Role of Charge Transfer States in P3HT-Fullerene Solar Cells

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ABSTRACT: By examining poly(3-hexylthiophene)-fullerene blend solar cells with controlled variations of the active layer using subgap external quantum efficiency combined with intensity dependent quantum efficiency at short circuit, a direct correlation between trap-assisted recombination parameters and the charge transfer state absorption strength is established. Most significantly, by comparing devices with different polymer molecular weight, regioregularity, C60 derivative chemistry, and film drying speed, we find that samples with higher trap-assisted recombination exhibit higher charge generation efficiency. Both findings are in support of the general view that the charge transfer states are involved in both processes. In addition, we find that the traps are full at about 100 mW/cm2, which suggests, together with the correlation with the charge transfer states, that the electrochemical potential difference in the bulk exceeds the open circuit voltage and that the loss of voltage is probably due to recombination associated with charge extraction at the electrodes.

1. INTRODUCTION

Organic photovoltaic cells (OPVs) are the subject of extensive research and development as they emerge to become a low cost, easy to produce, flexible, and efficient solution for converting solar energy into electrical power.1−4 One of the most studied structures of the organic solar cells is the bulk-heterojunction (BHJ) configuration, in which the donor and acceptor molecules are judiciously mixed to achieve high interfacial area.5,6 To design more efficient OPVs there is a need to identify the physical processes that govern the operation of these devices,7 quantify their relative importance, and understand how to manipulate and control them.8 Unfortunately, because multiple processes contribute to the observed response of the OPV devices, analysis using overly simplified models is often inadequate. For example, quantum efficiency measurement is a ratio of the measured photocurrent versus the expected photocurrent given the excitation intensity (electrons per photons). However, because various generation and recombination processes exhibit different intensity dependences on the photocurrent, different conclusions pointing to different physical processes can be drawn depending on the intensity range being considered.

To study the generation and recombination and more importantly to be able to differentiate the effects, we developed a technique that is based on sweeping the excitation intensity from ultralow intensity (10−4 Sun) and up to high intensity (a few Sun).9,10 The ultralow intensity regime is often considered irrelevant to solar cells since at such low intensity the "problems" associated with charge recombination within the device and/or at the contacts do not show up. This is exactly why we can use the ultralow intensity to directly measure the free-charge generation efficiency. As we ramp up the intensity the "problems" start to kick in one by one and from their evolution as a function of light intensity we can deduce the mechanisms driving the loss of efficiency. It is well-known that, for molecular systems, the relaxation in energy and the full occupancy of the density of states (DOS) is associated with charge transport required to reach the relevant states.11 When the motion is driven by low electric fields or diffusion this may be a very long process that will only become longer if the temperature is lowered making it very difficult to arrive at a steady state that is relevant to room temperature. Hence, we believe that scanning a wide range of intensity is more adequate to the characterization of working organic solar cells than scanning of temperatures or time scales.

In a recent publication12 we showed that the quantum efficiency loss with increasing intensity can be explained through the combination of Shockley-Read-Hall (SRH)13 type recombination, that is dominant at low excitation intensity, and bimolecular recombination which dominates the high intensity regime.14 We suggested that the bimolecular loss is not necessarily due to free electron−hole recombination (i.e., Langevin), but could also be due to exciton-polaron annihilation.15−18 It was also suggested that the SRH (“recombination center” assisted) recombination is associated with formation of charge transfer (CT) states at the donor−acceptor interface. In addition, the energy of the CT states, often found through the emission spectrum, has been shown to affect the open circuit voltage.8,19−21 Here we strengthen this notion by showing that the loss mechanisms associated with the...
As part of the introduction we briefly summarize the salient features of the model used in ref 12. The model relies on two assumptions that were shown to be valid.12 The first is that under sufficiently low excitation intensity the cell’s internal quantum efficiency is intensity independent and is directly related to the generation efficiency of free charges. The second is that the loss mechanisms associated with nongeminate recombination, as trap assisted or bimolecular, take place at higher excitation intensity. Thus, one can differentiate between the recombination mechanisms through their different intensity dependence.10,12 When considering trap-assisted recombination, this last statement encompasses a hidden assumption that in the dark all the traps are empty. This is of course not 100% true as the contacts do induce charge density near them. However, the detailed model we introduce toward the end of this paper and in Supporting Information show that under short-circuit conditions only ~25 nm close to the contact are filled to a significant extent, thus making the above assumption a reasonable approximation for the short-circuit conditions studied here. With these in mind the equations describing the evolution of excitons (n_ex) and free charges (n_h) can be written as12

