

Recombination in Polymer:Fullerene Solar Cells with Open-Circuit Voltages Approaching and Exceeding 1.0 V

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Polymer:fullerene solar cells are demonstrated with power conversion efficiencies over 7% with blends of PBDTTPD and PC₆₁BM. These devices achieve open-circuit voltages (V_{oc}) of 0.945 V and internal quantum efficiencies of 88%, making them an ideal candidate for the large bandgap junction in tandem solar cells. V_{oc} 's above 1.0 V are obtained when the polymer is blended with multiadduct fullerenes; however, the photocurrent and fill factor are greatly reduced. In PBDTTPD blends with multiadduct fullerene ICBA, fullerene emission is observed in the photoluminescence and electroluminescence spectra, indicating that excitons are recombining on ICBA. Voltage-dependent, steady state and time-resolved photoluminescence measurements indicate that energy transfer occurs from PBDTTPD to ICBA and that back hole transfer from ICBA to PBDTTPD is inefficient. By analyzing the absorption and emission spectra from fullerene and charge transfer excitons, we estimate a driving free energy of -0.14 ± 0.06 eV is required for efficient hole transfer. These results suggest that the driving force for hole transfer may be too small for efficient current generation in polymer:fullerene solar cells with V_{oc} values above 1.0 V and that non-fullerene acceptor materials with large optical gaps (>1.7 eV) may be required to achieve both near unity internal quantum efficiencies and values of V_{oc} exceeding 1.0 V.

respectively. While much synthetic research has focused on the development of lower bandgap materials with absorption spectra that better match the solar irradiation spectrum,^[1,2,5] new materials will also be required which maximize the photovoltage obtained from absorbed photons. Many organic photovoltaic materials have optical bandgaps in the range of 1.7–2.0 eV, which make them suitable for the large bandgap junction of a tandem solar cell. However, the highest efficiency all-organic tandem solar cells reported thus far only obtain open-circuit voltages (V_{oc} 's) of 0.9 V or less from the large bandgap junction.^[4,6]

Internal quantum efficiencies (IQEs) approaching 100% have been demonstrated in single junction polymer:fullerene BHJ solar cells.^[3,7] In order to generate and extract charges with high quantum efficiency from bound photogenerated excitons, a heterojunction is employed where the ionization potential and electron affinity of the fullerene are substantially higher than for the polymer, providing

sufficient free energy (ΔG) for charge transfer and exciton dissociation. Consequently, in the most efficient BHJ devices, the V_{oc} is 0.7–1.0 V less than the optical bandgap potential of the individual materials, E_g/q .^[1–3,5,7] The C₆₀ and C₇₀ fullerene derivatives currently employed in organic solar cells with efficiencies above 4% have an optical bandgap of 1.7 eV. Although there have been reports of polymer:fullerene devices with V_{oc} values above 1.0 V,^[8–10] and as high as 1.15 V,^[11] all of these

1. Introduction

Solution-processed organic solar cells offer the potential to provide solar energy at a lower cost than conventional photovoltaics due to scalable printing manufacturing and low materials costs. Polymer:fullerene bulk heterojunction (BHJ) solar cells have recently achieved power conversion efficiencies over 7%^[1–3] in single junction and 8%^[4] in organic tandem devices,

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devices suffer from poor currents and fill factors. The development of materials that produce V_{oc} values exceeding 1.0 V in single junction devices without sacrificing IQE will be crucial for improving the performance of multijunction organic solar cells.

It is not currently understood what fundamentally limits the minimum free energy for charge transfer in high quantum efficiency devices. Transient absorption studies have indicated that the yield of charges decreases as the magnitude of ΔG for electron transfer from the polymer to the fullerene is reduced.^[12,13] In high voltage devices, the polymer typically has a larger bandgap than the fullerene. Energy transfer has been demonstrated to occur from larger bandgap polymers to fullerenes in many blend combinations,^[14–16] and consequently the free energy of hole transfer from the fullerene to the polymer is crucial for charge generation.^[8,17] Recently, Coffey et al. examined the dependence of charge generation on the driving force for hole transfer from the fullerene to several optically transparent polymers using transient microwave photoconductivity (TRMC).^[18] Surprisingly, an optimal ΔG for charge generation was observed as the yield of carriers was found to increase with the magnitude of ΔG up to a point and then decrease with larger driving free energies for hole transfer. The ΔG needed for efficient charge generation, as estimated from the band energy offsets between the pure materials measured by cyclic voltammetry, has been reported to vary from -0.1 to -0.9 eV.^[13,18] However, no clear correlation has been observed between the required ΔG for efficient charge generation and any measurable material properties, limiting insight into how to engineer materials that minimize the magnitude of ΔG required for efficient charge generation.

In this article, we investigate charge generation in state-of-the-art high voltage BHJ solar cells based on poly(di(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene-*co*-octylthieno[3,4-*c*]pyrrole-4,6-dione) (PBDTTPD), which has attracted great interest since it was independently discovered by several research groups.^[19–21] We demonstrate a power conversion efficiency over 7%, an IQE of 88% and a V_{oc} of 0.945 V in blends of PBDTTPD and [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM), making PBDTTPD the most attractive polymer available for the large bandgap junction of a tandem device. We find that we can increase the voltage above 1.0 V by replacing PCBM with indene- C_{60} bis-adduct (ICBA); however, the fill factor and current are reduced. In PBDTTPD:ICBA blends, fullerene emission is observed in the photoluminescence (PL) and electroluminescence (EL) spectra, indicating that excitons are recombining on ICBA. Steady-state and time-resolved PL measurements indicate that energy transfer occurs from PBDTTPD to ICBA, and that the back hole transfer process to form charges is slow and inefficient.

We calculate the driving free energy for hole transfer by accurately measuring the difference in energy between the two states involved in the process, the fullerene singlet exciton and the interfacial charge transfer (CT) exciton, using a combination of EL and sub-bandgap photocurrent spectral measurements from polymer:fullerene blend devices and fullerene-only diodes. This method is able to account for the reorganization energy of excited states and the energetic interactions between the polymer and fullerene, providing a more accurate

measurement of ΔG than estimates based on the pure material band energies or EL spectra alone. We find that $\Delta G = -0.20$ eV in the efficient PBDTTPD:PCBM devices, while PBDTTPD:ICBA devices have $\Delta G = -0.02$ eV, which is too small for efficient hole transfer. These results suggest that the voltage cannot be raised above ~ 1.0 V without increased recombination of excitons on the fullerene, due to an insufficient driving force for hole transfer. Consequently, the open circuit voltage of efficient polymer:fullerene solar cells may be limited by the optical bandgap of fullerenes.

