

Electric Field and Mobility Dependent First-Order Recombination Losses in Organic Solar Cells

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The origin of photocurrent losses in the power-generating regime of organic solar cells (OSCs) remains a controversial topic, although recent literature suggests that the competition between bimolecular recombination and charge extraction determines the bias dependence of the photocurrent. Here the steady-state recombination dynamics is studied in bulk-heterojunction OSCs with different hole mobilities from short-circuit to maximum power point. It is shown that in this regime, in contrast to previous transient extracted charge and absorption spectroscopy studies, first-order recombination outweighs bimolecular recombination of photogenerated charge carriers. This study demonstrates that the first-order losses increase with decreasing slower carrier mobility, and attributes them to either mobilization of charges trapped at the donor:acceptor interface through the Poole–Frenkel effect, and/or recombination of photogenerated and injected charges. The dependence of both first-order and higher-order losses on the slower carrier mobility explains why the field dependence of OSC efficiencies has historically been attributed to charge-extraction losses.

OSCs often exhibit significant losses in the photocurrent, lowering the fill factor (FF) and hence the photovoltaic performance. Despite attempts to understand these losses under operational biasing, their origin remains unclear.^[3] In addressing this critical question, it is important to distinguish the different processes that can lead to photocurrent losses in forward bias: the most fundamental distinction being whether the charge recombination is non-geminate or geminate.

Recombination is non-geminate if the two charges in the encounter originated from different photoexcitations. In forward bias, the driving field for extraction decreases, which leads to a build-up of electron (n) and hole (p) density in the bulk of the heterojunction. Hence, the bimolecular recombination rate scales as $R \sim np$. As both n and p depend on the incident light intensity (I), the recombination

losses are nonlinear with respect to I . Bimolecular recombination is the most common explanation for photocurrent losses under operational bias.^[4–9] However, certain non-geminate recombination processes could conceivably lead to losses that are linear with I .^[10–13] In particular, the recombination of mobile carriers with trapped charges may be linear if one carrier type is trapped independent of the light intensity such that $R \sim N_{\text{trap}}p$. Similarly, photogenerated charges can recombine with a large excess of injected charges from the electrodes,^[14] or equilibrium charges (due to unintentional doping). Finally, non-geminate recombination can occur not only within the bulk of the heterojunction but also at the “wrong” electrode due to diffusion.^[14–16] The losses associated with these mechanisms increase with the applied voltage in forward bias; both because charge injection increases, and because charge diffusion becomes more dominant as the driving field diminishes.

In contrast, geminate recombination occurs if the two charges originate from the same photoexcitation. In both geminate and non-geminate cases, recombination occurs via a charge transfer state (CTS). The CTS consists of two separate charges, which can interact with a local or applied electric field (E). The E -field dependence of the CTS dissociation rate constant $k_d \sim (1+E+E^2/3+\dots)$ is described in the Braun model.^[17] However, assuming an initial charge separation of 1.5 nm,^[18] the Coulombic field between charges forming the CTS is >10 times stronger than a typical built-in electric field in a BHJ, which suggests the

1. Introduction

Bulk-heterojunction (BHJ) organic solar cells (OSCs) comprising blends of electron donating and accepting organic semiconductors continue to improve as a result of optimizations in molecular design, device engineering, and an increased understanding of how they work. A promising feature of BHJ solar cells is their high internal quantum efficiencies—the product of the charge generation (η_{GEN}) and collection (η_{COLL}) efficiencies, which in the best systems are close to 100% under short-circuit conditions.^[1,2] However, at the maximum power voltage (V_{MP}),

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electric field should only have a small impact. This hypothesis is consistent with the majority of transient charge extraction measurements on efficient blends^[2,6–8,19,20] and several absorption spectroscopy studies.^[21] Nevertheless, there are reports of field-dependent charge generation by measuring the CTS emission intensity, lifetime and transient absorption, or using steady-state photocurrent measurements,^[22–26] with the results often quantitatively explained with the Braun model. In addition to the field dependence of k_d , the Braun model suggests that k_d scales with the sum of the faster and slower carrier mobilities (μ_f, μ_s) although we note that higher local mobilities (μ^*) need to be assumed in the Braun model to explain the high dissociation rates as detailed in ref. [25]. Due to the electronically disordered nature of organic semiconductors, the mobility depends on temperature and often on the electric field, as shown by the Poole–Frenkel relation.^[27] Thus, apart from the interaction of the field with the CTS dipole, the field dependence of k_d can also originate from a field-dependent mobility, i.e., $k_d \sim \mu^*(E)$.

Motivated by these considerations, we investigate the photocurrent losses from short-circuit to V_{MP} , and, in particular, the dependence of the recombination losses on the light intensity, electric field, and mobility. We report on five organic semiconductor blends with very different hole mobilities, but similar electron mobilities. Light-intensity-dependent photocurrent measurements show that for these materials combinations, the majority of the photocurrent losses from short-circuit to operational bias scale with the first-order of the light intensity, rather than higher recombination orders (bimolecular). Furthermore, these first-order losses increase with decreasing slower carrier mobility. Our experiments indicate that the first-order losses are, in this bias regime, less affected by non-geminate recombination due to trapped or equilibrium charges with pseudo-first-order dynamics. Notwithstanding this point, these findings are counter to the conventional view that photocurrent losses in the power generating regime are predominantly bimolecular.