\[
\frac{d}{dt}n_{\text{ex}} = G - n_{\text{ex}}K_d - n_{\text{ex}}K_{ep}n_h
\]
\[
\frac{d}{dt}n_h = \alpha n_{\text{ex}}K_d - \mu \frac{V}{d}n_h - R_{\text{Loss}}
\]

\(G\) is the generation rate of excitons, \(n_{\text{ex}}\), through light absorption. These excitons may decay through either recombination or dissociation into free charges at a rate of \(K_d\). Another decay channel for the exciton is through exciton–polaron annihilation with a rate \(K_{ep}n_h\), \(\alpha\) is the fraction of excitons that decayed into free charges and hence \(\alpha n_{\text{ex}}K_d\) corresponds to generation rate of free charges. Equation 1 also shows that the generated charges may either exit the device to form the photocurrent \((\mu n_h V/d)\) or be lost through recombination at a rate \(R_{\text{Loss}}\) where \(V\) is the internal voltage drop.

On the basis of eq 1 and assuming steady state we can write the exciton generation current as

\[
J_G = Gqd = (n_{\text{ex}}K_d + n_{\text{ex}}K_{ep}n_h)qd
\]

If we restrict our analysis to \(V \gg kT\) (i.e., not too close to open circuit voltage where the bands at the center of the device are flat), then we can neglect diffusion currents and write5

\[
J_{PC} = q\mu_e \frac{V}{d}n_e = q\mu_h \frac{V}{d}n_h
\]

With these definitions the quantum efficiency can be written as

\[
\text{QE} = \frac{J_{PC}}{J_G} \equiv \frac{J_{PC}}{J_{PC} + J_{\text{Loss}}}
\]

The loss rates considered are shown in eq 5:

\[
R_{SRH} = C_N[n_hn_h - n_h^2] ; \quad J_{SRH} = R_{SRH}q_d
\]
\[
R_{Lang} = K_{Lang}(n_{\text{ex}}n_h - n_h^2) ; \quad J_{Lang} = R_{Lang}q_d
\]
\[
R_{ep} = n_{\text{ex}}K_{ep}n_h ; \quad J_{ep} = R_{ep}q_d
\]

At low light intensity the main loss mechanisms are sub 100% charge generation efficiency and SRH recombination. In the SRH theory \(C_n\) is the charge capture coefficient, \(N_i\) is the trap or recombination-center density, \(n\) is the intrinsic charge density, and \(\Delta E_i\) is the energy difference between the trap energy \((E_i)\) and intrinsic Fermi energy \((E_F)\) that is close to the middle of the gap. If \(\Delta E_i\) is much larger than \(kT\) one can apply the approximation

\[
2n_i \cos \left( \frac{\Delta E_i}{kT} \right) \approx n_i \exp \left( \frac{E_i - E_F}{kT} \right) = N_{eff} \exp \left( - \frac{E_i - E_F}{kT} \right)
\]

with \(N_{eff}\) being the effective density of states of mobile carriers and \(E_F\) the lowest uncoupled molecular orbital (LUMO) energy. At intensities approaching 100 mW/cm², a new loss mechanism appears with the signature of a bimolecular recombination.12 While this is generally assumed to result from Langmuir–type electron–hole recombination, we showed that the exciton–polaron recombination manifests itself in a very similar manner.12 Moreover, fitting using either model results in rate coefficients that are in agreement with more direct measurements reported in the literature. A third source for extra losses is observed at about 100 mW/cm² intensity due to screening of internal electric field and flattening of the bands,9,23 which becomes significant for charge mobility values below 10⁻² cm²/V s.9 In this paper we fit theQE loss to both SRH recombination and to exciton–polaron annihilation and find good agreement between fitted parameters and published values. We also introduce a full device model and compare its results with the model described above.

