The Role of Space Charge Effects on the Competition Between Recombination and Extraction in Solar Cells with Low-Mobility Photoactive Layers

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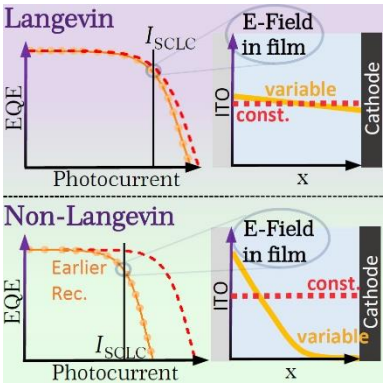
Abstract

The competition between charge extraction and non-geminate recombination critically determines the current-voltage characteristics of organic solar cells (OSCs) and their fill factor. As a measure of this competition, several figures of merit (FOMs) have been put forward, however, the impact of space charge effects has been either neglected, or is not specifically addressed. Here we revisit recently reported FOMs and discuss the role of space charge effects on the interplay between recombination and extraction. We find that space charge effects are the primary cause for the onset of recombination in non-Langevin systems, depending on the slower carrier mobility and recombination coefficient. The conclusions are supported with numerical calculations and experimental results of 25 different donor/acceptor OSCs with different charge transport parameters, active layer thicknesses or composition ratios. The findings represent a conclusive

understanding of bimolecular recombination for drift dominated photocurrents and allow to minimize these losses for given device parameters.



Organic semiconductors continue to be of great interest for photovoltaic energy conversion and light detection applications due to their solution processability, chemical tunability and mechanical flexibility. However, their disordered nature complicates the understanding of the critical mechanisms and pathways from the photoexcitation to free charges, and the subsequent extraction of these charges in a photovoltaic diode.[1,2] This complicates a more systematic improvement of their photovoltaic performance, and necessitates more research to understand the underlying photophysical mechanism which control charge generation and extraction.

Historically, a wide range of models have been proposed to describe the charge collection efficiency (η_{COLL}) of organic solar cells (OSCs) as a function of applied voltage. Some of these models were adapted from the inorganic semiconductor solid state physics, including the Shockley equation,[3,4,5] the Hecht equation,[6,7] or incorporating Shockley-Read-Hall (trap-assisted) recombination.[8,9] In particular, it has been shown that the current-density vs. voltage (JV) characteristics of low mobility solar cells deviate significantly from predictions of the Shockley equation.[10,11] For example, ideality factors evaluated from dark-JVs and from open-circuit voltage versus light intensity plots differ substantially.[12,13] The low carrier mobilities (typically not

exceeding 10^{-3} $cm^2V^{-1}s^{-1}$)[14] result in an efficient charge recombination when electron and hole encounter within their Coulomb radius, and the necessity of an electric-field to efficiently extract charge carriers in an organic light harvesting device. This leads to photocurrents that are dominated by carrier drift, rather than diffusion which is typically the case in inorganic *pn* junctions.[15] Indeed, significant progress has made in describing the efficiency of charge collection η_{COLL}, the fill factor (FF) and even entire IV-curves (provided that charge photogeneration is independent on the driving field)[16,17,18,19,20] of a large number of organic solar cells based on the competition between extraction and recombination.[10,11,14,21] Another consequence of the low carrier mobilities and the resulting accumulation of charge carries (space charges) is the redistribution/screening of the internal electric-field. It has become accepted wisdom that these so-called space charge effects play a crucial role in charge extraction, especially in devices with imbalanced mobilities.[6,22,23,24,25,26,27] However, recently proposed charge transport figures of merit (FOM) either neglect or do not specifically disentangle recombination due to the carrier meeting probability and space charge effects.[10,14,21,28,27]