2. Results and Discussion

2.1. Materials

We studied bulk heterojunction OSCs fabricated from five different donor: acceptor blends. **Figure 1a** shows the molecular structures and energy levels of each donor material with [6,6]-phenyl- C_{70} -butyric acid methyl ester (PC70BM)—the acceptor. The optimized blends for device performance have been previously reported and are:

- poly(2,5-(2-octyldodecyl)-3,6-diketopyrrolopyrrole-*alt*-5,5'-(2,5-di(thien-2-yl)thieno[3,2-b]thiophene) (DPP-DTT):PC70BM.^[28,29]
- poly[(4,8-bis{2-ethylhexyloxy}benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)(3-fluoro-2-[[2-ethylhexyl]carbonyl]-thieno[3,4-b]thiophenediyl)] (PTB7):PC70BM.^[30]
- poly[N-9"-heptadecanyl-2,7-carbazole-*alt*-5,5'-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole) (PCDTBT):PC70BM.^[31]
- $N^1, N^1, N^3, N^3, N^5, N^5$ -hexakis(4-methoxyphenyl) benzene-1,3,5-triamine (WJ1-06):PC70BM.^[32,33]

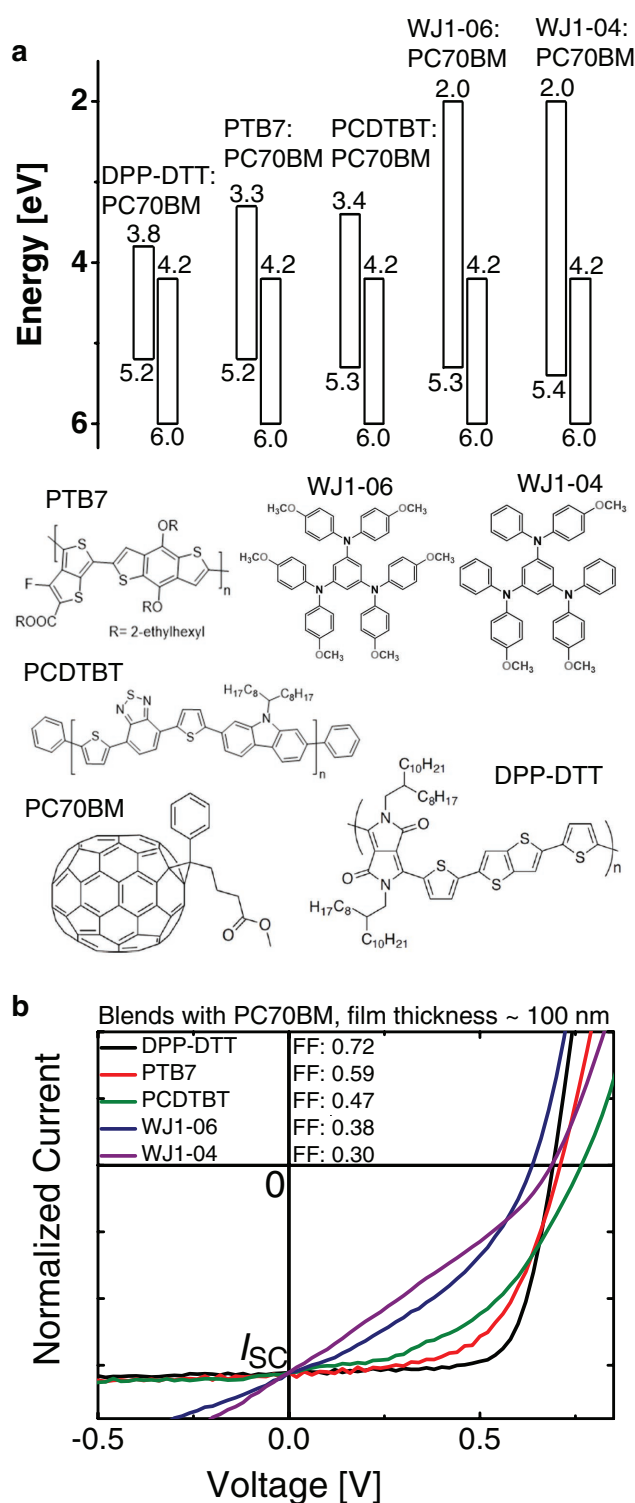


Figure 1. a) The chemical structures and energy levels of the materials that were studied in this work. Ionization potentials were measured by photoelectron spectroscopy in air, and the onset of the film absorptions were used to determine the electron affinities. b) Normalized and averaged photocurrent density versus voltage characteristics measured under standard AM 1.5G illumination highlighting the large differences for each blend in the device forward bias fill factors.

- (v) N^1,N^3,N^5 -tris(4-methoxyphenyl)- N^1,N^3,N^5 -triphenylbenzene-1,3,5-triamine (WJ1-04):PC70BM.^[34]

WJ1-04 and WJ1-06 are non-polymeric (small molecule) organic semiconducting donors, which were synthesized in house.^[32–34] WJ1-06 differs from WJ1-04 in terms of the number of alkoxy substituents on the surface of phenyl rings. The active layer thickness of all of the BHJ OSCs was 100 nm, which is a typical thickness used for high efficiency thin-film OSCs. However, we note that the key findings of this work are largely independent of the chosen active layer thickness. The devices were fabricated in the conventional architecture (see the Experimental Section).