In the main part of the paper, we use the above model to systematically study a range of devices in which we change one material or processing parameter at a time and study its effect on the balance of the different loss mechanisms. We vary the acceptor between [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) and indene C₆₀ bis-adduct (ICBA), the drying speed of the film by using chlorobenzene (CB) vs ortho-dichlorobenzene (DCB) as solvents, and P3HT of different molecular weight and regioregularity. We find correlation between the density of recombination centers and the generation efficiency suggesting that for this material system there is an inherent trade-off when increasing interface area to optimize device performance.

2. EXPERIMENTAL SECTION

2.1. Device Fabrication. All OPV devices are processed on top of UV-ozone (Procleaner Plus, Bioforce Nanoscience) cleaned ITO on glass (20 Ω/sq, Thin Film Devices). First, a 20-nm-thick film of ZnO nanoparticles is spin coated onto the cleaned ITO to function as electron transport layer.24 Then, different active layers are processed on top. For P3HT:PCBM devices, a blend of P3HT (Rieke Metals, RMI-001E, P3HT#1) and PCBM (Solenne BV) (1:1 by weight, 25 mg/mL each) in
CB is spin coated at 1200 rpm for 60 s to form a 220-nm-thick active layer. For the fast drying P3HT:ICBA condition, a blend of P3HT#1 and ICBA (Solenne BV) (1:1 by weight, 25 mg/mL each) in CB is spin coated at 1200 rpm for 60 s to form a 200-nm-thick active layer. For slow drying P3HT:ICBA condition, a 200-nm-thick active layer is spin coated from a blend of P3HT#1 and ICBA (1:1 by weight, 20 mg/mL each) solution in DCB at 600 rpm for 60 s, and left in a covered Petri dish to dry overnight. For the different P3HT molecular number (Mn) and regioregularity (H-T ratio) comparison, two slow dried P3HT:ICBA devices were made by the same spin coating procedure, one using P3HT#1:ICBA, the other using a blend of P3HT (Plextronics, OS2100, P3HT#2) and ICBA (1:1 by weight, 17 mg/mL each) solution in DCB. For all processing conditions, the active layers are thermally annealed at 170 °C for 10 min in N₂, followed with evaporation of 5 nm MoO₃ and then 100 nm Ag to complete the device. The area of each device diode is 0.11 cm², and at least 6 diodes were averaged for device parameters per fabrication condition.

2.2. Measurement procedures. The J–V measurements were performed in N₂ filled glovebox under AM1.5G 100 mW/cm² illumination from a class AAA solar simulator (Abet Technologies) using a low-noise sourcemeter (2635A, Keithley) controlled by a LabView program.

The QE measurement setup consisted of a powerful white light LED (Quad SugarCUBE LED Illuminator by Nathaniel Group) the intensity of which could be computer controlled through the LED current level. To broaden the intensity range over 4 orders of magnitude we also used neutral density (ND) filters (Newport). For each excitation intensity the device J–V curve was measured using Keithley 2400 source meter. The intensity scan was done from low to high excitations to minimize the time needed for equilibration at each point and the light intensity was monitored using a calibrated Si photodetector. Care was taken to ensure that the light spot falls within the pixel so as to avoid any potential edge effects. QE was measured from at least 4 diodes to determine the characteristic QE signature for each device type.

3. RESULTS AND DISCUSSION

The energetics for SRH recombination through the CT state is schematically displayed in Figure 1. As shown in Figure 1a, we consider the donor–acceptor blend as an effective medium with band gap determined by the LUMO level of the acceptor and the highest occupied molecular orbital (HOMO) level of the donor. For the general trap assisted recombination model (Figure 1b), one often assumes a single trap or level that is separated from the intrinsic Fermi level (E_F) by ΔE_t and from the nearest transport level by E_b. We show the trap above E_F, but since the SRH formalism is symmetric around E_F, it could equivalently be positioned below E_F. Figure 1c makes use of the fact that recombination losses have been shown to be associated with CT state recombination8,19–21 and the finding reported below of correlation between trap recombination and CT state EQE signature strength. Hence, it shows the same physical chemistry as Figure 1b but in the molecular picture where the total energy of a state, E_CT, is measured relative to the ground state energy. The highest energy is of free electron and hole polarons. The recombination center is the charge transfer state which is shown to have a binding energy (with respect to the free electron–hole) of E_b, and hence an absolute energy of E_CT. The position of E_b/2 is shown for reference only in this sub figure.

