two are examples of materials that outperform P3HT when blended with PCBM as a result of a either deeper HOMO energy, enabling higher photovoltage (PCDTBT), or a lower optical gap, enabling higher photocurrent (SiPCPDTBT). We find that the fullerene has a twofold effect on photocurrent generation. First, it influences charge pair generation through the effect of the higher lying fullerene LUMO on the driving force for charge separation. Secondly, it influences collection through the impact adducts have on fullerene packing and consequently on electron transport. Moreover we find that the latter phenomenon is also influenced by the type of polymer. Together, these factors are sufficient to explain the mismatch between the expected and observed performance of the blends studied here.

2. Results and Discussion

2.1. Studies of Charge Generation Efficiency of the Blend Films

Charge generation in polymer:fullerene solar cells is usually efficient if the LUMO-LUMO or HOMO-HOMO offsets do not drop below a certain critical energy that depends among others on the definitions of the energy levels^[36] and the properties of polymer and fullerene.^[17] A recent study by Vandewal et al.^[17] showed that a high internal quantum efficiency of nearly 90% is still possible when the electroluminescence emission energies of polymer and charge transfer state are only 0.1 eV apart showing that large offsets are not necessary for charge separation. To study whether insufficient offsets at the heterojunction affect the performance of our series of blends with fullerene multiadducts, we use a similar definition for the energy levels. We define the energy of the charge transfer state by the peak of its electroluminescence emission $E_{CT,EL}$ and estimate the energy of a relaxed exciton by the absorption onset of the polymer or fullerene. Combining both values gives us two energetic offsets at the heterojunction:

$$\Delta E_{LUMO} = E_{opt,polymer} - E_{CT,EL} \quad (1)$$

related to the offset of lowest unoccupied molecular orbital (LUMO) of donor and acceptor and

$$\Delta E_{HOMO} = E_{opt,fullerene} - E_{CT,EL} \quad (2)$$

related to the difference in highest occupied molecular orbital (HOMO) of donor and acceptor. Here, E_{opt} is defined as the absorption onset for polymers and fullerenes (see Table 1). As most photons are absorbed by the polymer, ΔE_{LUMO} is usually considered the relevant offset for charge generation, a process that occurs on a timescale of femtoseconds.^[24]

Combining the different fullerene adducts with the selected polymers enables us to vary the energy offsets ΔE_{HOMO} and ΔE_{LUMO} at the heterojunction. Table 1 shows the energetic offset ΔE_{LUMO} for blends containing P3HT, SiPCPDTBT and PCDTBT,

Table 1. Absorption onsets (typical error 0.02 eV) for polymers and fullerenes as well as values of ΔE_{LUMO} (shaded cells) for polymer:fullerene blends (typical errors are 0.03 eV – 0.05 eV).^[36,39]

	Fullerene	PCBM	bis-PCBM	ICBA	ICTA
Polymer	E_{opt} [eV]	1.70	1.70	1.70	1.70
P3HT	1.93	1.06	0.96	0.80	0.60 ^{a)}
SiPCPDTBT	1.52	0.53	0.37	0.26	0.06 ^{a)}
PCDTBT	1.90	0.73	0.60	0.52	0.32

^{a)}Values are estimated from the LUMO level difference observed in DPV and are therefore less reliable.

determined according to Equation (1a). For both SiPCPDTBT and PCDTBT, the energetic offset is smaller than for P3HT. This is the result of efforts to tune the polymer energy levels so as to maximize V_{oc} when used with PCBM.

In a previous study,^[37] we have shown that in blends with P3HT, charge generation is not affected by substituting the *bis*- or *tris*-PCBM for PCBM despite the reduction of the energetic offset (from ≈ 1.0 eV to ≈ 0.8 eV) and a strongly reduced mobility for these multiadducts. The selection of SiPCPDTBT and PCDTBT as donor polymers and ICBA and ICTA as electron acceptors now allows us to evaluate the effect of a reduced ΔE_{LUMO} on charge generation for a wider range values of ΔE_{LUMO} , from 1 eV to almost zero.