2. Results and Discussion

2.1. Device Performance Comparison with Two Different Fullerenes

PBDTTPD has previously demonstrated power conversion efficiencies of 6.8% in bulk heterojunction devices with $PC_{61}BM$,^[19] and recently a power conversion efficiency of 7.1% and V_{oc} of 0.93 V were achieved using a combination of two solvent additives.^[22] We were able to achieve a slightly improved voltage (0.945 V) and efficiency (7.3% record, 7.1% average) with a higher molecular weight ($M_n = 41$ kDa, PDI = 1.8) batch of the polymer using a weight blend ratio of 1:1.5 (polymer:fullerene) and an optimal active layer thickness of 100 nm (Figure 1). We found that we did not need to use any solvent additives to optimize these devices, unlike the previous reports.^[19,22] The external quantum efficiency (EQE) and IQE of the PBDTTPD:PCBM devices are shown in Figure 2a. The IQE was determined from a combination of integrating sphere measurements and transfer matrix simulations in order to accurately account for light scattering and parasitic absorption by the electrodes.^[23] We calculate a wavelength independent IQE of 88% which rivals the highest performing polymers to date.^[3,7] These devices have a similar photocurrent action spectral range as poly-3-hexylthiophene (P3HT)-based devices, but have values of V_{oc} that are about 0.10 V higher than those obtained with the P3HT:ICBA devices commonly used in the highest performing tandem solar cells.^[4] Consequently, we expect PBDTTPD:PCBM to be a superior candidate for the large-bandgap junction of tandem devices.

ICBA has a lower electron affinity than PCBM and has been shown to improve the V_{oc} and efficiency of P3HT solar cells by reducing the energy lost during the charge transfer process.^[24,25] We fabricated PBDTTPD:ICBA devices to determine whether the voltage and power conversion efficiency of PBDTTPD-based devices could similarly be increased. While the voltage of the devices increased to 1.09 V, both the short-circuit current density and fill factor dropped significantly, reducing the power conversion efficiency to 2.7%. To confirm that the low efficiency of the PBDTTPD:ICBA devices was not a consequence of impurities in our ICBA, we fabricated P3HT:ICBA devices that performed comparably to literature reports and obtained power conversion efficiencies of 6.0%, with V_{oc} of 0.84 V.^[26]

To determine the cause of the reduced current and fill factor in PBDTTPD:ICBA devices, the EQE and IQE were measured as a function of wavelength and light intensity (Figure 2). The

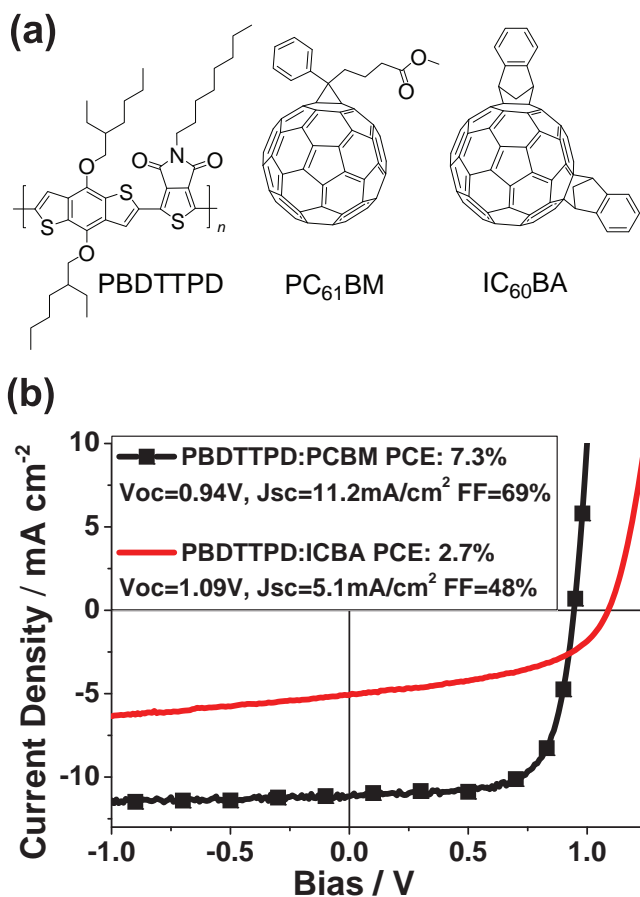


Figure 1. a) Chemical structures of PBDTTPD, PCBM and ICBA. b) Current-voltage behavior of 1:1.5 (by weight) PBDTTPD:ICBA and PBDTTPD:PCBM.

ICBA devices optimized at a slightly thinner thickness (90 nm) than the PCBM devices (100 nm), and had a similar absorption. However, the ICBA devices had an IQE of about half (46%) that of the PCBM devices (88%) (Figure 2a), indicating that the difference in performance is a result of inefficient electrical or excitonic processes in PBDTTPD:ICBA devices. The impact of light intensity on the external and internal quantum efficiencies was investigated by illuminating the devices with a white light bias of variable intensity (I), in addition to illuminating with a weak optically chopped monochromatic probe beam. This method provides a measurement of the differential internal quantum efficiency, ΔIQE ,^[27] which is the IQE of an additional photon absorbed by the device at a given light intensity and wavelength. ΔIQE was found to be relatively independent of white light bias intensity for both device blends (Figure 2b). The average IQE of all photons absorbed in the active layer can then be computed by calculating the average value of ΔIQE up to the light intensity of interest (Equation 1):

$$IQE(I) = \frac{\int_0^I \Delta IQE(I') dI'}{I} \quad (1)$$

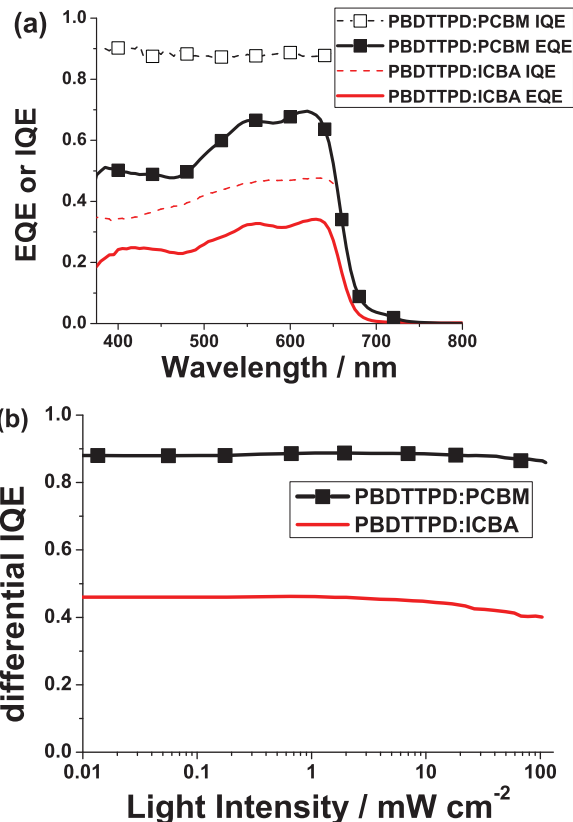


Figure 2. a) External quantum efficiency (solid line) and internal quantum efficiency (dashed) spectra of PBDTTPD:PCBM and PBDTTPD:ICBA devices. b) Differential IQE of both devices at 550 nm as a function of white light bias intensity (I).