The material systems were chosen based on the large differences in their slower carrier mobilities (ranging from $\approx 1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $\approx 6 \times 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ as measured by resistance-dependent photovoltage). This delivers a large variation in the forward-bias photocurrent losses and FFs. Figure 1b shows representative white-light current–voltage (J – V) performance curves obtained under standard AM 1.5G illumination. We note that multiple devices were fabricated and tested for each blend combination to confirm the reproducibility of the results. The J – V curves are normalized to their short-circuit current to highlight the differences in photocurrent losses in the power-generating regime of the cells. The original J – V curves and the key photovoltaic parameters are provided in Figure S1 and Table S1 (Supporting Information), respectively.

2.2. Light-Intensity Dependence of Photocurrent Losses from Short-Circuit to the Maximum Power Point

In order to disentangle first-order and higher-order photocurrent losses under operational solar cell conditions, we

performed intensity-dependent photocurrent (IPC) measurements at an excitation wavelength of 532 nm. From the IPC measurements we calculated the EQE and examined it as a function of the photocurrent, which increases with the applied laser intensity. Details of this methodology are given in the literature.^[34,35] First, we measured IPC at short-circuit (0 V) and then subsequently at the maximum power point under 1-sun equivalent conditions (V_{MP} applied). The results of these IPC measurements are presented for WJ1-04:PC70BM in Figure 2a, while the results for the other blends are shown in Figure S2 (Supporting Information). Figure 2a presents the EQE of the WJ1-04:PC70BM device as a function of the photocurrent at 0 V (black data points) and at V_{MP} (red data points). The EQE was normalized to 100% at 0 V, which eliminates losses in the generation efficiency and the absorption efficiency at short-circuit from the analysis. The following analysis is, however, not limited in any way by this normalization but allows for direct and convenient comparison of first- and second-order losses. The 1-sun short-circuit current (I_{SC}) and maximum power point current (I_{MP}) are marked by circles. The plot shows that the WJ1-04:PC70BM blend is strongly limited by bimolecular recombination under 1-sun conditions, as seen by the decrease of the EQE at relatively low photocurrents ($< \approx 10^{-5} \text{ A}$).^[35] The reason for this behavior is the relatively low slower carrier mobility in this blend ($6 \times 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), which creates a strong mobility imbalance, a build-up of slower carriers in the junction, and subsequent high encounter probability of non-geminate charge carriers.^[35]

The EQE under forward bias has two characteristic features. First, we observe that the constant EQE value (prior to deviation) is less compared to the EQE at 0 V, which we define as a first-order recombination loss (more clearly observable in the original IPC plot in Figure S3a, Supporting Information). The