Transient absorption spectroscopy (TAS) is a widely used and well-established tool to measure charge generation in photovoltaic blends.^[21,23,40] It allows the user to estimate the relative yield and decay dynamics of photo-induced polarons in most polymer:fullerene blends by measuring the polaron absorption in a pump-probe setup. If free charge carriers are generated, the TAS decay is limited by diffusion of free charge carriers towards sites containing opposite charges. Such behavior is visible in a monotonic decay with the polaron signal typically being proportional to $t^{-\alpha}$. It has been suggested that the parameter α can be related to the density of states of the blend component with the slower charge diffusion.^[41]

Figure 2 shows the normalized polaron absorbance decay in blends of P3HT, SiPCPDTBT and PCDTBT combined with four different fullerene adducts: PCBM, *bis*-PCBM, ICBA and ICTA. In blends with P3HT (Figure 2a), the acceptors PCBM, *bis*-PCBM and ICBA show a similar charge generation yield (signal amplitude), while the polaron yield of the blend with ICTA is reduced. It is likely that in the latter case the reduced energy offset, $\Delta E_{\text{LUMO}} = 0.60$ eV, limits yield. Effects inherent to *tris*-adducts, such as a possible reduction in charge separation due to the effect of the multiple side chains, can be excluded, since P3HT blended with the *tris*-adduct of PCBM, *tris*-PCBM, shows a charge generation yield equal to the blend with PCBM at a ΔE_{LUMO} of 0.85 eV.^[37] In the case of SiPCPDTBT (Figure 2b), the energetic offsets are much smaller, 0.53 eV in the blend with PCBM and 0.26 eV in the blend with ICBA. Despite these offsets being smaller than 0.6 eV, the charge generation yield is still high in these blends. In the films with PCDTBT (Figure 2c) as donor material, charge generation is continuously reduced as the energetic offset decreases from 0.73 eV to 0.32 eV. In the blends of PCDTBT with ICBA and ICTA, an additional fast

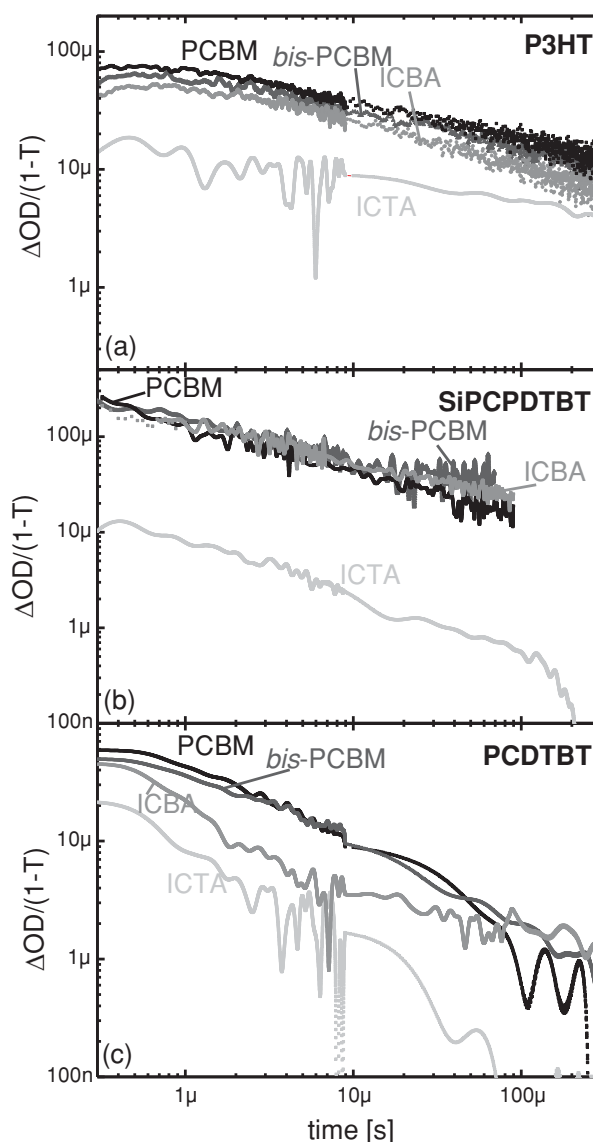


Figure 2. Decay of transient absorption assigned to positive polarons in polymer-fullerene blends decay normalized relative to the film absorptivity at the pump wavelength: (a) P3HT, (excited at 520 nm and measured at a probe wavelength of 980 nm) (b) SiPCPDTBT (excited at 650 nm and measured at a probe wavelength of 1310 nm), and (c) PCDTBT (excited at 600 nm and measured at a probe wavelength of 980 nm), each blended with PCBM, *bis*-PCBM, ICBA and ICTA. Note that the curves are smoothed; the original data is in the supporting information, Figure S9.