At 550 nm and 100 mW cm⁻², we calculate an 87% IQE for the PCBM devices and 43% for the ICBA devices. Comparing these values to the IQE measured at low-light intensities, we estimate bimolecular losses to account for 1.3% of the recombination in the PCBM devices and 3.1% in the ICBA devices at short-circuit. These amounts of recombination, and the difference between them, are too small to explain the large difference in short-circuit current and indicate that neither bimolecular recombination nor space charge effects are responsible for the poor performance of the ICBA devices.

2.2. Recombination of ICBA Excitons at the Heterojunction Interface

Steady-state photoluminescence (PL) quenching studies were performed on the polymer:fullerene blends to probe the exciton harvesting efficiency and to determine which excited state species form. At the excitation wavelength of 515 nm, the polymer is responsible for 85% of the device absorption. Over 99.7% of the polymer photoluminescence is quenched in PBDTTPD:PCBM, and 99.4% is quenched in PBDTTPD:ICBA, indicating that nearly all excitons in the polymer phases are created close enough to an interface to be quenched in both devices

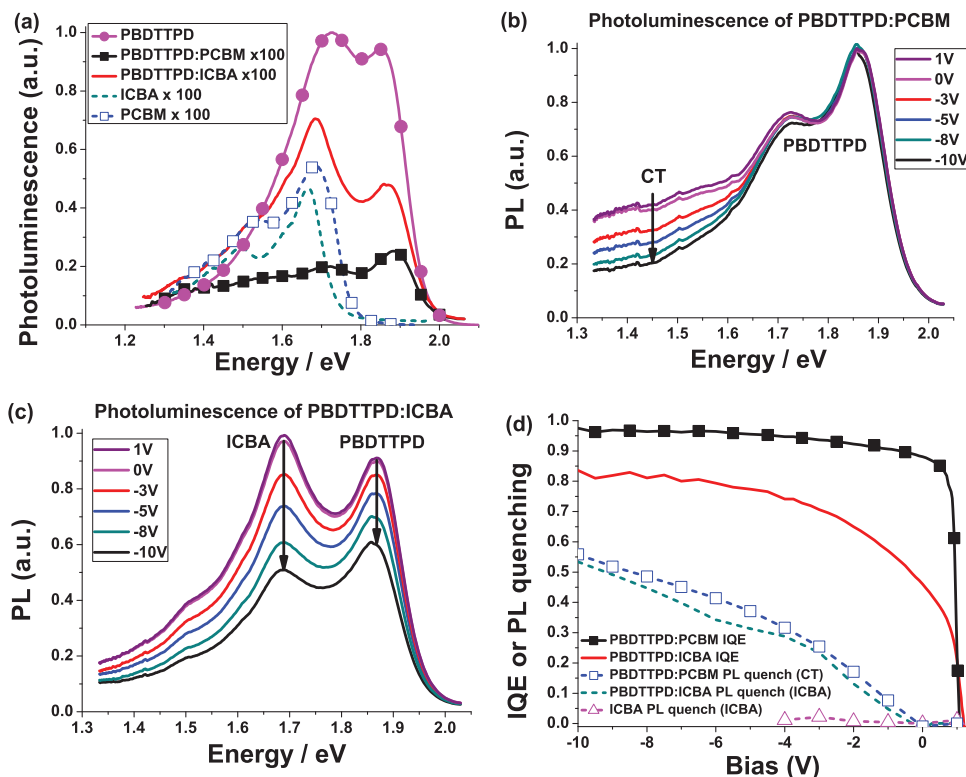


Figure 3. a) Photoluminescence of films, accounting for the fraction of excitation light (at 515 nm) absorbed in each sample. Voltage dependent photoluminescence spectra of b) PBDTTPD:PCBM and c) PBDTTPD:ICBA devices. d) Voltage dependence of the IQE at 550 nm for PBDTTPD:PCBM and PBDTTPD:ICBA devices and PL quenching of CT emission (at 1.45 eV) in PBDTTPD:PCBM and ICBA emission (at 1.69 eV) in the PBDTTPD:ICBA devices and ICBA only devices. The PL quenching fraction was computed from the ratio of the PL at each voltage to the PL at open-circuit voltage.

(Figure 3a). By carefully examining the shape of the residual PL spectrum we can identify the emissive excited species that are formed. The PL from PBDTTPD:PCBM shows luminescence predominately from the polymer, which comes from regions of the film that are too far from the interface with fullerenes for exciton dissociation to occur. The PL from PBDTTPD:ICBA blends has a component that is similar to the polymer emission from the PBDTTPD:PCBM, but also has a component centered at 1.69 eV that is similar to the PL from a pure ICBA film. By deconstructing the PBDTTPD:ICBA PL spectra into emission from the pure polymer and fullerene (Figure S1), we estimate that the ICBA emission from the blend is ~78% as strong as from pure ICBA films. It is remarkable that the fullerene PL quantum efficiency emission is so high from PBDTTPD:ICBA blends considering that 85% of excitons start on the polymer. These results indicate that excitons initially generated on the polymer are undergoing energy transfer to ICBA in high yield and are inefficiently quenched by the heterojunction.

There are two possible causes for inefficient quenching of fullerene excitons. The excitons may be formed in large fullerene domains and are unable to reach the heterojunction before they recombine, or they may reach the heterojunction but are unable to undergo hole transfer before recombining. Given that most of the excitons on ICBA are initially generated on the polymer in PBDTTPD:ICBA, it seems unlikely that the ICBA excitons would have difficulty reaching the heterojunction interface.

To confirm that the ICBA emission from PBDTTPD:ICBA blends is a result of inefficient hole transfer at the interface, the photoluminescence spectra were measured as a function of the applied bias voltage and compared to those of the high efficiency PCBM devices. Reverse bias voltages have been shown to help dissociate interfacial states at the heterojunction, resulting in increased quenching of the luminescence from these states.^[28–31] On the other hand, an applied bias has a much weaker effect on the emission of excitons in the bulk of pure materials, as the electric field is insufficiently strong to efficiently dissociate the tightly bound Frenkel excitons without the help of a heterojunction interface. In the efficient PBDTTPD:PCBM devices (Figure 3b), the photoluminescence from the polymer above 1.65 eV is voltage independent which we attribute to excitons formed in the largest polymer domains that are unable to reach the heterojunction interface before emitting. At lower emission energies, the photoluminescence is quenched with increasing reverse bias which can be explained by field-assisted dissociation of luminescent charge transfer excitons, a phenomena which has been previously reported for other polymer:fullerene devices.^[28–30]

In contrast, for the PBDTTPD:ICBA devices (Figure 3c), the higher energy features at 1.69 eV and 1.87 eV, identified as emission from the fullerene and polymer respectively, are both voltage dependent. We note that the photoluminescence quantum efficiency of ICBA is about two orders of magnitude lower than that

of PBDTTPD (Figure 3a), indicating that significantly more excitons end up on the fullerene than on the polymer. We will thus focus on understanding the cause for ICBA emission which is a more significant problem in these devices. Applying a bias to ICBA-only diodes does not appreciably quench the PL emission (Figure 3d) until voltages were reached where appreciable leakage current ($>10 \text{ mA cm}^{-2}$) reduced the photoluminescence efficiency. This observation shows that the applied electric field is not sufficient to efficiently dissociate excitons in the interior of a fullerene phase. It therefore confirms that the substantial fullerene emission in PBDTTPD:ICBA is not the result of emission from fullerene excitons formed far from the fullerene-polymer interface. We find that quenching of the fullerene emission in PBDTTPD:ICBA devices has a similar voltage dependence as the quenching of CT emission in PBDTTPD:PCBM devices (Figure 3d). These results demonstrate that the observed ICBA emission originates from excitons at the heterojunction interface, which unlike those in pure ICBA films, can be more easily dissociated by an electric field, in a similar manner to CT states in efficient PBDTTPD:PCBM devices. A reverse bias is also expected to reduce the recombination of charge pairs or CT states, which may regenerate excitons^[32] on the fullerene, resulting in the observed fullerene emission.