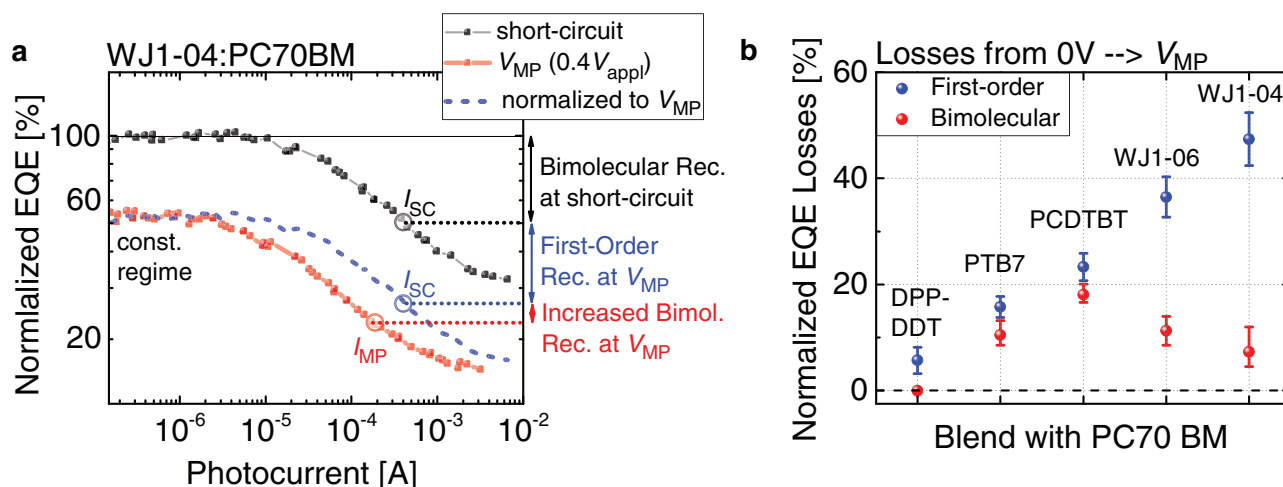


Figure 2. a) Photocurrent-dependent external quantum efficiencies (EQEs) measured on the WJ1-04:PC70BM blend at 0 V applied (black data points) and the maximum power voltage (V_{MP}) (red data points). The 1-sun short-circuit current (I_{SC}) is marked by the black circle and the photocurrent at V_{MP} by the red circle (I_{MP}). The dotted blue line (denoted as EQE*) represents the EQE at 0 V normalized (parallel shifted) to the EQE at V_{MP} . This procedure allows estimation of the first-order losses from $\text{EQE}(I_{\text{SC}}) - \text{EQE}^*(I_{\text{SC}})$ and bimolecular recombination losses from $\text{EQE}^*(I_{\text{SC}}) - \text{EQE}(I_{\text{MP}})$. b) The first-order and bimolecular recombination losses of the blends from short-circuit to V_{MP} . The actual photocurrent losses at V_{MP} can be obtained by multiplying the I_{SC} by the plotted first-order and bimolecular recombination losses. The error bars of the first-order losses were estimated from the standard deviations of the constant EQE regimes at 0 V and V_{MP} , considering also an uncertainty of 40 mV in the V_{MP} and expected shifts of the constant EQE values due to this uncertainty. The error bars of the bimolecular losses were estimated from the standard deviations of the EQEs at 0 V and V_{MP} , including a 10% uncertainty in both I_{SC} and I_{MP} .

magnitude of these first-order losses strongly depends on the effective driving voltage V (built-in minus the applied voltage; Figure S3b, Supporting Information). Second, the deviation from constant EQE occurs at lower photocurrents, indicating increased bimolecular recombination losses. Qualitatively we can therefore say that both first- and second-order losses are increased under forward bias in this blend.

In order to estimate the increased recombination at V_{MP} , we normalized the EQE at 0 V to the EQE at V_{MP} in the constant EQE regime, as illustrated by the blue dotted line in Figure 2a. This allows the first-order recombination losses to be calculated from the difference between the EQE value at I_{SC} (black circle) and the normalized EQE^* at I_{SC} (blue circles), i.e., $EQE(I_{SC}) - EQE^*(I_{SC})$. Similarly, the increased bimolecular recombination losses can be obtained from $EQE^*(I_{SC}) - EQE(I_{MP})$.

Figure 2b summarizes the increase in first-order and bimolecular recombination losses from short-circuit to V_{MP} for each of the blends (noting the $EQE(I_{SC})$ is normalized to 100%). The graph demonstrates that the increase in first-order losses is higher for each blend. In addition, it is interesting to note that the gap between the first-order and second-order recombination losses is larger in blends that are already strongly limited by bimolecular recombination at short-circuit (WJ1-06:PC70BM and more pronounced in WJ1-04:PC70BM). On the other hand, the DPP-DTT blend, which is not limited by bimolecular recombination at short-circuit nor at V_{MP} , exhibits only small first-order recombination at V_{MP} . OSCs that are at the boundary of being limited by bimolecular recombination at 1-sun under short-circuit conditions, such as PCDTBT:PC70BM and PTB7:PC70BM, exhibit similar losses in first-order and bimolecular recombination, with the former being slightly higher (outside experimental error). We further confirmed this observation for the same blends with different active layer thicknesses (Figure S4, Supporting Information).

While the generality of these observations, and the exact trends over the whole power generating regime, cannot be simply implied, the important conclusion is that first-order recombination plays an important role for the J - V curve, particularly at V_{MP} in OSCs.

2.3. Mobility Dependence of the First-Order Photocurrent Losses

To elucidate the origin of the first-order losses, we compared the charge carrier mobilities with the first-order losses at a fixed reduction of the driving field. The charge transport parameters were studied using a transient photovoltage technique.^[36,37] The left column of Figure 3 shows the transient photovoltage responses for each blend (see Figure 1) after a short (≈ 5 ns) laser excitation at 532 nm at different load resistances. The technique allows visualization of the arrival of charge carriers at the electrodes after transiting the whole active layer thickness from the shoulders in the photovoltage transient signal. The data show that the slower carrier arrival times, as marked by the arrows, differ by many orders of magnitude (i.e., $<1 \times 10^{-7}$ s to 2×10^{-4} s). Accordingly, the mobility of the slower carrier type varies from $\approx 1 \times 10^{-3}$ cm² V⁻¹ s⁻¹ in the DPP-DTT:PC70BM

blend to 6×10^{-7} cm² V⁻¹ s⁻¹ in the WJ1-04:PC70BM blend. The other blends lie between these two limiting cases. In blends with significantly imbalanced mobilities (≥ 10 times imbalanced) the faster and slower carrier transit time can be identified unambiguously. The arrival of faster carriers can be observed from the first shoulder in the photovoltage signal. The faster carrier can be assigned to electrons in PCDTBT:PC70BM, WJ1-06:PC70BM, and WJ1-04:PC70BM.^[34,36] In PTB7:PC70BM and DPP-DTT:PC70BM devices however, the electron and hole mobilities are superimposed. Nevertheless, it can be seen that the electron mobility is very similar in each blend (varying between 2×10^{-3} cm² V⁻¹ s⁻¹ and 3×10^{-4} cm² V⁻¹ s⁻¹), in contrast to the hole mobility which varies substantially more among these blends.