In this article we discuss how different previously introduced FOMs are related and analyse the effect of space charge effects on the charge collection yield. To this end we first apply numerical simulations without space charge effects, examine the onset of bimolecular recombination, and address the role of the slower and faster carriers, and the recombination coefficient on the efficiency of charge extraction. We then enable space charge effects and discuss their impact on Langevin and Non-Langevin type systems with balanced and imbalanced mobilities. While space charge effects have little effect in Langevin system, in Non-Langevin systems they are the primary cause for the early onset of bimolecular recombination. Lastly, with explicit consideration of space charge, we can successfully describe the charge collection efficiency of *25 BHJ solar cells*, with

different (i) slower carrier mobilities, (ii) active layer thicknesses, (iii) blend compositions, as well as (iv) Langevin reduction factors. The work presents a satisfying understanding of detrimental bimolecular recombination of free charge carriers for drift limited photocurrents, and allows to minimize those losses for given device parameters such as film thickness, applied voltage and the slower carrier mobilities.

The FOM proposed by Bartesaghi et al.[14] which the authors called the θ parameter, considers the ratio of the rate constants for recombination k_r and extraction k_{ex}

$$\frac{k_r}{k_{ex}} = \frac{t_{tr}^{s}}{\tau^{s}} = \frac{t_{tr}^{f}}{\tau^{f}} \sim \theta = \frac{Gd^4\beta}{\mu_s\mu_f U'^2} \quad (1)$$

where $t_{tr}^{f(s)}/\tau^{f(s)}/\mu_{f(s)}$ are the faster (slower) carrier transit time/lifetime/mobility, G is the generation rate, d the active layer thickness, β the bimolecular recombination rate coefficient which equals the Langevin coefficient divided by a reduction factor (β_L/γ), and U' is the effective driving voltage at short-circuit (defined in ref.[10] as the difference between the ionization potential of the donor and the electron affinity of the acceptor minus 2*0.2 V to account for band bending at the electrodes). Importantly, the θ was derived under the assumption of a uniform electric-field in the bulk. Also, to calculate k_r the average hole distribution was written as $p_{av} = (Gd^2)/(4\mu_f U')$, which is only a valid assumption when charge carrier recombination is insignificant. We note that in a recent article Kaienburg et al.[27] proposed another electronic quality factor which was based on the FOM of Bartesaghi et al. with a stronger weight on the slower carrier mobility. Additionally the authors demonstrated the impact of space charges effects in thick (several hundred nm) and doped (N_D >5x10^{16}cm^{-3}) active layers, although this wasn't described analytically. Similarly, the FOM of Neher et al.[10] $\alpha^2 = \frac{q^2Gd^4\beta}{4\mu_s\mu_f(k_BT)^2}$ was derived under the

assumption of a constant quasi-Fermi level tilt in the bulk, meaning that space charge effects were not considered. The parameter α has been used in a modified Shockley-type equation to correct the ideality factor for transport losses, which enables to fit the entire IV curve analytically with a good match. Evidently, α is directly related to θ via the thermal and the built-in voltage. In an apparent contrast, Stolterfoht et al.[21] proposed that the device is limited by the accumulation of the slower carriers causing space charge effects. Specifically, the non-geminate charge recombination rate was shown to become significant (roughly 10% to 20% of the extraction rate) when the photocurrent approaches the space charge limited photocurrent $I_{\mathrm{SCLC}} = CU/t_{\mathrm{tr}}^{\mathrm{s}}\gamma^{1/2}$, where CU is the charge that can be stored in the dark on the electrodes in order to cancel the effective driving field and γ the reduction factor. We note that the driving voltage was defined in ref.[21], in contrast to Bartesaghi et al., as $U = U_{\mathrm{BI}} - U_{\mathrm{appl}}$, i.e. the superposition of built-in and applied voltage (and this definition was adopted in this work). However, limitations due to charge transport and space charge effects were not disentangled.