phase is observed in the decay. At short timescales ($t < 1 \mu\text{s}$), the decay can be approximated by a monoexponential decay with a lifetime of 90 ns for PCDTBT:ICBA and 60 ns for PCDTBT:ICTA. This fast phase may be caused by recombination of polaron pairs that are either still Coulombically bound or that are confined to small domains and that therefore do not separate into free polarons. Geminate recombination dynamics of Coulombically bound, emissive charge transfer states in polymer:polymer blends have been reported to occur on the 50 ns timescale.^[42,43] Such bound charge pairs tend to absorb

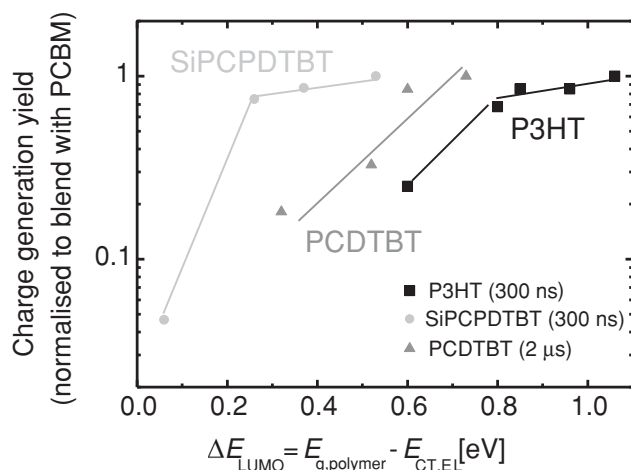


Figure 3. Charge generation yield in various polymer-fullerene blends, measured with TAS at 300 ns (2 μ s for PCDTBT due to the fast decay component). The data is normalized to the yield with PCBM, the lines are a guide to the eye. Data for P3HT: *tris*-PCBM ($\Delta E_{\text{LUMO}} = 0.85$ eV) was taken from a previous study.^[40] For each series the data points represent (from low to high ΔE_{LUMO}) the fullerenes ICTA, ICBA, *tris*-PCBM (only for P3HT), *bis*-PCBM and PCBM.

the probe light at the same wavelength as the free polarons thus contributing to the TAS signal but not to photocurrent. Despite the signal in PCDTBT:ICBA being similar to PCDTBT:PCBM at short times ($t < 0.2$ μ s), the yield in free charges at $t = 2$ μ s is only about a quarter as large.

Figure 3 shows a summary of the charge generation yields as a function of ΔE_{LUMO} for all of the blends we studied. The charge generation yield is defined here as the normalized polaron absorbance at a given time for each blend, relative to the normalized polaron absorbance for the blend of that polymer with PCBM. This comparison shows that there is no universal threshold for charge generation and that energetics are not enough to understand charge generation.^[24,44] If ΔE_{LUMO} is reduced by replacing PCBM with the fullerene multiadducts, remarkable differences between the systems emerge. In the P3HT:fullerene blends, the polaron yield is already reduced at $\Delta E_{\text{LUMO}} = 0.60$ eV, while in blends with SiPCPDTBT, an energetic offset $\Delta E_{\text{LUMO}} = 0.26$ eV still results in a high polaron yield. A possible explanation for this strong material-dependence is the difference between potential energy and Gibbs free energy. ΔE_{LUMO} represents the potential energy, but according to Marcus theory, the rate in electron transfer that drives charge generation is strongly affected by the difference in Gibbs free energy ΔG^0 between bound and separated state.^[13,44,45] Factors other than ΔE_{LUMO} , such as nanomorphology,^[46] energetic disorder,^[38] aggregation or crystallinity^[21] and differences in donor – acceptor distances^[47] can contribute to ΔG^0 . These results are in agreement with recent spectroscopic studies of polymer:fullerene systems where we find that materials crystallinity does have a strong impact upon the recombination dynamics of the initially generated polarons.^[48]

At high energetic offsets (high ΔE_{LUMO}) the offset in potential energy might dominate the Gibbs free energy, making other contributions less important, but as ΔE_{LUMO} is lowered, these material-dependent quantities will become more pronounced.