The right column of Figure 3 presents EQEs as a function of the measured photocurrent for each blends at short-circuit (black data points) and under forward bias (blue data points). For a fair comparison between the blends with different built-in voltages (U_{BI}), the applied voltage was chosen to decrease the built-in field by roughly 3.5 times (the applied voltage varied between 480 to 550 mV, which is similar to or slightly above the V_{MP} of each device). This factor was chosen based on a trade-off between a large as possible reduction of the driving field, while maintaining a small injection current (the highest injection current was observed for the PTB7:PC70BM blend with ≈ 8 μ A (or 40 μ Acm⁻²); Figure S5, Supporting Information). The first-order losses in forward bias are plotted in Figure 4 as a function of the slower carrier mobility. These photocurrent losses increase from 4% in the DPP-DTT:PC70BM blend, which has the highest slower carrier mobility and highest FF (0.72), to 64% in WJ1-04:PC70BM films, which has the lowest slower carrier mobility and FF (of 0.3). Again, all other systems lie between these two extreme cases.

2.4. Impact of Non-Geminate Recombination on the First-Order Photocurrent Losses

The experimental results show the critical impact of the first-order photocurrent losses depending on the slower carrier mobility of the BHJ blend, while bimolecular recombination plays a minor role, at least between 0 V and V_{MP} . Referring back to the Introduction, Street et al.^[12] (and others^[10]) have assigned the first-order photocurrent losses to a non-geminate recombination process of free charges with (light-intensity-independent) trap states. In contrast, our results show that trapped charges are, in the studied bias regime, not present independent of the light intensity, with very few trapped charges present at the lowest intensities especially (much less than CV, where C is the device capacitance; Figure S6, Supporting Information). This implies that trapped carriers do not lead to significant first-order recombination under steady-state conditions at the lowest light intensities (and consequently in the linear IPC regime) due to the low recombination probability of free and trapped charges. The effect of charge-carrier-trapping would be to lower the effective slower carrier mobility, which in turn leads to increased bimolecular recombination losses at lower photocurrents. This is clearly seen in Figure 3 from the downward deviation of the EQE, which shifts to lower photocurrents depending