3.1. Different Acceptors. The device parameters, fabrication details, and measurement procedures were detailed in the experimental section. The general device structure (Figure 2b inset) consists of the following layer sequence: ITO/ZnO nanoparticles (~20 nm)/active layer (~200 nm)/eMoO₃ (5 nm)/Ag (100 nm). The active layer is composed of a blend of P3HT, donor, and a C₆₀ derivative, acceptor. We
start by comparing two types of devices which are identical in all parameters except for the acceptor material being either PCBM or ICBA. Figure 2a shows the current–density voltage (J–V) characteristics of two such cells. The extracted open-circuit voltage, short-circuit current density, and power conversion efficiency \( (V_{OC}, J_{SC}, PCE) \) for P3HT:PCBM and P3HT:ICBA are \((0.57 \text{ V}, 10.6 \text{ mA/cm}^2, 3.5\%)\) and \((0.79 \text{ V}, 9.9 \text{ mA/cm}^2, 5.1\%)\), respectively. These differences in performance are well documented in the literature.\(^{24}\) To shed light on the loss mechanism leading to the above differences we measured, shown in Figure 2b, the quantum efficiency (QE) of the cells, whose \( J–V \) are shown in Figure 2a, under short-circuit conditions and as a function of excitation light intensity.

When we compare the QEs of P3HT:PCBM (Figure 2b, red solid triangles) and P3HT:ICBA (Figure 2b, blue solid squares) by normalizing both to the low intensity limit for P3HT:PCBM, we find that the P3HT:PCBM device has higher generation rate than the P3HT:ICBA device, consistent with its higher \( J_{SC} \). To analyze the QEs using our model, we normalized the QE for P3HT:ICBA to its low intensity limit (Figure 2b, red open triangles), which exhibits a different shape compared to the P3HT:PCBM curve, indicating a different balance of loss mechanisms. We also note that the data in Figure 2b may appear at first glance to not be in agreement with the systematic studies reported in refs 20 and 25, which showed flat lines. However, our experiments were measured over a wider range of excitation intensities, with maximum values exceeding 100 mW/cm\(^2\), and we zoom in the Y axis to be able to view the fine details.

To extract the loss parameters we fitted the two top curves in Figure 2b to the model described briefly in the Introduction and detailed in ref 12. The curve fits are shown as lines going through the symbols. To extract the energetics parameters shown in Figure 1 we assume the material parameters shown in Table 1. Regarding the parameters in Table 1, one should be aware that reported values for the energy levels of organic semiconductors cover a large range. For example, PCBM is reported to have LUMO between 3.5 eV\(^{26,27}\) and 4.3 eV\(^{28}\) below the vacuum level, but the important parameter for the current paper is that the LUMO of ICBA is \(~0.2 \text{ eV higher}~\) than that of PCBM.\(^{29}\) Similarly, for the HOMO of P3HT there is a range around 5 \text{ eV}.\(^{26,28}\) We choose PCBM LUMO of 3.6 eV and P3HT HOMO of 5 \text{ eV} as the effective bandgap of 1.4 eV matches the value measured in our lab. For the effective density of states we use the common value\(^{11}\) of \(10^{21} \text{ cm}^{-3}\), but we note that an order of magnitude lower density of states would result in a binding energy, eq 6, that is lower by \(2.3kT\) (60 meV).

The independent parameters that can be extracted using the fitting procedures are \( N_{eff} \exp(-E_b/kT) \), \( K_{pp} \alpha K_b \) and \( C_{nN}/\mu \). \( N_{eff} \exp(-E_b/kT)\) is the density of free charges for which the Fermi level coincides with the trap level. In the molecular picture one would say that we find the charge density for which the electrochemical potential difference coincides with the effective or average energy of the charge transfer state. The first column of Table 2 shows this charge density, and since we assume that \( E_b \gg kT \), we may use the Boltzmann approximation to relate the charge density with the binding energy \( (E_b = E_L - E_F) \); see eq 6. Assuming the total density of states to be \(10^{21} \text{ cm}^{-3}\) (Table 1) we deduce \( E_b \) to be 0.3 and 0.35 eV for the P3HT:ICBA and P3HT:PCBM blends, respectively (Table 2, second column). Finally, using the energy levels given in Table 1 we can calculate the effective band gap and deduce the \( E_{CT} \) to be 1.3 and 1.05 eV for the P3HT:ICBA and P3HT:PCBM blends, respectively (Table 2, third column). The uncertainty for the \( E_{CT} \) is quite high due to the large spread of HOMO/LUMO values in the literature. However, we note that \( E_{CT} \) for P3HT:PCBM is in good agreement with values reported by Tvingstedt et al.\(^{30}\) and Veldman et al.\(^{21}\) based on the electroluminescence of the charge transfer state.