The push-pull copolymer SiPCPDTBT shows a high generation yield at the lowest offset, in agreement with previous reports that show low energetic losses^[17,49] and high charge generation yields^[50] at low energetic offsets in push-pull (donor-acceptor) copolymers containing benzothiadiazole (BT) or diketopyrrolopyrrole (DPP). One reason for this could be the strength of the acceptor (pull) unit and the resulting charge-transfer nature of the polymer exciton.^[51] Another contributing factor could be the relation of polymer and fullerene optical gaps. Fullerenes are very efficient energy transfer acceptors,^[52,53] and if the polymer optical gap is larger than the fullerene optical gap ($E_{\text{opt,polymer}} > 1.7$ eV), the exciton population could branch off and populate the fullerene singlet. The driving force for charge separation for these excitons on the fullerene, ΔE_{HOMO} , is smaller than ΔE_{LUMO} in this case and could be insufficient for charge generation.^[36] In blends with high-bandgap polymers, the fullerene singlet can also act as an additional recombination channel through activation of the fullerene singlet that appears at $\Delta E_{\text{HOMO}} < 0.35$ eV and can reduce fill factor as well as open-circuit voltage.^[36]

2.2. Studies of Charge Collection Efficiency of the Blend Films

A comparison of Figure 3 and Figure 1 shows that in certain cases (PCDTBT:*bis*-PCBM, SiPCPDTBT:ICBA, SiPCPDTBT:*bis*-PCBM) a high apparent charge yield is not accompanied by good photovoltaic performance. In these cases the low device performance for the blends containing multiadducts *bis*-PCBM and ICBA cannot be explained by reduced charge generation due to a lower driving force. To further study the relation between charge generation and charge collection, we have measured the voltage-dependent charge collection efficiency using the corrected photocurrent measurement. In this method the corrected photocurrent is defined as the device current under illumination as a function of voltage after subtraction of the corresponding dark current. It is a widely used tool to analyze device parameters.^[54–57] We use a pulsed, almost simultaneous measurement of light and dark currents^[55] through which temperature- and time-dependent effects are avoided and the photocurrent $J_{\text{ph}} = J_{\text{light}} - J_{\text{dark}}$ can be measured much more accurately than by subtracting separately measured current-voltage curves. J_{ph} is then corrected for a photoshunt as explained in the supplementary information and is normalized to its saturation value at high reverse biases, the saturation current J_{sat} . It is assumed that the charge carrier collection efficiency is 100% in this limit. The normalized current is then plotted versus the electrostatic potential difference $V_0 - V$ between the two contacts, where V_0 is the voltage at which the corrected photocurrent becomes zero. The ratio of J_{ph} to J_{sat} represents the product of charge generation and collection efficiencies. Collection efficiency can then be estimated by comparing $J_{\text{ph}}/J_{\text{sat}}$ with the relative charge yield estimated from TAS. Figure 4 shows $J_{\text{ph}}/J_{\text{sat}}$ for the blends of P3HT, SiPCPDTBT and PCDTBT with PCBM, *bis*-PCBM and ICBA over a range of biases from small forward ($0 < V < V_0$) to strong reverse ($V \ll 0$).

The measured values of J_{sat} vary by up to 30% for blends with P3HT, 20% for blends with SiPCPDTBT and less than 10% for blends with PCDTBT, but these variations are small enough to be completely explained by differences in thickness and optical