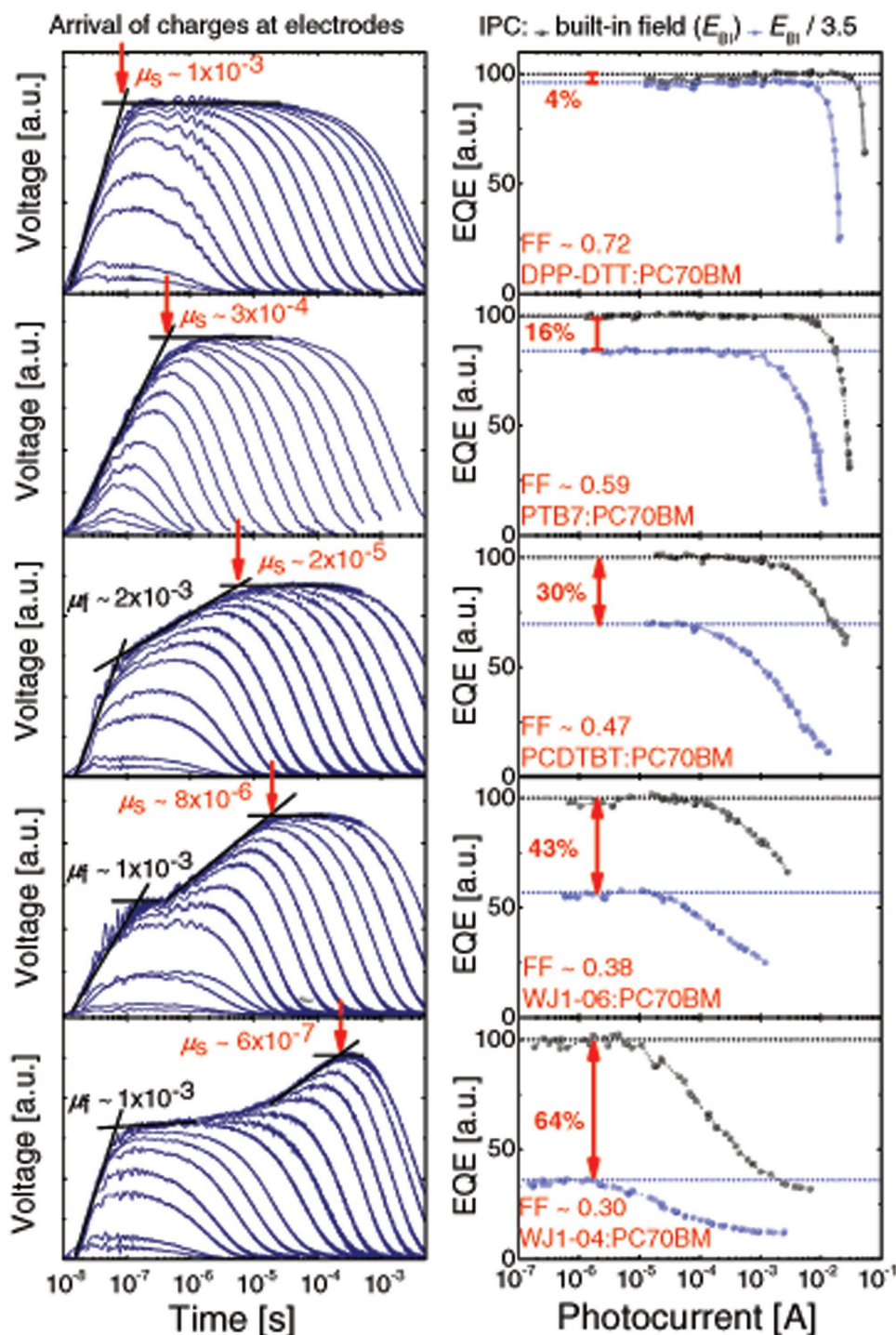


Figure 3. Left column: Resistance-dependent photovoltage (RPV) transient signals for each blend revealing the arrival of charge carriers at the device electrodes. The magnitude of the transients increases (progressive photovoltage traces) with the load resistance, which was varied from 1 Ω to 1 M Ω . The slower carrier mobility/transit time, as indicated by the red arrows, varies by four orders of magnitude from DPP-DTT:PC70BM (top) to WJ1-04:PC70BM (bottom). The faster carrier mobility (electrons), as observed from the first shoulder in the transient responses, is similar among all devices. The mobility values are specified in cm² V⁻¹ s⁻¹. Right column: The photocurrent-dependent EQEs of the blends measured at short-circuit and in forward bias corresponding to an ≈ 3.5 times reduction of the internal driving field. The first-order photocurrent losses in forward bias are observed from the shift of the constant EQE value and are marked by the arrows.

on the slower carrier mobility of the system. This occurs when the bimolecular recombination rate becomes comparable to the extraction rate, or equivalently when the photocurrent reaches

the space charge (and transport) limited photocurrent (I_{SCLC}), which is mainly defined by the active layer thickness, effective driving voltage, and slower carrier mobility.^[35] This was also

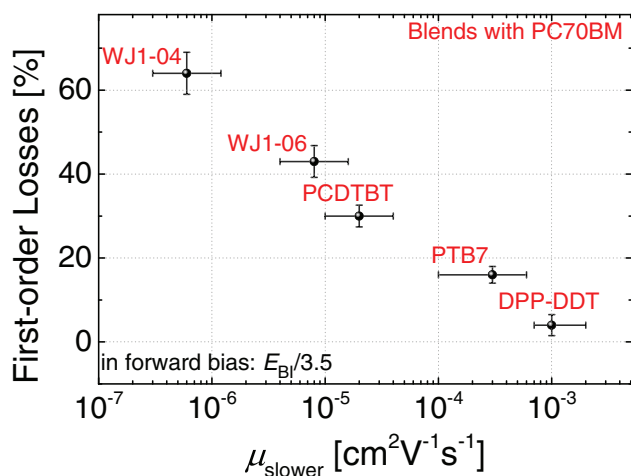


Figure 4. The first-order losses in forward bias where the built-in field is 3.5 times reduced as a function of the slower carrier mobility in the blends. The losses decrease with increasing slower carrier mobility from 64% in films of WJ1-04:PC70BM to 4% in DPP-DDT:PC70BM, which suggests the importance of the slower carrier mobility on these losses. The x-error bars were estimated from the uncertainty of the carrier arrival times as observed in RPV (see the Experimental Section). The y-error bars of the first-order losses are standard deviations of the constant EQE regimes at short-circuit and in forward bias, considering also an uncertainty of 40 mV in the V_{MP} as described in the caption of Figure 2.

confirmed for the blends studied in this work (Figure S7, Supporting Information).

Similarly, Dibb et al.^[14] pointed out that non-geminate recombination will exhibit first-order dynamics if the amount of injected charges greatly exceeds the amount of photogenerated charges. While this is correct in principal, we note that our previous study demonstrated that this first-order recombination rate will be negligible compared to the extraction rate as long as the amount of charges—which are present independent of the light intensity—remains significantly below 1 CV.^[34] Although we cannot presently rule out the role of recombination of photogenerated charges with injected charges, we note that the injection current at V_{MP} is roughly —two to three orders of magnitude lower than the magnitude of the first-order photocurrent losses, and that we observe an opposite trend between the injection current and the first-order losses (Figure S5, Supporting Information). Lastly, we note that the observed first-order losses are also independent of the excitation wavelength (Figure S8, Supporting Information) and corresponding photo-carrier generation profiles,^[38] which may indicate that losses at the contacts either due to reverse diffusion or charge injection of charges play a minor role.

2.5. Impact of Geminate Recombination on the First-Order Photocurrent Losses

If the Coulomb barrier for CTS dissociation is substantially lower than expected from the simple calculation presented in the Introduction, then the contribution of the internal electric field could make the decisive difference to a successful

CTS dissociation event. Indeed there are several processes that could lower the Coulomb barrier for dissociation, for example an entropic driving force that could be more effective together with the effect of the electric field.^[39–42] We note that a majority of transient extraction and absorption spectroscopy studies have found a field-independent photogeneration yield in relatively efficient blends such as PCDTBT:PC70BM^[19,21] and PTB7:PC70BM,^[20] which suggests that the first-order losses are not related to geminate recombination in these systems. Nevertheless, the electric-field dependence of the CTS-dissociation rate k_d can also originate through the field dependence of the local charge carrier mobility $k_d \sim \mu^*(E)$.^[27] The effective mobility increases with increasing electric field due to detrapping of charges. Thus, the primary role of the internal electric field could be to mobilize trapped charges, especially the slowest charge carriers; and enable them to leave the donor:acceptor interface.