The other parameters we extracted using the model’s fit are shown in Table 3. The exciton polaron annihilation parameter \( (K_{pp})\) is identical for the two devices suggesting that the bimolecular loss dominating the high intensity regime is not very sensitive to the change in acceptor. To deduce the trap density based on the extracted \( C_nN/\mu \) one has to know \( C_n \) and \( \mu \) or at least their ratio. For example, if we use literature values\(^{12,31}\) for \( C_n \) \((~10^{-12} \text{ cm}^2 \text{ s}^{-1})\) and \( \mu \) \((10^{-15} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})\) to derive \( N_i \) we arrive at \( N_i \) values shown as (1) in Table 3. Alternatively, if we follow the suggestion by Kuij et al.\(^{32}\) that the capture is different \((C_n \mu = q/e)\), which then gives values for \( N_i \) shown as (2) in Table 3. We are not in a position to state which method is more realistic. Since the ratio of the two results is a constant and we are primarily interested in comparing devices we will report in the following only the values deduced by the second method which relies on \( C_n \mu = q/e )\)\(^{32}\).

The extracted parameters show that P3HT:ICBA exhibits a higher density of recombination centers \( (N_r) \) which we attribute to the smaller tendency of ICBA to phase separate resulting in a higher interface area.\(^{33}\) On the basis of the deduction that the ICBA produces higher interface area one may expect that the charge generation rate \( (\alpha K_b) \) would also be higher. However, the opposite is true (Table 3) due to the different energy levels of PCBM vs ICBA, which we discuss in detail below.

As we have already indicated, a large part of the discussion in this paper revolves around the CT states. To that end we show in Figure 3 the external quantum efficiency (EQE) as a function of excitation intensity.
of excitation energy for P3HT:PCBM and P3HT:ICBA devices. We note an absorption edge at about 2 eV associated with the P3HT absorption and a shoulder at about 1.7 eV that is associated with the acceptor absorption. At a lower energy there is the response associated with multiple types of CT states. The flattening of the response at energies below 1.3 eV for P3HT:ICBA (Figure 3, red triangles) may be the signature for the deep CT states. However, the low sensitivity of our system below 1.3 eV does not allow us to definitively resolve this point. While the data shows more sub-bandgap absorption for P3HT:PCBM (Figure 3, blue squares), we cannot quantify the relative CT state density in the two systems because our instrument do not have sensitivity down to 1.05 eV, the predicted CT state of P3HT:PCBM. We only state that while our use of a model employing a single energy level for the CT state generates a good fit to the normalized EQE data, it is clear that there is a broad distribution which will have to be included if more sophisticated models are to be used.

3.2. Different Processing Conditions. We have thus far shown that the combined SRH and exciton–polaron recombination model detailed in ref 12 can adequately explain the different dependence of QE on excitation intensity for P3HT:PCBM and P3HT:ICBA devices. However, one may justifiably claim that a change in acceptor simultaneously modifies the energy levels, morphology, and transport within the active layer, such that the good fit to the model may be coincidental. To overcome this issue we examined P3HT:ICBA devices where we either changed only the solvent and drying conditions or the structural parameters of the P3HT (molecular weight and regioregularity). Comparing $J$–$V$ curves of P3HT:ICBA devices show that slow drying (Figure 4a, black solid circles) gives higher $J_{SC}$ than fast drying (Figure 4a, red solid triangles). When intensity-dependent QE curves for both devices are normalized to the low intensity limit of the slow drying device, the slow-dry device (Figure 4b, black solid circles) exhibits higher generation rate than the fast-dry device (Figure 4b, red solid triangles), consistent with the higher $J_{SC}$. When the QE curve for the fast-dry device is normalized to its low intensity limit (Figure 4b, red open triangles) and overlaid on the slow-dry device, a striking difference between the two curves is observed. Indeed, the significant decrease in QE between 1 and 20 mW/cm² for the slow-dry device is a signature for increased recombination center (“trap”) assisted recombination. The leveling of the signal at 20 mW/cm² indicates that the electrochemical potential difference is reaching the energy of the recombination-center and that the

![Figure 3](image1)

Figure 3. External quantum efficiency as a function of excitation energy for P3HT:PCBM (blue squares) and P3HT:ICBA (red triangles) devices.