We note that the PL quantum efficiency of fullerenes is less than 0.1%,^[33] and consequently fullerene PL quenching studies are only able to probe a small fraction of photogenerated excitons. We compared the voltage dependence of the IQE to the quenching of the fullerene photoluminescence to determine if the observed recombination of luminescent excitons on the fullerene can account for the reduction in current in PBDTTPD:ICBA devices. The ICBA PL quenching has a different voltage dependence than the IQE, and is more field dependent in reverse bias (Figure 3d). With PBDTTPD:PCBM devices, we also see that the CT PL is more field dependent than the photocurrent in reverse bias, as has been previously demonstrated for other polymer:fullerene devices.^[28,30] These results indicate that the behavior of fullerene PL cannot quantitatively explain the recombination in the PBDTTPD:ICBA devices. Due to the low PL quantum efficiency of fullerenes, dark states not observed from PL studies, such as fullerene triplet excitons, are expected to play a large role in the recombination process. These non-emissive states may generate charges with a weaker voltage dependence than emissive states.

2.3. Energy Transfer to ICBA and Inefficient Back Hole Transfer

Time-resolved photoluminescence measurements by time-correlated single photon counting (TCSPC) suggest that fullerene exciton quenching in PBDTTPD:ICBA devices is slower than in efficient PBDTTPD:PCBM devices (Figure 4a). The emission at 1.69 eV, which is at the peak of the fullerene emission but also where the polymer emits, decays with a lifetime of 0.65 ns in the PBDTTPD:ICBA blend devices during the first few nanoseconds. This is faster than the unquenched ICBA radiative lifetime (1.5 ns), but slower than the decay rate at 1.69 eV in PBDTTPD:PCBM devices that are instrument response limited at early times. We note that photoinduced charge transfer is well known to occur on sub-picosecond time scales in devices

with a large driving free energy for charge transfer.^[34] The slow, nanosecond time scale for quenching of the ICBA fluorescence may suggest that there is a quantum mechanical mixing of charge transfer exciton and fullerene exciton states at the interface which are close to each other both in energy and spatially. Applying a reverse bias to PBDTTPD:ICBA devices results in an increased initial fullerene PL decay rate (Figure 4b), suggesting that the electric field helps dissociate interfacial ICBA excitons that are having difficulty undergoing hole transfer to the polymer.

Based on the steady-state and time-resolved PL measurements, we propose a mechanism to explain the observed fullerene emission and poor current generation in PBDTTPD:ICBA devices. In PBDTTPD:PCBM devices, excitons on the polymer can undergo energy transfer to the fullerene followed by efficient back hole transfer due to the large driving free energy for charge transfer (Figure 4c). In PBDTTPD:ICBA devices, the difference in ionization potential between the two materials is smaller (Figure 4d). Consequently, hole transfer from ICBA to the polymer is less efficient, and a significant fraction of excitons on the fullerene recombine before they are able to undergo charge transfer. A similar pathway has been proposed for polymer:fullerene devices based on a family of large bandgap polyfluorene polymers where charge generation was observed to be less efficient when the driving force for hole transfer was small.^[14,16]

The photoluminescence studies show that over 99% of the polymer PL is quenched, indicating the absence of very large polymer domains. Although the fullerene emission in the ICBA-based device is not substantially quenched, we have shown that this is not emission from coarse fullerene phases. Instead, the emission results from energy transfer from the polymer to fullerene molecules near the interface, followed by ineffective hole transfer back to the polymer. We therefore can conclude that the morphologies for both PCBM and ICBA devices are sufficiently fine to ensure that photogenerated excitons reach an interface. On the other hand, morphologies that are too finely mixed can impede charge extraction and have been shown to result in increased geminate recombination in some polymer:fullerene devices.^[34,35] We have recently demonstrated that ICBA intercalates between the side chains of the polymer PBTTT in a configuration in which the fullerene substituents may hinder electron transport.^[36] While PBDTTPD:fullerene blend films are too disordered to discern variations in packing structures with different fullerenes, we observe from transmission electron microscope (TEM) images that PBDTTPD:ICBA blend films have a less defined morphology than PBDTTPD:PCBM (Figure S2). It is possible that a suboptimal PBDTTPD:ICBA blend morphology, in addition to a slow hole transfer rate from ICBA to PBDTTPD due to an insufficient driving free energy for hole transfer, may also play a role in the increased geminate recombination of these devices.

2.4. Determination of Charge Transfer Energy and Driving Free Energy for Hole Transfer

To determine the free energy required for efficient hole transfer and photocurrent generation in PBDTTPD:fullerene devices,