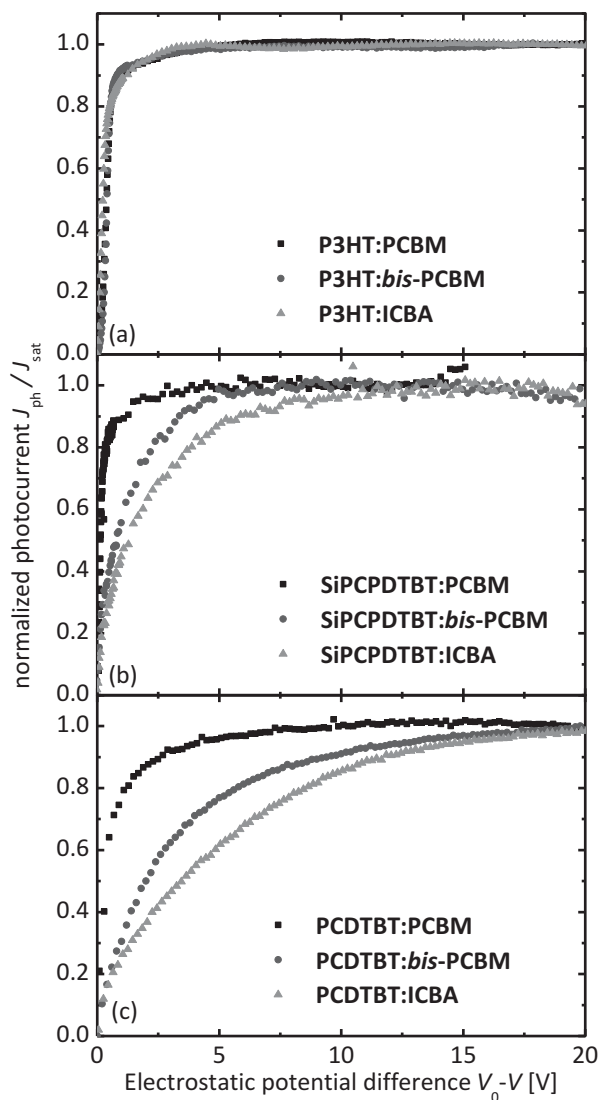


Figure 4. Corrected photocurrent data as a function of the potential difference $V_0 - V$, where V_0 is the voltage at which the currents measured in the dark and under illumination are equal. Data are presented for (a) P3HT, (b) SiPCPDTBT, (c) PCDTBT blended in turn with PCBM (squares), *bis*-PCBM (circles) and ICBA (triangles).

interference. At high reverse biases the photocurrent saturates in all blends, suggesting that almost all generated charges are collected. At low $V_0 - V$, i.e. at low electric field, however, the three polymer systems show very different behavior in terms of charge collection.

In the blends with P3HT (Figure 4a), the collection probability is equally high for blends with PCBM, *bis*-PCBM and ICBA, evident through the very similar behavior of the normalized J_{ph} as a function of internal voltage. Combined with the increased open circuit voltage of the blends containing *bis*-PCBM and ICBA, this similar photocurrent generation results in superior device performance of the blends with fullerene multiadducts.^[3,5] Studies have shown that blends containing SiPCPDTBT show reduced, but still relatively good performance in blends with *bis*-PCBM and ICBA. Azimi et al. reported

a SiPCPDTBT:*bis*-PCBM device with PCE = 4.0% compared to 5.0% for the blend with PCBM,^[11] attributing the loss in fill factor and photocurrent to reduced mobilities.^[35] We find high charge collection only at a reverse bias of −5 V in the blend with *bis*-PCBM and at −10 V in the blend with ICBA (Figure 4b). PCDTBT (Figure 4c) features a very high short-circuit internal quantum efficiency with PCBM,^[58] but shows low photocurrent and fill factor with both fullerene multiadducts. High reverse biases of 20 – 30 V are needed to ensure high charge collection.

While the corrected photocurrents presented in Figure 4 clearly show that multiadducts suffer from collection problems, the pure current/voltage curves do not reveal whether the collection is reduced due to reduced mobilities, reduced charge carrier lifetimes or due to field dependent dissociation probabilities for the excitons in the polymer or the charge transfer state. Thus, we measured the current/voltage curves of single carrier devices in addition to studying charge transport. Figure 5 shows the (a) hole and (b) electron mobilities for polymer:fullerene blend devices (containing 50% fullerene by weight in the case of P3HT and 67% fullerene by weight in the case of the other two polymers). The mobilities were derived by fitting a drift-diffusion solver as described in refs.^[59,60] to a set of electron only, hole only and solar cell current/voltage curves (see supporting information for the current/voltage curves, the fits and the parameters). This has the advantage that charged defects that lead to deviations from space-charge-limited-current-type behavior ($J \sim V^2$) can be taken into account. This improves the analysis especially of the electron only data relative to fits based on drift-only models.^[61]

In the following we will explain the changes in corrected photocurrent as seen in Figure 4 with the mobilities presented in Figure 5 and with the changes in charge carrier lifetime between blends with the three different polymers that have been reported in literature.^[27] Let us first compare the corrected photocurrents and mobilities of the P3HT based devices with the SiPCPDTBT based devices. While there are substantial differences in the corrected photocurrent (Figure 4a,b), the mobilities (Figure 5) are reasonably similar for both polymers. While the electron mobility decreases when going from PCBM to *bis*-PCBM and ICBA (Figure 5b), the hole mobility even goes up when exchanging PCBM with ICBA (Figure 5a). Thus, while the reduction in the collection efficiency when going from SiPCPDTBT:PCBM to SiPCPDTBT:*bis*-PCBM and SiPCPDTBT:ICBA could be explained by the reduced electron mobilities, Figure 5 by itself does not explain why the same reduction is not seen in the blends with P3HT. This only becomes apparent, when considering that charge carrier lifetimes as measured with transient photovoltage in P3HT:PCBM are known to be substantially longer than in SiPCPDTBT:PCBM.^[27,62] This increased lifetime also explains why P3HT:PCBM devices can be fabricated without substantial loss of efficiency at much higher thicknesses than devices made from blends of other polymers including SiPCPDTBT.^[63,64]