Interestingly, the FOM by Bartesaghi can be rewritten in a form similar to the one by Stolterfoht et al. by considering a few simple expressions: 1) $t_{\mathrm{tr}}^{\mathrm{f}} = d^2/(U\mu_{\mathrm{f}})$ that relates the transit time to the mobility of the faster carriers, 2) $\tau^{\mathrm{f}} = 1/(n^{\mathrm{s}}\beta)$ that relates the lifetime of faster carriers to a uniform density of slower carriers n^{s}, and 3) $\beta_{\mathrm{L}} = e(\mu_{\mathrm{f}} + \mu_{\mathrm{s}})/(\epsilon\epsilon_0)$, where e is the elementary charge, and $\epsilon\epsilon_0$ the product of vacuum permittivity and relative dielectric constant. We then arrive at a slightly different FOM for transport limited photocurrents:

$$FOM_{\mathrm{transp}} = \frac{k_{\mathrm{r}}}{k_{\mathrm{ex}}} = \frac{t_{\mathrm{tr}}^{\mathrm{f}}}{\tau^{\mathrm{f}}} = \frac{d^2 n^s \beta_{\mathrm{L}}}{\mu_{\mathrm{f}} U\gamma} = \frac{e n^{\mathrm{s}} d}{\gamma(\frac{\epsilon\epsilon_0}{d})U}\frac{(\mu_{\mathrm{f}} + \mu_{\mathrm{s}})}{\mu_{\mathrm{f}}} = \frac{Q^s}{\zeta CU\gamma}, \tag{2}$$

where Q^{s} is the slower carrier charge in the junction. Importantly, **Equation 2** is valid for different driving voltages U. Therefore, the theory can describe the power-generating regime of OPVs, however, beyond the maximum power point there will be a regime where these predictions do not hold anymore since charge diffusion become dominant. In **Equation 2**, we also introduced a correction factor $\zeta = \mu_{\mathrm{f}}/(\mu_{\mathrm{f}}+\mu_{\mathrm{s}})$ which equals 1/2 in case of balanced mobilities, and 1 in case of strongly imbalanced mobilities. Expanding the nominator and dominator of **Equation 2** with $t_{\mathrm{tr}}^{\mathrm{s}}$ leads to another similar - but experimentally better accessible - FOM

$$FOM_{\mathrm{transp}} = \frac{Q^{\mathrm{s}}}{\zeta CU\gamma} = \frac{I}{I_{\mathrm{transp}}}, \tag{3}$$

Here, I is the external photocurrent (which consists in equal parts of the drift current of the two carrier types: $I = 2Q^{\mathrm{s}}/t_{\mathrm{tr}}^{\mathrm{s}}$, and from the measured light minus dark current obtained from the measured light minus dark current), and

$$I_{\mathrm{transp}} = 2\zeta CU/t_{\mathrm{tr}}^{\mathrm{s}}\gamma\,, \tag{4}$$

the transport limited photocurrent. We use the term 'transport limited' to refer to the amount of charge that could be transported in the absence of space charge effects, i.e. if the electric field $E = U/d$ was uniform. Therefore, transport limitation sets in if $I > I_{\mathrm{transp}}$. Importantly, I/I_{transp} equals the θ parameter (**Equation 1**) when I is set to edG. We also note that I_{transp} depends linearly on the reduction factor γ while I_{SCLC} depends on the square root of γ. **Equation 4** underlines the important conclusion that also in the case of a constant electric field the charge transport efficiency is essentially given by the slower mobility of the two carrier types, consistent with our previous publication[21] and others.[22,23] We note that the dependence on the slower carrier

mobility might be in apparent discrepancy to the θ parameter, however the faster carrier mobility in θ factors out with the mobility dependence of β in the nominator. A subtle, but important prediction of **Equation 4** is, that the often cited detrimental effect of a mobility imbalance[25,29] is basically irrelevant for the transport efficiency because only the slower carrier mobility matters. It is also interesting that I_{transp} without the reduction factor equals the unipolar space charge limited current, which means that the onset of recombination and space charge effects coincide in Langevin systems, as previously reported by Tessler and Rappaport et al.[23,24]