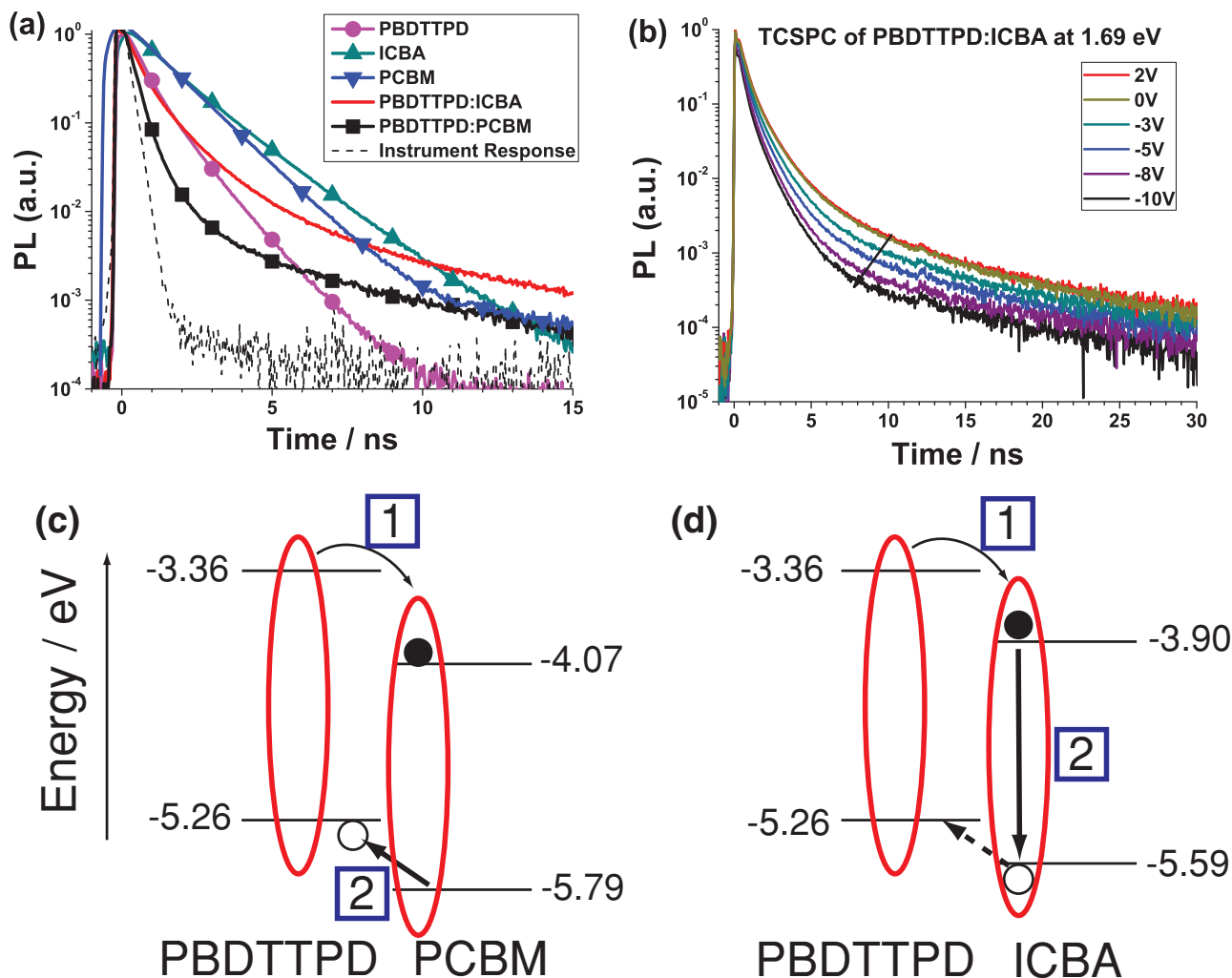


Figure 4. a) Time correlated single photon counting (TCSPC) of optical films, with an excitation energy of 2.58 eV and emission energy of 1.69 eV. The instrument response is also shown and the measurement has a resolution of 0.2 ns. b) TCSPC at the fullerene peak emission (at 1.69 eV) from PBDTTPD:ICBA devices under different bias voltages. Proposed charge generation and recombination mechanism for c) PBDTTPD:PCBM devices and d) PBDTTPD:ICBA devices on a band energy diagram. The PBDTTPD band energies were determined by a combination of photoelectron spectroscopy in air and the optical bandgap, while the fullerene band energies were determined from the cyclic voltammetry reduction potential^[56] and the optical bandgap. The PCBM containing devices can undergo energy transfer from the polymer to the fullerene followed by efficient back hole transfer. In the PBDTTPD:ICBA devices, hole transfer from the ICBA to polymer is slow and recombination of fullerene excitons is observed.

the energy of the fullerene singlet exciton and the CT state involved in the hole transfer process were determined from the absorption and emission spectra of these states.^[37] Although the CT energy is often approximated by the difference in energy between the polymer's highest occupied molecular orbital (HOMO) and the fullerene's lowest unoccupied molecular orbital (LUMO), this method does not account for interactions between the polymer and fullerene, such as interface dipoles^[38] or morphological or conformation changes upon mixing,^[39,40] which will shift the CT energy. The CT and fullerene emission spectra were measured using electroluminescence. An advantage of electroluminescence over photoluminescence in observing CT emission is that it is more likely to generate excitations at the donor-acceptor interface instead of generating excitons in the interior of polymer of fullerene domains.^[30]

Since CT states are only weakly emitting in polymer:fullerene blends, their PL spectra can be hard to resolve when there is significant residual PL from the pure materials.

The EL spectra of the PBDTTPD:PCBM devices show a distinct CT emission peak at 1.24 eV which is easily distinguished from the EL from either PBDTTPD (~1.73 eV) or fullerene (~1.67 eV for both PCBM and ICBA) only diodes (Figure 5). On the other hand, the EL spectra from the PBDTTPD:ICBA devices shows a mixture of broad CT emission, peaking between 1.4–1.5 eV, and ICBA emission. We estimate the CT state EL emission spectra in the PBDTTPD:ICBA devices by subtracting the EL spectrum of the ICBA-only diodes from the PBDTTPD:ICBA EL spectra.

The presence of ICBA emission in the PBDTTPD:ICBA EL spectra indicates that injected charges are recombining

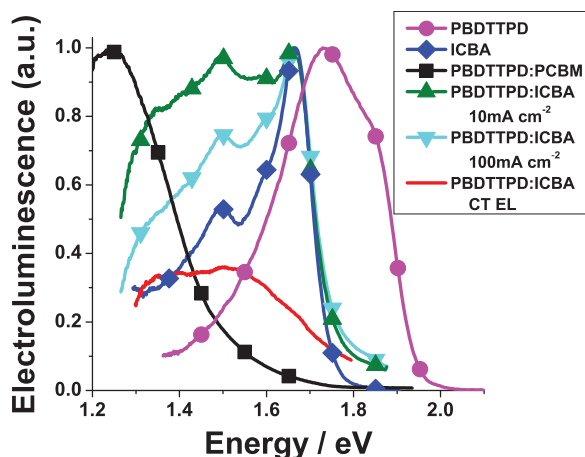


Figure 5. Electroluminescence spectra of PBDTTPD, ICBA, PBDTTPD:PCBM and PBDTTPD:ICBA. The bias current was 100 mA cm^{-2} except where specified otherwise. The electroluminescence from CT states in the PBDTTPD:ICBA devices (red) was estimated by subtracting the EL spectrum of the ICBA only diodes from the PBDTTPD:ICBA EL spectra.

bimolecularly on ICBA under forward bias conditions similar to open-circuit voltage (injected dark current $\sim 10 \text{ mA cm}^{-2}$). While the EL spectra can provide some insight to the excited states formed under photovoltaic operation,^[8] it is difficult to estimate the yields of these excited states, unlike from PL measurements. Electroluminescence quantum efficiencies^[37] and spectral shapes^[28] can be highly bias voltage dependent. We find that applying a higher forward bias current (100 mA cm^{-2}) to PBDTTPD:ICBA results in a larger amount of EL from the ICBA relative to CT states (Figure 5), which may be the result of increased injection of holes into the fullerene at large forward biases that are not relevant for solar cell operation. Charge transport also appears to have a complicating impact on the shape of the EL spectra by influencing the phases through which injected charges are transported and recombine. We find that the amount of fullerene EL is increased when the fullerene content of the blend film (and thus charge transport through the fullerene) is increased (Figure S6b). When PBDTTPD was blended with several multiadduct fullerenes known to have worse electron transport than PCBM,^[41] strong EL was observed from the polymer (Figure S5b) despite PBDTTPD having a larger bandgap than the fullerenes. These results demonstrate that the states observed from EL measurements might not be representative of the states involved in recombination under normal photovoltaic device operation (low injection currents).