![Figure 4](image2)

Figure 4. (a) $J$–$V$ characteristics of slow-dry (black solid circles) and fast-dry (red solid triangles) P3HT:ICBA solar cells under AM1.5G illumination. (b) Light intensity dependence of the QE at short circuit conditions for slow drying device normalized to its low intensity limit (black solid circles), fast drying device normalized to the low intensity limit for slow drying device (red solid triangles), and fast drying device normalized to its low intensity limit (red open triangles). Sold lines represent best fits to the model. Dashed lines represent best fits using only SRH recombination.

CT states serving as recombination-traps are considered full. This last point will be discussed in the summary and conclusions section.

To quantify the difference we fitted the data using the model and achieved good agreement (Figure 4b, solid lines). We also fitted the data using only SRH recombination (Figure 4b dashed lines), which shows that below 10 mW/cm² the losses are dominated by trap (recombination center) assisted recombination. Following the same analysis procedure described in the context of Figure 2b we extracted the parameters of the two devices and these are presented in Table 4. We note that since the material system is unchanged, $E_{CT}$ is not changed. Also, $K_{ep}$ is found to be unchanged too. Comparing $N_0$ and $\alpha K_{d}$ we find that for both parameters the values for the slow-dry device are about 2.8 times higher compared to the fast-dry device. The close correlation between $N_0$ and $\alpha K_{d}$ ratios suggests that states at the donor–acceptor interface are active both in the process of dissociating the excitons into free carriers and in the process of nongeminate charge recombination, as also suggested in ref 34.

External quantum efficiency (EQE) measurements at below gap energies (Figure 5) further support the assignment of CT states as the traps for SRH recombination. In particular, the CT state signature is higher for the slow-dry device (Figure 5, black circles) compared to the fast-dry device (Figure 5, red triangles) We also note that the CT state intensity for the slow-drying device at 1.3 eV is about 2.5x higher than the fast-dry device (Figure 5, inset). While precise measurement of CT state densities requires decomposition of the EQE signal to different contributions, the similarity in the ratios of CT state intensity ratio, $N_0$ at $E_{CT}$ again offer support to the theory that CT states are responsible for both charge generation and trap assisted recombination.

Table 4. Parameters Extracted from the Fit to Figure 4b

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fast Dry</th>
<th>Slow Dry</th>
</tr>
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<tbody>
<tr>
<td>$N_0$ [1/cm³]</td>
<td>$2 \times 10^{14}$</td>
<td>$5.5 \times 10^{14}$</td>
</tr>
<tr>
<td>$E_{CT}$ [eV]</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>$K_{ep}$ [cm³/s]</td>
<td>$10^{-8}$</td>
<td>$10^{-8}$</td>
</tr>
<tr>
<td>$\alpha K_d$ [1/s]</td>
<td>$4.4 \times 10^{10}$</td>
<td>$4 \times 10^{10}$</td>
</tr>
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increased generation efficiency and the recombination-center assisted recombination for the P3HT#1 device, the QE curves normalized to their respectively low intensity limits are fitted.

The parameters extracted using the fit are displayed in Table 5 and show that both $N_i$ and $aK_d$ are higher for the P3HT#1 device compared to the P3HT#2 device, although the ratios are different at 3.7 and 1.5, respectively. The energy dependent external quantum efficiency of the two devices (Figure 7) exhibit similar shapes. At 1.3 eV, the ratio between the two curves is $\sim 2.6$ (Figure 7, inset), in good agreement with the ratios found for $N_i$ and $aK_d$.