To confirm the applicability of **Equation 4** to the situation of transport-limited currents we performed drift-diffusion simulations where the internal electric field (E-field) was set constant throughout the active layer. The external quantum efficiency (EQE) versus the (intensity dependent) external photocurrent in **Figure 1**(**a**) demonstrates that the downward deviation of the EQE increases linearly with increasing slower carrier mobility, thereby confirming the benefit of increasing the slower carrier mobility on I_{transp}. In contrast **Figure 1**(**b**) shows that the same advantage cannot be achieved by increasing the faster carrier mobility, and therefore a mobility imbalance has no effect. **Figure 1**(**c**) shows that increasing the reduction factor linearly improves the linear dynamic range of the device, as expected from **Equation 4** while **Figure 1**(**d**) shows that the recombination rate becomes similar to the extraction rate if the photocurrent reaches I_{transp}. Therefore, under the conditions considered here, for constant electric field, all simulations shown in panel (**a**, **b**, **c**) collapse into one curve, meaning that FOM_{transp} provides an accurate description of the onset of bimolecular recombination under neglect of space charge effects.

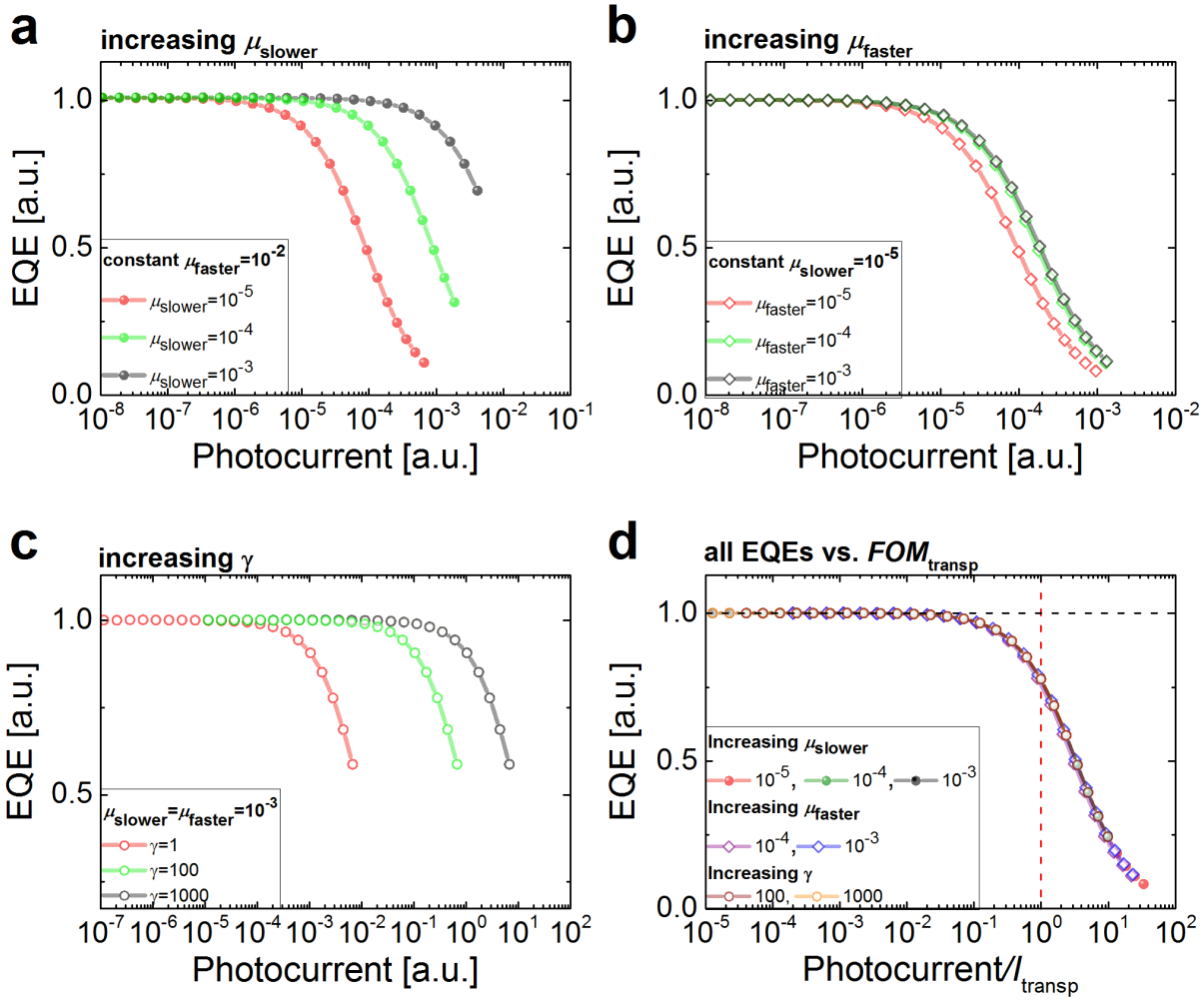


Figure 1. Space charge effects neglected - constant internal electric field. *Drift-diffusion simulations of external quantum efficiency (EQE) as a function of the light intensity dependent photocurrent. (**a**) Systems with higher slower carrier mobility sustain higher photocurrents before bimolecular recombination causes the downward deviation of the EQE (i.e. higher transport limited photocurrents I_{transp}). (**b**) Increasing the faster carrier mobility has essentially no effect on I_{transp}. (**c**) Reducing the recombination rate coefficient with respect to the Langevin coefficient allows to increase I_{transp} as well. (**d**) The EQE plotted versus the figure of merit ($FOM_{\mathrm{transp}} = I/I_{\mathrm{transp}}$) mark the critical point where the recombination rate becomes comparable to the extraction rate for simulated systems shown in the panels (**a**), (**b**) and (**c**).*