To test the dependence of the mobility on the field, we performed additional one-carrier J - V measurements on the DTT:PC70BM, PCDTBT:PC70BM, and WJ1-04:PC70BM blends to identify the electric field dependence of the slower carrier mobility (Figure 5), following the methodology presented in ref. [43] (see Supporting Information Figure S9 for the raw data). The results confirm a stronger field dependence of the mobility in blends with low mobilities (WJ1-04:PC70BM and to a lesser extent, PCDTBT:PC70BM) due to significant charge carrier trapping. Therefore, the Poole–Frenkel-assisted mechanism could also explain the larger field dependent first-order recombination losses in blends with low slower carrier mobilities. This is also consistent with a previous study that demonstrated the importance of the ability of the slower carrier to escape the donor:acceptor interface for efficient CTS separation.^[44]

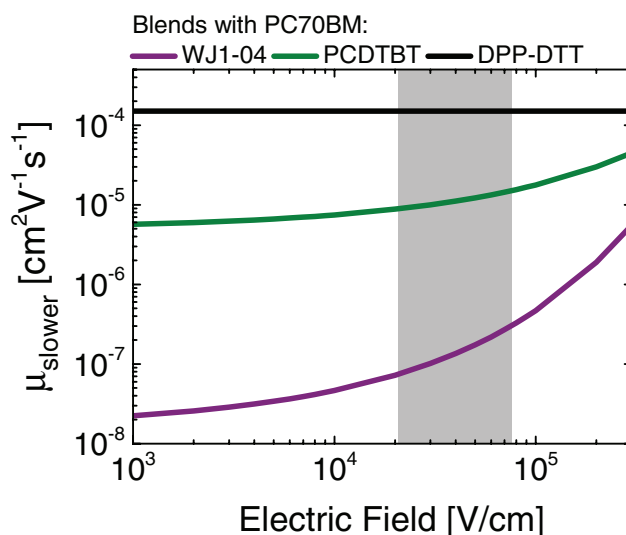


Figure 5. Slower carrier mobility versus electric field as obtained from space charge limited current (SCLC) measurements for DPP-DDT:PC70BM, PCDTBT:PC70BM, and WJ1-04:PC70BM highlighting the stronger field dependence of low mobility blends. The gray area corresponds to the mobility and field of the measurement conditions from Figure 3 (i.e., the short-circuit and forward bias conditions).

3. Conclusion

We have studied the electric field, light intensity, and mobility dependence of the carrier recombination dynamics in BHJ OSCs from short-circuit to operational biasing conditions. We observe significant first-order photocurrent losses, which increase with applied forward bias. This leads to the conclusion that significant photocurrent losses at V_{MP} do not originate solely from the competition between charge extraction and recombination of free charge carriers. Instead, substantial photocurrent losses at operational bias originate either from inefficient and electric-field-dependent CTS dissociation and/or recombination of photo-generated charges with injected charges despite the negligible dark current around V_{MP} . Both of these effects have first-order kinetics. We further find that these processes with first-order kinetics are more susceptible to a reduction of the built-in electric field in systems with low slower carrier mobilities; this manifests as typically poor fill factor in such systems. Considering that in relatively efficient blend systems, transient extraction and absorption spectroscopy studies consistently find field-independent photogeneration yields suggests that the losses with first-order kinetics are not related to geminate recombination in efficient polymer:fullerene blends (DPP-DTT:PC70BM, PTB7:PC70BM, and PCDTBT:PC70BM). However, the data show that geminate recombination of CT states is a dominant loss mechanism in low efficiency blends where the slower carrier mobility is small. Our results highlight that both first-order and higher-order loss mechanisms are similar in the sense that they both are limited by the mobility of the slower carrier type. This could explain the difficulty in understanding the losses associated with free carrier extraction and CTS dissociation in the power generating quadrant of the J - V curve. Our results underline the importance of optimization of CTS dissociation via increasing the mobility of both charge carriers to maximize the generation yield and the fill factor in bulk-heterojunction organic solar cells.

4. Experimental Section

Device Preparation: Substrates with an ≈ 80 nm indium tin oxide (ITO) layer (purchased from Kintec) were cleaned by sonicating in sequence with Alconox, deionized water, acetone, and 2-propanol for 5 min, respectively. Subsequently, the substrates were coated with 30 nm of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS; Baytron P VPAI4083) for the DPP-DTT, PTB7, and PCDTBT composite devices, or with 15 nm of thermally vacuum deposited MoO_3 for the WJ1-04 and WJ1-06 composite devices. The PEDOT:PSS-coated substrates were dried at 170 °C for 10 min.

DPP-DTT:PC70BM Blends: Blend films of DPP-DTT ($\bar{M}_w = 350$ kDa and PDI = 2.8, synthesized as described in ref. [29]) and PC70BM (American Dye Source, Inc., Canada, $\bar{M}_w = 1032$ g mol $^{-1}$) were prepared from a chloroform solution using a total concentration of 24 mg cm $^{-3}$. An optimized blend ratio of 1:3 by weight was used.