3.4. Discussion. By examining pairs of organic solar cells with different acceptors, drying conditions, and donor molecular weight and regioregularity, we find strong evidence indicating that the recombination centers are also charge transfer states, with a measured binding energy of $\sim 0.3$ eV with respect to the free charge carriers. We note that the issue of the CT state binding energy is under debate in the literature. We are also aware that there are several types of CT states.

Table 5. Parameters Extracted from the Fit to Figure 6b and the P3HT Parameters

<table>
<thead>
<tr>
<th></th>
<th>P3HT #1:ICBA</th>
<th>P3HT #2:ICBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_i$ [1/cm$^3$]</td>
<td>2) $5.5 \times 10^{14}$</td>
<td>2) $1.5 \times 10^{14}$</td>
</tr>
<tr>
<td>$E_C$ [eV]</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>$K_p$ [cm$^3$/s]</td>
<td>$10^{-4}$</td>
<td>$10^{-4}$</td>
</tr>
<tr>
<td>$\alpha K_d$ [1/s]</td>
<td>$4 \times 10^{19}$</td>
<td>$2.6 \times 10^{20}$</td>
</tr>
<tr>
<td>$M_i$ [kg/mol]</td>
<td>37</td>
<td>55</td>
</tr>
<tr>
<td>$H-T$ Ratio [%]</td>
<td>$&gt;96$</td>
<td>$&gt;98$</td>
</tr>
</tbody>
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LUMO levels of P3HT are not changed by Mn or regioregularity, $E_C$ should remain unchanged, allowing for quantitative comparison of recombination parameters. $J-V$ characteristics under AM1.5G 100 mW/cm$^2$ illumination shows that device containing P3HT#2 (higher Mn and higher regioregularity) (Figure 6a, blue solid circles) exhibits slightly lower $V_{OC}$ and $J_{SC}$ compared to device containing P3HT#1 (Figure 6a, red solid squares).

The data in Figure 6a suggests that there is little difference between the two devices. In contrast, intensity dependent QE for the two devices reveals qualitative differences in carrier recombination for devices with different P3HT. When QE curves are normalized to the low intensity for the P3HT#1 device, at intensity $\sim 100$ mW/cm$^2$ the difference between the QE for the P3HT#2 device (Figure 6b, blue solid circles) and the P3HT#1 device (Figure 5b, red solid squares) is fairly small. However, comparing the curves over the entire intensity range, we find that the device based on P3HT#1 has significantly higher QE at low intensity, which decreases more rapidly between 1 and 10 mW/cm$^2$. This is a clear indication that measurement of QE over a wide range of excitation intensities can reveal the interplay between different recombination mechanisms, which would otherwise remain hidden if one examines QE only at 100 mW/cm$^2$. To quantify the

Figure 6. (a) $J-V$ characteristics of P3HT:ICBA solar cells with P3HT#1 (red solid squares) and P3HT#2 (blue solid circles) under AM1.5 illumination. (b) Light intensity dependence of the QE at short circuit conditions for P3HT#1 device normalized to its low intensity limit (red solid squares). P3HT#2 device normalized to the low intensity limit for P3HT#1 device (blue solid circles), and P3HT#2 device normalized to its low intensity limit (blue open circles). Solid lines represent best fits to the model.

Figure 7. External quantum efficiency as a function of excitation energy for P3HT:ICBA devices with P3HT#1 (red squares) and P3HT#2 (blue circles).
and/or traps and that our analysis probes only those most effective in the charge recombination process. However, the debate regarding the binding energy is partly due to the method of calculating it and measurements of the donor HOMO and acceptor LUMO energy levels to deduce $E_b = |HOMO_D - LUMO_A| - E_{CT}$, which is hampered by the widespread of values for the HOMO/LUMO energies. Unlike previous reports, our method directly fits for the binding energy, and the uncertainty in the HOMO/LUMO energies only affects $E_{CT}$, which in the present paper coincides with values found in some reports based on EL.

Having said that, one may question the ability of charges to escape a trap with $\sim 0.3$ eV depth. However, charges have been shown to thermalize out of traps with 0.2–0.3 eV depth at room temperature. Also, in the context of disordered organic materials it is common to attribute the charge transport as hopping to a transport energy, which requires an activation energy on the order of 0.2–0.3 eV.