The CT absorption spectra were determined by measuring sub-bandgap photocurrent generation in the blend devices. Sub-bandgap EQE spectra were taken on the two blend devices as well as on diodes containing either the pure polymer or fullerene. Devices with efficient charge generation have been shown to have a strong CT absorption band in the sub-bandgap region.^[17] The PBDTTPD:PCBM devices show a shoulder below 1.6 eV that is not present for either the PBDTTPD or the PCBM diodes, and is attributed to photocurrent generation from directly exciting CT states (Figure 6a). In contrast, no

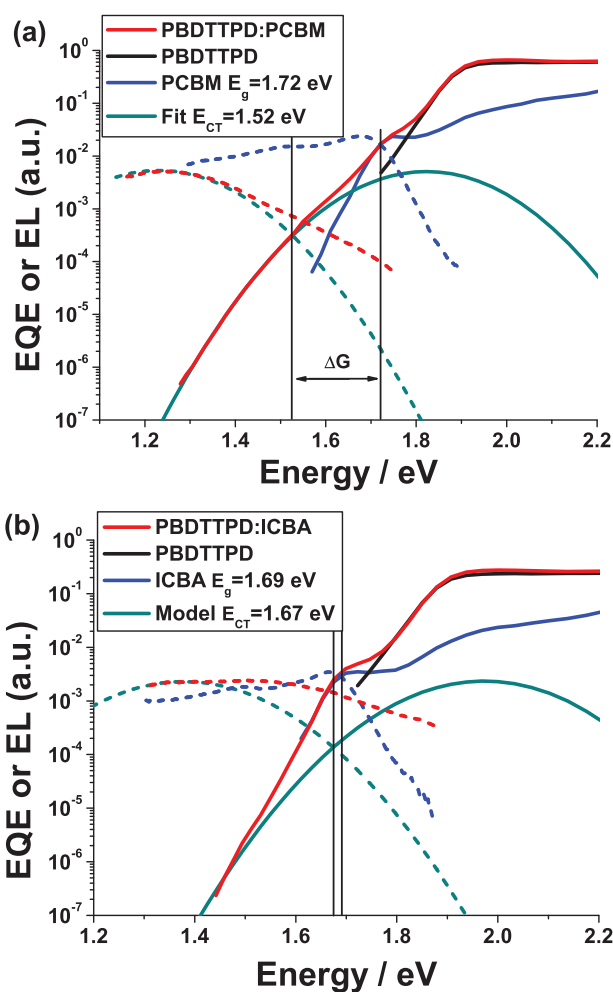


Figure 6. a) EQE (solid lines) and EL (dashed lines) of PBDTTPD:PCBM, PBDTTPD and PCBM-only devices, and a fit to determine the charge transfer energy. b) EQE (solid lines) and EL (dashed lines) of PBDTTPD:ICBA, PBDTTPD and ICBA only devices, and the modeled CT emission and absorption spectra assuming a charge transfer energy of 1.67 eV. The EL spectra shown for the PBDTTPD:ICBA blend is the CT emission spectra estimated by subtracting the ICBA EL from the PBDTTPD:ICBA EL spectra (see Figure 5). The EQE spectra of the pure material devices were scaled in magnitude to overlay the features in the blend spectra.

distinct CT absorption band is observed in the EQE spectrum of PBDTTPD:ICBA devices; the spectrum resembles a combination of the pure polymer and fullerene spectra (Figure 6b).

We use both the absorption (EQE) and emission (EL) spectra to estimate the energies (relative to the ground state) of the excited states involved in the hole transfer process in order to determine the free energy, ΔG , for charge transfer. In organic materials, the peak emission from an electronic state is red-shifted to the absorption peak by the Stokes shift. Fullerenes typically exhibit small ($<30 \text{ meV}$) Stokes shifts,^[42,43] due to their rigidity and symmetry. Considerably larger Stokes shifts (0.2–2 eV) are typically observed for CT states of donor-fullerene dyads in organic solvents.^[44] For solid-state polymer:fullerene blends Stokes shifts of about 0.4–0.6 eV have been observed.^[37]

A good estimate for the energy of an excited state is halfway between the absorption and emission peaks for that excited state, which accounts for the energy lost through reorganization of the molecule during both absorption and emission.^[45]

Using this method, we estimate the energy of PCBM and ICBA singlet excitons to be 1.72 eV and 1.69 eV, respectively (Figure 6a and 6b). Determination of the energy of the CT state is complicated by the fact that the CT absorption bands for the blends are partially or fully hidden under the absorption spectra of the blend's pure constituents. For PBDTTPD:PCBM, we can fit the CT absorption shoulder and emission to a model based on Marcus theory,^[37] (see Supporting Information) giving the charge transfer state energy a value of $E_{CT} = 1.52$ eV. This value is 0.58 eV larger than the V_{oc} , which is in agreement with previous observations of E_{CT} being 0.55–0.59 eV larger than the V_{oc} of other polymer:fullerene devices.^[37,46] For PBDTTPD:ICBA devices, it was not possible to unambiguously fit the CT emission and absorption spectra due to substantial overlap with features from the fullerene. If we assume that the charge transfer energy in PBDTTPD:ICBA devices is also 0.58 eV higher than the voltage achieved in these devices, then $E_{CT} = 1.67$ eV, which results in modeled EL and EQE spectra that agree with the measured spectra.

These results suggest that a difference of ~ 0.02 eV between the PBDTTPD:ICBA CT state (~ 1.67 eV) and the ICBA bandgap (1.69 eV) is too small for efficient hole transfer to occur from the fullerene to the polymer. In the PBDTTPD:PCBM devices there is a 0.20 eV difference between the CT state (1.52 eV) and the PCBM singlet state (1.72 eV), which is large enough for efficient charge generation. We also examined the EL and EQE spectra of PBDTTPD:bis-PC₆₁BM (Figure S5c) which has an intermediate CT energy of ~ 1.64 eV and a fullerene bandgap of 1.72 eV. These devices also have low photocurrent and fullerene emission in the blend PL and EL spectra (Figure S5a,b), indicating that ~ 0.08 eV is also insufficient for efficient hole transfer. These results suggest that for PBDTTPD, a driving free energy for hole transfer of 0.14 ± 0.06 eV is required for efficient charge generation.