To demonstrate the impact of possible space charge effects we performed the same simulation with and without space charge effects enabled. First, we compare in **Figure 2**(**a**) the effect of space charge in Langevin systems with different mobility ratios (10 and 1000). It can be seen, that in Langevin systems, the additional screening effect of the field will have little or no impact because bimolecular recombination sets in when the amount of charge in the device becomes comparable to 1 *CU* where space charge effects are small. In other words, FOM_{transp} provides an appropriate description for Langevin systems, even in case of highly imbalanced mobilities. However, it is also well known that Non-Langevin systems can sustain more charge than 1 CU in the device.[30] This might suggest that, for these systems, space charge effects will have significant impact prior to the onset of bimolecular recombination. Indeed, the simulations in **Figure 2**(**b**) clearly show that the deviation of the EQE happens much earlier than in the case of a constant electric-field. Therefore, it can be concluded that the space charge effects are highly relevant for Non-Langevin systems and that they are the primary cause for an early onset of bimolecular recombination. We therefore propose that

$$FOM_{\mathrm{SCLC}} = \frac{I}{I_{\mathrm{SCLC}}}, \tag{5}$$

provides a more universal measure of the onset of bimolecular recombination, particularly for future high efficiency systems with strongly suppressed recombination.[31] Naturally, FOM_{SCLC} will become equal to FOM_{transp} when γ approaches one (Langevin systems) but will differ markedly from the transport FOM for highly suppressed recombination. We also note that the dependence of the I_{SCLC} on the square root of the reduction factor also applies to the double injection current.[32,33,34]