Finally, blends with PCDTBT have the most severe reduction in collection efficiency as presented in Figure 4c, but the explanation seems to be a combination of effects. PCDTBT:PCBM clearly has lower electron and hole mobilities than P3HT:PCBM and SiPCPDTBT:PCBM. In addition it is known to have faster recombination dynamics than P3HT:PCBM.^[27] To reproduce the

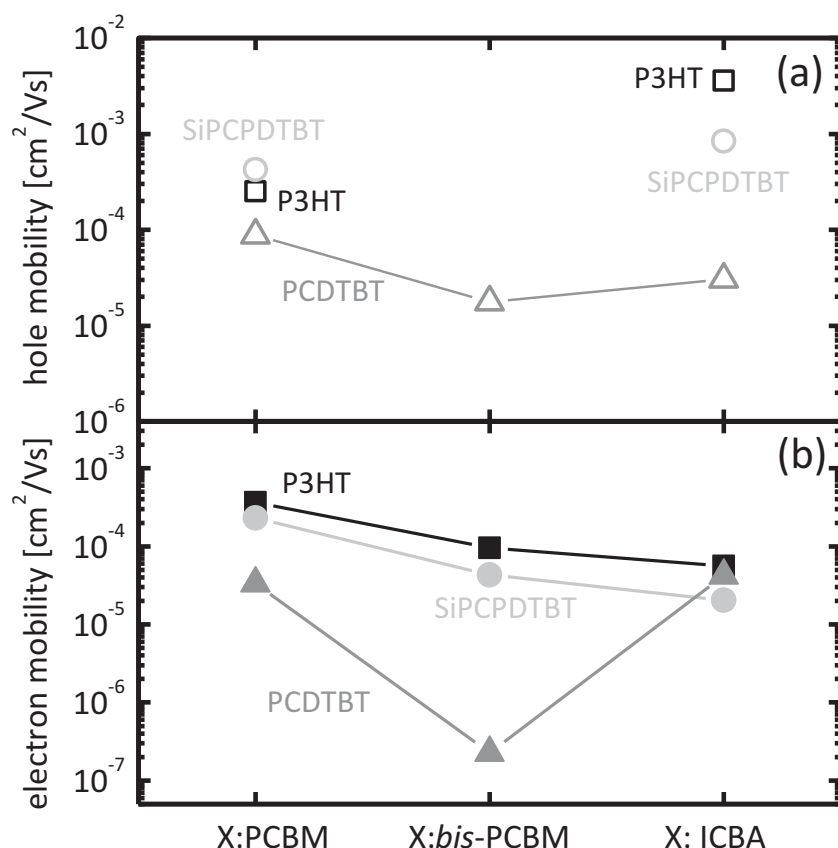


Figure 5. Charge carrier mobilities for polymers (X = P3HT (squares), SiPCPDTBT (circles) and PCDTBT (triangles)) and their blends with fullerene acceptors PCBM, ICBA and *bis*-PCBM. (a) SCLC hole and (b) SCLC electron mobilities. The ranking of hole mobilities depends predominantly on the polymer used, with some evidence for a relative increase in mobility for ICBA with P3HT and SiPCPDTBT. The electron mobilities seem to be strongly reduced for blends with multiadducts. Electron and hole mobilities are generally lower for the two more disordered (less crystalline) polymers PCDTBT and SiPCDTBT.

inefficient collection in PCDTBT:*bis*-PCBM and PCDTBT:ICBA as well as the single carrier device data, the fit converged either at extremely low electron mobilities (PCDTBT:*bis*-PCBM) or substantially faster non-geminate recombination (PCDTBT:ICBA).

By fitting the single carrier devices and the solar cell current/voltage curves simultaneously, we obtain not only the mobilities that are presented in Figure 5, but we also predict the recombination constants that are necessary to reproduce the photocurrents with the mobilities constrained by the single carrier device measurements. These predicted recombination constants are presented in Figure S8 in the supporting information and they confirm the observation from literature that non-geminate recombination in P3HT based devices is substantially slower than in PCDTBT or SiPCPDTBT based devices. In addition, we reproduce the observation in literature that recombination at room temperature is similarly fast in P3HT blended with different fullerenes as shown by Guerrero et al.^[65] and Busby et al.^[66] and that SiPCPDTBT:PCBM and SiPCPDTBT:*bis*-PCBM have similar lifetimes as shown by Azimi et al.^[35] The only cases, where the fullerene has a strong effect on the predicted recombination constants are the cases of SiPCPDTBT:ICBA and PCDTBT:ICBA, which seem to have much faster recombination

than the other blends. Note that we cannot exclude effects like field dependent charge generation in these cases, which would have a similar effect than non-geminate recombination: Field dependent charge generation would decrease the fill factor and short circuit current of the solar cells without affecting the current/voltage curves of the single carrier devices.