This minimum energy required for efficient hole transfer is considerably smaller than the value that would be obtained if we estimated ΔG from the difference between the fullerene and CT EL emission peaks, ΔE_{EL} , which is 0.22 ± 0.05 eV for PBDTTPD:ICBA and 0.43 ± 0.02 eV for PBDTTPD:PCBM. Since the Stokes shift of the fullerene is small compared to the CT state Stokes shift, an estimate for ΔG from ΔE_{EL} will overestimate the driving force for charge transfer by roughly half the Stokes shift, i.e. the reorganization energy, of the CT state. We measure a reorganization energy of 0.30 eV for PBDTTPD:PCBM, which is comparable to previously reported values in other polymer:fullerene blends.^[37] These results with PBDTTPD are consistent with a recent study by Faist et al. who reported a minimum ΔE_{EL} of 0.35 ± 0.05 eV for efficient charge generation.^[8]

2.5. Negligible Recombination via Polymer Triplet Excitons

We also investigated the possibility that a triplet recombination mechanism may be responsible for the low current in

PBDTTPD:ICBA devices. It has been proposed that recombination via triplet states becomes a significant loss mechanism when the energy of the triplet lies sufficiently below that of the lowest charge transfer state.^[47] Based on an optical bandgap of 1.90 eV for PBDTTPD, determined from the midpoint between the lowest energy absorption peak and the highest energy photoluminescence peak, and assuming an exchange energy of 0.6 V for a donor–acceptor type polymers,^[35,48] we estimate a triplet energy of ~ 1.3 eV. This value is consistent with photoinduced absorption measurements of the polymer in chlorobenzene solution, where we observed that PBDTTPD triplets were quenched by tetracene ($E_T = 1.27$ eV^[49]) rubrene ($E_T = 1.14$ eV^[49]) and oxygen ($E_T = 0.98$ eV), indicating that triplet excitons will transfer from the polymer to those molecules. Since the CT energy of PBDTTPD:PCBM devices (1.52 eV) and PBDTTPD:ICBA devices (~ 1.67 eV) lie above the triplet energy of the polymer (~ 1.3 eV), we might expect triplet recombination to occur in these devices, and possibly to occur to a different extent (Figure 7a,b).

To determine if charges are being lost to triplet excitons on PBDTTPD in ICBA blend devices, steady-state photo-induced absorption (PIA) measurements were obtained for the pure polymer and blend films using an excitation wavelength of 515 nm. All of the PBDTTPD containing film spectra show a photoinduced Stark effect around the bandgap at 1.9 eV and ground state bleaching at higher energies (Figure 7c). PBDTTPD only films exhibit a T_1 - T_N absorption feature at 0.85 eV, which is lower in energy than many conjugated polymers. This feature was identified as the triplet because it disappeared when the sample was exposed to oxygen. The blend films exhibit a polaron absorption band from 1.3 eV to 1.8 eV with a sharp feature at 1.4 eV. These features are in agreement with the absorption change from oxidatively doping solutions of PBDTTPD with SbCl₅ (Figure S3). We note that the clear separation of the triplet and polaron absorption features is relatively rare for photovoltaic polymers, and the ease of spectral identification and high device efficiency may make this polymer valuable for photophysical study.

No triplet absorption is observed in PBDTTPD:PCBM blends, while the PIA spectra for PBDTTPD:ICBA blend films show a weak triplet absorption around 0.85 eV. The low triplet absorption indicates that the steady state triplet population in PBDTTPD:ICBA films is nearly an order of magnitude less than for pure PBDTTPD. We note that a large excitation power (100 mW cm^{-2}) and a low temperature (15 K) were required to generate enough triplets and slow their recombination in PBDTTPD:ICBA blends to clearly observe the triplets. By measuring the triplet absorption signal at different optical chopping frequencies, we estimate the PBDTTPD triplet lifetime in the pure films to be 100 μs at 15 K (Figure S4). Assuming a triplet absorption cross section of $140,000 \text{ M}^{-1}\text{cm}^{-1}$, estimated from quantum calculations at the TD-B3LYP/6-31G** level, we calculate a triplet yield of $\sim 6\%$ in the pure films, which is comparable to triplet yields in some other fluorescent polymers.^[50] Assuming that the triplet lifetimes in the ICBA blend and pure polymer films are similar, we estimate that the yield of polymer triplets in PBDTTPD:ICBA blends is about 1%, which cannot account for the 50% reduction in photocurrent compared to the PCBM devices. These results indicate that the existence of low

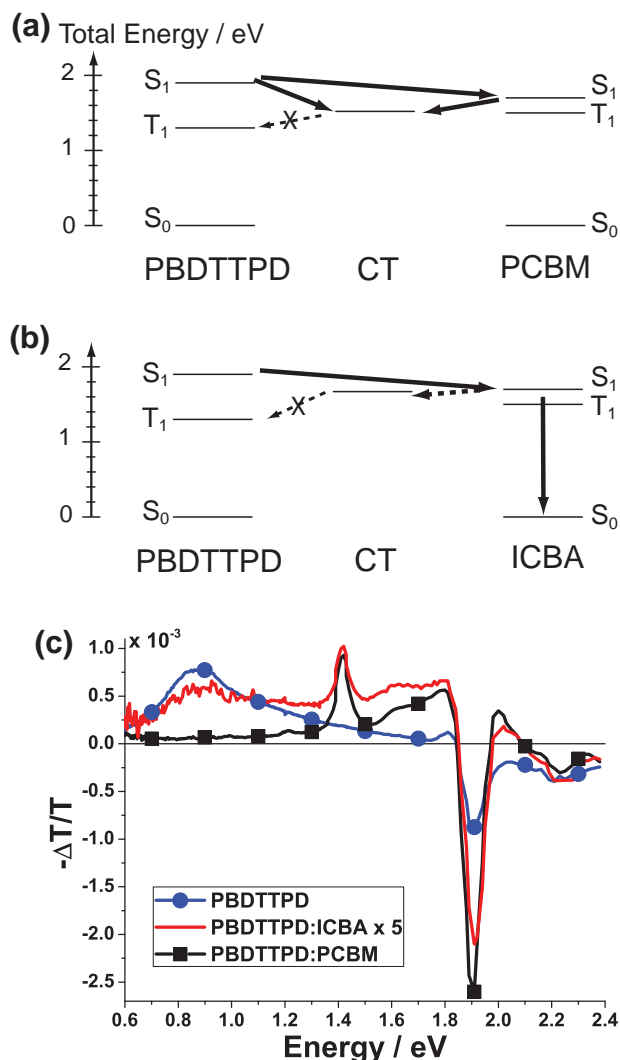


Figure 7. Proposed charge generation and recombination mechanisms in a) PBDTTPD:PCBM and b) PBDTTPD:ICBA, on a Jablonski diagram. Although PBDTTPD triplet formation from CT states, or from fullerene triplets, should be energetically favorable in both blend films, the quasi-steady state photoinduced absorption (PIA) spectra of PBDTTPD containing films (at 15 K using a 2250 Hz optical chopping frequency) c) indicate that triplets are not formed in PBDTTPD:PCBM blends, and few are formed in PBDTTPD:ICBA.

energy triplet states below the charge transfer energy does not necessarily imply that triplet recombination is a significant loss mechanism.

Fullerene triplet excitons have been shown to form as a result of inefficient hole transfer from the fullerene to the polymer in several large bandgap polyfluorene-based polymer:fullerene blends where the charge transfer energy was above 1.6 eV.^[14,16] We are unable to determine if triplets are forming and recombining on ICBA in PBDTTPD:ICBA devices since the weak photoinduced absorption by the fullerene triplet occurs around 1.7 eV^[16] and would be buried by the significantly stronger polymer polaron absorption. The triplet exciton energy of the fullerene ($E_T = 1.5$ eV^[35]) is higher than that of PBDTTPD

($E_T \sim 1.3$ eV), so we might expect ICBA triplets to transfer to PBDTTPD where they would be easily detected. This suggests that not many triplets are formed on ICBA or that the triplet transfer rate from ICBA to PBDTTPD is slow compared to the recombination of triplet excitons. It is currently unclear if fullerene triplet excitons, in addition to the fullerene singlet excitons observed from PL and EL studies, are responsible for the loss in current in PBDTTPD:ICBA devices.