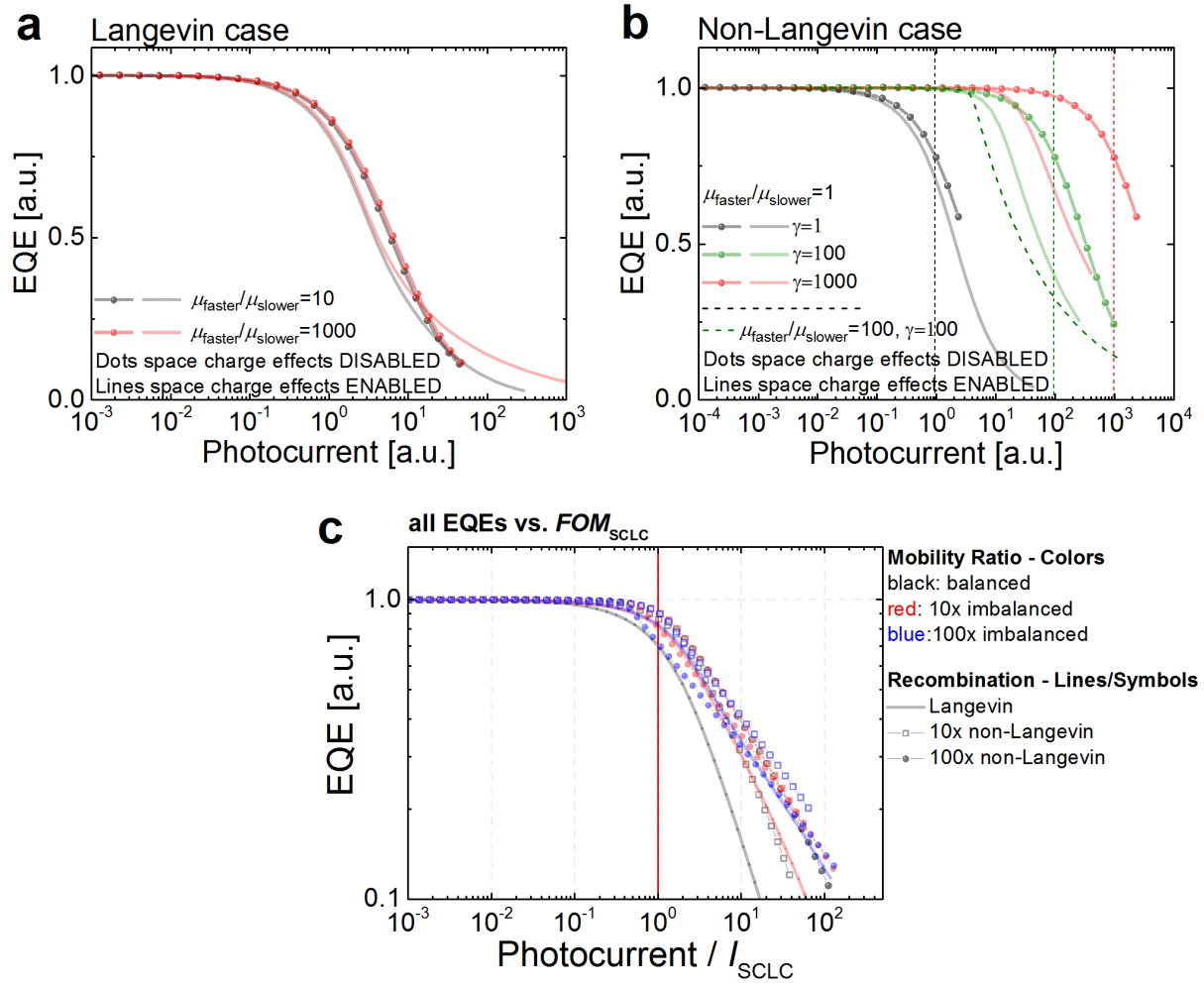


Figure 2. Space charge effects enabled – redistribution of the internal electric field. *Drift-diffusion simulations of External Quantum Efficiencies (EQE) as a function of the photocurrent. (**a**) Comparing simulations with space charge effects enabled (lines) and disabled (dotted lines) shows that space charge effects have essentially no impact on the onset of the bimolecular recombination losses in Langevin systems. (**b**) In contrast, in strongly Non-Langevin systems, the same comparison demonstrates that the space charge lead to an earlier recombination onset compared to the case of a uniform field. The reason is that non-Langevin systems can sustain more than ~1 CU charge (where C is the device capacitance and U the effective driving voltage) in the device without bimolecular recombination. Charge in excess of ~1 CU will, however, cause*