The fact that the electron mobility is higher for the semi-crystalline P3HT than for the more amorphous polymer PCDTBT can be understood by more complete phase separation in the blends with P3HT that leads to a better network for electron transport.^[67] Further, it has been shown that some polymer:fullerene combinations show intercalation of fullerenes in the blend, which decreases the electron mobility by trapping fullerenes in closely mixed domains rather than making them available for fullerene network formation.^[8,68,69] Hence, for the polymer/fullerene combinations studied here, we conclude that the blend morphology is normally most favorable for electron transport in blends with P3HT, which displays high crystallinity and strong phase separation,^[20,67,70,71] and least favorable for PCDTBT, which is the most disordered of the polymers, and one for which there is evidence of intercalation of PCBM.^[8,72]

The fact that the electron mobility is reduced in P3HT:*bis*-PCBM relative to P3HT:PCBM is consistent with studies on the phase behavior of P3HT blended with mono-, *bis*- and *tris*-PCBM^[73] which indicate that *bis*- and *tris*-PCBM have a reduced

tendency to form crystalline networks in P3HT, compared to PCBM.

On the basis of the above results, we propose that the reduced charge collection efficiency in fullerene acceptor blends with SiPCPDTBT and PCDTBT relative to P3HT is due to reduced charge carrier lifetimes and reduced charge carrier mobilities. Moreover, we propose that the reduced electron mobilities in blends of disordered polymers with fullerene multiadducts result from the fullerenes' failure to segregate sufficiently to form coherent networks for electron transport.

These results indicate the criteria that must be satisfied in order to achieve useful PV performance with fullerene multiadducts. In addition to having a sufficiently high LUMO energy offset for charge generation (a property that is polymer specific) the blend must exhibit sufficiently strong phase segregation so as to define relatively pure pathways for charge percolation. This is particularly challenging for multiadducts since their weakened inter-fullerene interactions lead to lowered electron mobility within the fullerene phase in comparison to PCBM. A strongly crystalline polymer like P3HT succeeds in defining effective percolation paths but less crystalline polymers such as the PCDTBT studied here apparently fail to define such paths,

resulting in parasitic, isolated fullerene domains that don't contribute to collection.

3. Conclusions

In summary, we have studied the performance of the fullerene multiadducts *bis*-PCBM, and ICBA blends with three conjugated polymers that are relevant for organic photovoltaic devices. We found that the energy level offset, ΔE_{LUMO} (measured as the energy difference between the polymer absorption onset and the peak in electroluminescence from the charge transfer state), at which efficient charge generation first occurs is different for each polymer system. SiPCPDTBT shows efficient charge generation at a threshold $\Delta E_{\text{LUMO}} \approx 0.26$ eV (with ICBA), for PCDTBT the threshold is closer to $\Delta E_{\text{LUMO}} \approx 0.6$ eV (with *bis*-PCBM), while for P3HT it is closer to $\Delta E_{\text{LUMO}} \approx 0.80$ eV (with ICBA).

Despite high charge generation in blends with the fullerene multi-adducts *bis*-PCBM and ICBA, charge collection and hence device performance is significantly reduced in blends of SiPCPDTBT and PCDTBT with fullerene multi-adducts. We find not only that the charge collection efficiency becomes worse for blends with a given fullerene when exchanging P3HT for SiPCPDTBT or PCDTBT, but also that the collection efficiency penalty for using a fullerene multi-adduct becomes more severe with those polymers. Space-charge-limited current measurements on hole-only devices suggest that there is a reduction in the hole mobility in blends when substituting P3HT or SiPCPDTBT with PCDTBT. However, the blend hole mobility was not negatively affected by exchanging PCBM for a fullerene multiadduct. SCLC measurements on electron only devices show that the electron mobility depends both on the fullerene and on the crystallinity of the polymer. Thus, blends with *bis*-PCBM and especially ICBA lead to lower electron mobilities than blends with PCBM while blends of any fullerene with disordered polymers normally show lower electron mobilities than blends with more crystalline polymers. In addition, we note that the increased charge carrier lifetimes in P3HT relative to the two other polymers contribute to the improved performance of P3HT with fullerene multiadducts and makes P3HT less vulnerable to the losses in electron mobility due to the multiadducts.