The leveling of the charge transfer state mediated recombination loss implies that at high excitation densities the electrochemical potential difference in the bulk is such that a significant fraction of the density of states of the relevant CTs is filled. Namely, the electrochemical potential difference is approaching the energy of the effective recombination band gap and the energy of these states is not necessarily what limits the open circuit voltage. This last statement seems too strong for the rate equation model used to arrive at this conclusion. On one hand, the advantage of such a rate equation model is that it does not require many details to capture the big picture. On the other, this is also why it may prove not so useful when the details of the physical picture are sought. To somewhat rectify this we repeated the fitting and data extraction using a more elaborate device model developed for this purpose. We rely on the drift-diffusion model presented in ref 41 which incorporates self-consistently the contact energy position. For the current paper the model was augmented with trap states as well as charge generation profile that follows the absorption profile. For more details see the Supporting Information.

Using the drift-diffusion model we fitted the data measured for the slow-dry P3HT:ICBA device, and present the results in Figure 8a. Compared to the experimental data (Figure 8a, circles), the drift-diffusion model achieves good agreement with $N_t = 5.5 \times 10^{14}$ cm$^{-3}$ and $E_b = 0.36$ eV (Figure 8a, black solid line). Increasing $E_b$ from 0.3 to 0.42 eV increases the contribution from trap assisted recombination, as expected. When $N_t$ is increased to $1 \times 10^{15}$ cm$^{-3}$ with $E_b = 0.36$ eV (Figure 8a, green dot-dash line), the fit becomes poor. Comparing to the simple rate equation model we find good agreement with the deduced trap density. However, the binding energy is found to be higher by about 60 meV. Using the drift-diffusion model, we also calculated the energy band diagram under open circuit conditions using $E_b = 0.36$ eV and $N_t = 5.5 \times 10^{14}$ cm$^{-3}$ (Figure 8b). We note that the contact barrier (0.2 eV) creates band banding that leads to about 0.16 eV loss in open circuit voltage. This is due to the induced charge density close to the contacts.

The bottom inset of Figure 8b shows the electrochemical potential difference at both short-circuit and open-circuit conditions. The declining curve toward the contacts indicates that even under open circuit conditions there is current flowing toward the contacts. Since no current is exiting the device it indicates an enhanced recombination rate close to the contacts. Last, the top inset of Figure 8b shows the band diagram at short-circuit conditions under 100 mW/cm$^2$ illumination. The reduced slope at the center of the device is the manifestation of the electric field screening, present in low mobility solar cells, that reduces the extracted current and thus enhances the effect of recombination. Examining Figure 8a we see that this loss amounts to about 10% or ~1 mA/cm$^2$ of short-circuit current. As the drift-diffusion model implemented only SRH type recombination, this is the source of the high excitation density loss which has the signature of a bimolecular loss.

4. SUMMARY AND CONCLUSIONS

Using a simple and CW measurement technique we have presented self-consistent analysis of the loss mechanisms in BHJ solar cells. The study was based on the fabrication of several families of devices where one parameter was changed at a time between pairs of devices using different acceptors (PCBM vs ICBA), fast vs slow drying speeds, and donor (P3HT) of two different molecular weights and regioregularity.

By correlating the density of recombination centers and the strength of the subgap EQE signal we show that the loss due to trap assisted recombination is taking place through the charge transfer states which act as a recombination center. We also found a correlation between the density of the recombination centers and the generation efficiency, strengthening the notion that the recombination centers are residing at the donor–acceptor interface and that their density can be used to quantify relative differences in the effective donor–acceptor interface area.

Through the analysis of multiple devices, we have shown a simple CW technique that spans across orders of magnitude of excitation intensity allowing us to obtain deep insight into the morphology dependent physical processes and their balance at the operating conditions of the solar cell. This is in contrast to techniques that span orders of magnitude of time scales or a very broad temperature range, which are also able reveal the various processes but do not lend themselves to easily quantifying the relative importance under solar cell operating conditions. Using both the simple rate equation approach and a full dynamic drift-diffusion, trapping, and recombination model we arrive at the conclusion that the open circuit voltage is largely limited by the contacts’ properties and that the short-
circuit current under 100 mW/cm² illumination is limited by the electric field screening, which is a consequence of the low mobility.

**ASSOCIATED CONTENT**

**Supporting Information**

Details of the dynamic drift diffusion device model are described. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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