PTB7:PC70BM Blends: Blends of PTB7 (1-Material, $\bar{M}_w = 97.5$ kDa, PDI = 2.1) and PC70BM were prepared from a 1,2-dichlorobenzene (DCB) with 3% 1,8-diodooctane solution using a total concentration of 31 mg cm $^{-3}$. An optimized blend ratio of 1:1.5 by weight was used.

PCDTBT:PC70BM Blends: PCDTBT (SJPC, Canada, $\bar{M}_w = 122.2$ kDa, PDI = 5.4) and PC70BM active layer blends were prepared from a DCB solution using a total concentration of 30 mg cm $^{-3}$. An optimized blend ratio of 1:4 by weight was used.

WJ1-06:PC70BM Blends: WJ1-06 ($\bar{M}_w = 760$ g mol $^{-1}$) was synthesized in house.^[32,33] WJ1-06 was dissolved along with PC70BM in chloroform using a total concentration of 20 mg cm $^{-3}$. An optimized blend ratio of 1:1 by weight was used.

WJ1-04:PC70BM Blends: WJ1-04 ($\bar{M}_w = 670$ g mol $^{-1}$) was synthesized in house.^[34] WJ1-04 was dissolved with PC70BM in chloroform using a total concentration of 20 mg cm $^{-3}$. An optimized blend ratio of 1:10 by weight was used.

In all cases, the solutions were spin-coated onto the substrates, with the spin speed varied to achieve a target active layer thickness of ≈ 100 nm. The active layer thicknesses were measured with a DekTak 150 profilometer. The DPP-DTT, PTB7 and PCDTBT, and (WJ1-04 and WJ1-06) based devices were completed by vacuum evaporation of 1.2 nm of samarium (15 nm of calcium) followed by 75 nm of aluminum under a 10^{-6} mbar vacuum. The device area was 0.2 cm 2 . All device fabrication took place within a glove box with <1 ppm O_2 and H_2O , and the J - V and EQE measurements were also performed inside a glove box. The devices were then encapsulated for the IPC and resistance-dependent photovoltage (RPV) measurements.

Current Density–Voltage Characteristics: J - V curves were obtained in a 2-wire source-sense configuration and an illumination mask was used to prevent photocurrent collection from outside of the active area. An Abet Class AAA solar simulator was used as the illumination source providing ≈ 100 mW cm $^{-2}$ of AM1.5G light. The exact illumination intensity was used for efficiency calculations, and the simulator was calibrated with a standard traceable NREL photodiode. The AM1.5G short-circuit current of the devices, which were not limited by bimolecular recombination under 1-sun equivalent conditions, matched the integrated product of the EQE spectrum (as measured using a PV Measurements Inc. QEX7 system) as a further characterization check.

Light-Intensity-Dependent Measurements: Steady-state intensity dependent photocurrent measurements were obtained with a 532 nm continuous wave laser (Ningbo Lasever Inc.) providing a power of 1 W. Optical filters (Thorlabs) were used to attenuate the laser power and the photocurrent transients were recorded with an Agilent semiconductor device analyzer (B1500A). The IPC responses in forward bias were corrected by subtracting the dark (injection) current. Each measured data point corresponds to a steady-state photocurrent measurement at the respective incident laser power, which was simultaneously measured with a Silicon photodetector to improve the accuracy of the measurement. The EQE was obtained from the ratio of the photocurrent and the laser power.

Transient Photovoltage: Photovoltage transients for mobility measurements were recorded with an oscilloscope (LeCroy WaveRunner 6200A) at different external load resistances (R_{Load}) ranging from 1 Ω to 1 M Ω . A pulsed Nd:Yag laser (Brio Quantel) with a pulse length of 5 ns and excitation wavelength of 532 nm was used to generate the charge carriers, while neutral optical density filters were used to attenuate the ≈ 50 mJ energy output. Low laser pulse intensities (resulting in a photovoltage close to 100 mV at an R_{Load} of 1 M Ω) were applied to avoid space charge effects and to maintain quasi short-circuit conditions during extraction.^[36] R_{Load} was varied in order to check the saturation of the maximum photovoltage with increasing load resistance.^[36] All transients exhibit a saturated maximum photovoltage at 1 M Ω , which is a requirement to correctly estimate the mobility. The saturated photovoltage at highest laser fluences and a load of 1 M Ω was taken as built-in voltage of each device, which was in all cases a few tens of mV larger than the V_{OC} . The error bars in the mobility values as measured by RPV indicate the uncertainty of the carrier transit times. The uncertainty of the transit time was approximated from the range over which the photovoltage signals deviate and saturate to tangents fitted to the rise and plateau regions of the photovoltage transients.

Space Charge Limited Current: SCLC measurements on WJ1-04:PC70BM and PCDTBT:PC70BM were performed using a hole-only architecture with ITO/ MoO_3 as the anode electrode and MoO_3 /Silver as the top cathode. SCLC measurements on DPP-DTT were performed using an electron-only device structure, using ITO/Al as the anode and Al as the cathode. The active layer thicknesses were chosen around 250 nm.

Photoelectron Spectroscopy in Air: PESA measurements were performed using a Riken Keiki AC-2 spectrometer. For all samples a power intensity of 5 nW was used. The data were fitted as the square root of the electron count versus energy. The energy levels as obtained using a combination of PESA (IP) and film absorption onset have been partially previously reported in ref. [34,45].

Supporting Information

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

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