Therefore, we expect that in order to show a high performance in a blend with fullerene multi-adducts, a polymer must exhibit both a fairly high hole mobility, long charge carrier lifetimes, and a strong tendency towards phase separation in order to minimize the reduction in the electron mobility in the fullerene multi-adduct phase. Whilst this does not necessarily require high polymer crystallinity like that shown by P3HT, the literature experience, along with our findings, suggests that this is the only effective way to ensure sufficient charge collection in both donor and acceptor phases.

4. Experimental Section

Materials: Poly[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl (PCDTBT) was purchased from 1-material, Poly(3-hexylthiophene) (P3HT) was purchased from

Merck, PCBM was purchased from Nano-C, Poly((4,4'-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole)-2,6-diyl-alt-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5'-diyl) (SiPCPDTBT) was provided by Konarka and the indenofullerenes (ICMA, ICBA, ICTA) were provided by Plextronics.

Device fabrication: Bulk heterojunction solar cells were prepared by cleaning patterned ITO in detergent, acetone and isopropanol. A layer of PEDOT:PSS was spin coated onto the ITO substrates at 2000 rpm and annealed at 150 °C for 20 minutes. Subsequently, the active layer solution was spin-coated on top (P3HT:PCBM (dissolved in chlorobenzene at 1:1 wt%, 40 mg/ml), PCDTBT (dissolved in chloroform at 1:2 wt%, 15 mg/ml), SiPCPDTBT (dissolved in ortho-dichlorobenzene, 1:2 wt%, 40 mg/ml). Vacuum-deposited calcium/aluminium was used as cathode. All the devices were encapsulated in a nitrogen-filled glovebox.

Electroluminescence (EL) was measured at current densities of 1.25 – 1250 mA/cm² using a Princeton Instruments Acton SP 2500 monochromator combined with a liquid nitrogen cooled InGaAs photodiode array (Acton OMAV:1024). Spectral intensity was corrected with the spectrum from a calibrated halogen lamp.

The corrected photocurrent was determined by pulsed $J(V)$ measurements to minimize the influence of temperature changes between the light and dark measurements and device degradation effects. Illumination was provided by 12 white LEDs which could be pulsed by interrupting their power supply using a fast MOSFET switch; in these measurements, the light remained on for 2 ms and off for 420 ms. The cell was held at applied bias using a Keithley 2400 source-measure unit, and the current was measured across a 50 W resistor using a Tektronix TDS3032B oscilloscope.

Transient absorption decays were measured by exciting the sample film, under a nitrogen atmosphere. Excitation pulses were generated with a commercially available optical parametric oscillator (Opportelle) pumped by a Nd:YAG laser (Lambda Photometrics). The excitation wavelength used was the absorption maximum for each blend, with a pump intensity of 0.4 – 2.0 J/cm² and a repetition frequency of 20 Hz. A 100 W quartz halogen lamp (Bentham, IL 1) with a stabilized power supply (Bentham, 605) was used as a probe light source, with a probe wavelength depending on the donor polymer (P3HT: 980 nm, SiPCPDTBT: 1310 nm, PCDTBT: 980 nm). The probe light passing through the sample film was detected with a silicon photodiode (Hamamatsu Photonics, S1722-01). The signal from the photodiode was pre-amplified and sent to the main amplification system with an electronic band-pass filter (Costronics Electronics). The amplified signal was collected with a digital oscilloscope (Tektronix, TDS220), which was synchronized with a trigger signal of the pump laser pulse from a photodiode (Thorlabs Inc., DET210). To reduce stray light, scattered light and sample emission, two monochromators and appropriate optical cut-off filters were placed before and after the sample.

Space charge limited current measurements: All the single carrier devices were prepared on patterned ITO coated glass similar to solar cells above. Hole only devices were prepared with ITO/PEDOT:PSS as a bottom contact/hole injection layer and PEDOT:PSS/Ag as top contact. For the electron only devices we replaced PEDOT:PSS with TiO_x for the electron injection layer and the top contact was TiO_x/Al. The concentrations of polymer:fullerene blend solutions used to prepare active layer films for single carrier devices were kept the same as for the solar cells. The mobilities were determined by fitting a drift-diffusion solver as described in refs.[59,60] to the diode current/voltage curves under illumination and the e-only and h-only current/voltage curves. The effective mobility was defined as $\mu_{n,p} = \mu_{f,n,p} n_f/n_{\text{tot}}$, where $\mu_{f,n,p}$ is the mobility of free carriers, n_f is the concentration of free electrons or holes at short circuit and n_{tot} is the total concentration of free and trapped electrons or holes at short circuit.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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