3. Fullerene Exciton Recombination in Other Material Systems

To determine how general is the problem of ineffective hole transfer in high voltage solar devices, we examined several other combinations of polymers and fullerenes with low electron affinity that can be used to make solar cells with $V_{oc} > 1.0$ V. In blends of PBDTTPD with multi-adduct fullerenes bis-PC₆₁BM, and bis-PC₇₁BM ($V_{oc} = 1.06$ V), we observe a decrease in photocurrent and fill factor, disappearance of a CT absorption band, and the appearance of EL and PL from the fullerene (Figure S5). We have also measured fullerene emission when ICBA is blended with another high-efficiency polymer PCDTBT (Figure S6). The short-circuit current of PCDTBT:ICBA devices was about half that of the PCDTBT:PCBM devices. Emission from the fullerene in photoluminescence spectra and/or electroluminescence spectra has been recently reported in blends of bis-adduct fullerenes with the polymers PFODTBT,^[8] MDMO-PPV,^[8] PhanQ,^[9] and PF10TBT,^[10] when the V_{oc} is at or above 1.0 V. Fullerene emission in the PL and EL spectra has also been reported for blends of indene C₆₀ mono-adduct (ICMA) with the polymer PFODTBT, which achieves a V_{oc} of just over 1 V, indicating that emissive recombination of fullerene excitons is not specific to multi-adduct fullerenes.^[8]

The prevalence of recombination on the fullerene in high-voltage solar cells suggests that the use of fullerenes may be limiting the voltage that can be obtained in these devices. Our studies of PBDTTPD-based devices suggest that a minimum free energy of 0.14 ± 0.06 eV is required for efficient charge generation, while 0.58 ± 0.01 eV is lost going from the E_{CT} to the potential energy at open-circuit voltage, qV_{oc} . Previous studies on polymer:fullerene devices suggest that roughly 0.25 eV of this loss is due to thermodynamically unavoidable radiative recombination losses, whereas the remaining 0.33 eV is due to nonradiative recombination losses that are not well understood.^[37] Given $E_g = 1.72$ eV for PC₆₁BM, and that other C₆₀ and C₇₀ derivatives have similar bandgaps, this suggests that there is an empirical limit of 1.00 ± 0.07 V for the V_{oc} of polymer:fullerene solar cells. Obtaining larger V_{oc} 's thus may require the development of larger bandgap, non-fullerene acceptor materials where the band energy levels can be more easily changed by chemical functionality modifications than for fullerenes. Through energy level engineering, non-fullerene acceptor organic solar cells have achieved V_{oc} values significantly higher than fullerene solar cells,^[51,52] and as high as 1.4 eV.^[53] With the highest efficiency non-fullerene device reaching 3.4% to date,^[54] continued research is required to understand how to improve the quantum efficiency of these devices.

4. Conclusion

We have demonstrated V_{oc} values of 0.94 V with BHJ solar cells of PBDTTPD:PCBM, making these devices the highest voltage single junction organic solar cells that can achieve 7% power conversion efficiency. We find values of V_{oc} of almost 1.1 V can be obtained in PBDTTPD:ICBA devices, but the current and fill factor are reduced. We observe voltage dependent emission from the fullerene in the PL and EL spectra from these devices as well as the disappearance of a CT absorption band, suggesting that the CT energy is too close in energy to the fullerene bandgap for there to be a sufficient driving force for efficient hole transfer from the fullerene to the polymer. Through detailed analysis of the EQE and EL spectra, and accounting for the large Stokes shift of the CT state, we estimate that a driving free energy of 0.14 ± 0.06 eV is required for efficient charge generation. We calculate an empirical maximum for the open-circuit voltage of 0.72 ± 0.07 V less than E_g/q for both materials used in the device. These observations suggest that the voltage may be limited by the fullerene bandgap and that non-fullerene acceptors materials may be required for devices to achieve voltages above 1.0 V and near unity quantum efficiencies.

5. Experimental Section

Materials: ICBA and ICTA were generously provided by Plextronics, while PCBM and bis-PCBM were purchased from Nano-C. **PBDTTPD** synthesis and purification: 1,3-dibromo-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (400 mg, 945 μ mol), (4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (708 mg, 917 μ mol) and chlorobenzene (16 mL) were combined in a 100 mL Schlenk flask and degassed with nitrogen for 25 min. Tris(dibenzylideneacetone) dipalladium(0) (26.0 mg, 28.4 μ mol) and tri-*o*-tolylphosphine (34.5 mg, 113 μ mol) were added to the flask and the reaction mixture was stirred for 24 h at 110 °C. Strong complexing ligand N,N-diethyl-2-phenyldiazene-carbothioamide (250 mg, 1.13 mmol) and chloroform (20 mL) were added to the reaction mixture at 55 °C to remove residual catalyst before precipitating the reaction contents into methanol (300 mL). The precipitate was filtered through a Soxhlet thimble and purified via Soxhlet extraction for 2 h with methanol, 9 h with dichloromethane and was finally collected in chlorobenzene. The chlorobenzene solution was then concentrated by evaporation, precipitated into methanol (400 mL) and filtered to yield 648 mg of a dark purple solid (97%). SEC analysis: $M_n = 41$ kDa, $M_w = 75$ kDa, PDI = 1.8.

Device Fabrication: ITO patterned glass substrates (Xinyan Technologies LTD) were cleaned by sequential ultrasonic baths in detergent, water, acetone and isopropanol, followed by UV-ozone treatment. PEDOT-PSS (Clevios P VP Al 4083) was spun-cast and baked at 140 °C. The active layers were spun-cast at 115 °C from solutions of 1:1.5 by weight PBDTTPD:fullerene in chlorobenzene, which had been dissolved overnight. A total solution concentration of 20 mg mL⁻¹ was used for the PBDTTPD:PCBM devices to produce active layer thicknesses of 100 nm, while 15 mg mL⁻¹ was found to be optimal for the multiadduct fullerene blends (active layer thicknesses ~90 nm). 7 nm of calcium, followed by 150–200 nm of aluminum, was thermally evaporated under vacuum ($< 10^{-7}$ torr) to provide the cathode electrode.

Spectroscopic Characterization: Photoluminescence and electroluminescence spectra were measured using a spectrograph (Acton Research SpectraPro 500i) equipped with a silicon CCD array detector (Hamamatsu), and were corrected for the instrument response and the Jacobian for converting from wavelength to energy. External quantum efficiency^[46] and time-correlated single photon counting (TCSPC)^[55] were performed as described in the references herein. Quasi-steady state

photoinduced absorption measurements^[56] were performed on films on quartz substrates at 15 K with an excitation power of 100 mW cm⁻² at 488 nm and a chopping frequency of 2250 Hz.

Supporting Information

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

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