significant screening effects and the formation of field-free regions, which triggers more recombination. The green dotted line demonstrates that mobility imbalance will increase the detrimental space charge effects. ***(c)*** *EQE plotted as a function of the photocurrent normalized to the space charge limited current (I_{SCLC}) for different system with varying mobility ratios (1 - 100), and reduction factors γ of the bimolecular recombination coefficient (1 - 100). Within this range and ideal conditions, the square root dependence of the I_{SCLC} on γ holds.*

In this work, we further tested the validity of the square root dependence numerically in the ideal case of uniform charge generation with no charge injection (perfectly selective contacts). The numerical simulation show that the square root dependence holds within a broad mobility ratio and a reduction factor range from 1 to 100 (**Figure 2c**). However, it should be added that several factors can influence the formation of space charge effects and this dependence, such as doping, film thickness, carrier distribution, and significant charge injection ($\sim CU$) as pointed out by Kirchartz et al.[6] Even in the ideal case we find that the square root dependence of the limiting photocurrent breaks down for large reduction factors > 100 in combination with imbalanced mobilities > 10 (**Supplementary Figure 1**). In these extreme cases, the accumulation of slower carriers creates a zero-field region in which both carriers recombine independent on the recombination coefficient. This is because the charges are effectively "stuck" in this region as long as it takes to recombine them away. In such a scenario the photocurrent is entirely determined by the properties of the slower carrier with a characteristic 3/4 dependence on the light intensity.[25,35]

So far we presented several analytical and theoretical predictions of the competition between recombination and extraction under the influence of space charge effects. Next we will show that these results can be experimentally verified for a large number of BHJs solar cells (25) under different experimental conditions. We recently demonstrated the huge impact of the slower carrier

mobility for 5 BHJ solar cells with fixed active layer thicknesses (100 nm), similar faster carrier mobilities and different slower carrier mobilities,[36] as shown in **Figure 3**(**a**) (please refer to the **Supplementary Figure 2** for the details of the molecular structures). **Figure 3**(**b**) confirms that, at short-circuit, recombination becomes significant for all systems if the current hits the I_{SCLC}. **Figure 3**(**c**) demonstrates the impact of the reduction factor γ on the limiting photocurrent for a Langevin system such as WJ1-06:PC70BM and strongly non-Langevin systems, such as PTB7:PC70BM (1:1.5) ($\gamma \sim 50$ as obtained using transient extracted charge measurements[37]) and BTR:PC70BM (1:1) ($\gamma \sim 133$ using the same technique[31]). To highlight the effect of the reduction factor, we plot in **Figure 3**(**c**) the EQE of these 3 systems as a function of $I/(CU/t_{\mathrm{tr}}^{\mathrm{s}})$ to cancel the differences in the slower carrier transit time and CU among these systems. Plotting the EQE as a function of the I/I_{SCLC} as shown in **Figure 3**(**d**) confirms experimentally that the space charge limited photocurrent depends on the square root of the reduction factor.

Moreover, we have recently shown for PCDTBT:PC70BM and PTB7:PC70BM blends how electron and hole mobility vary as a function of the blend ratio, i.e. the slower carriers are holes at low donor concentrations, and electrons at high donor concentrations.[38] **Figure 3**(**e**) shows for PCDTBT:PC70BM blends that depending on the slower carrier mobility, the downward deviation of their normalized EQE occurs at different photocurrents, regardless of the carrier type. **Figure 3**(**f**) confirms, once more, that the critical current is the space charge limited current. Analogous results are shown in **Supplementary Figure 3** for PTB7:PC70BM blends.

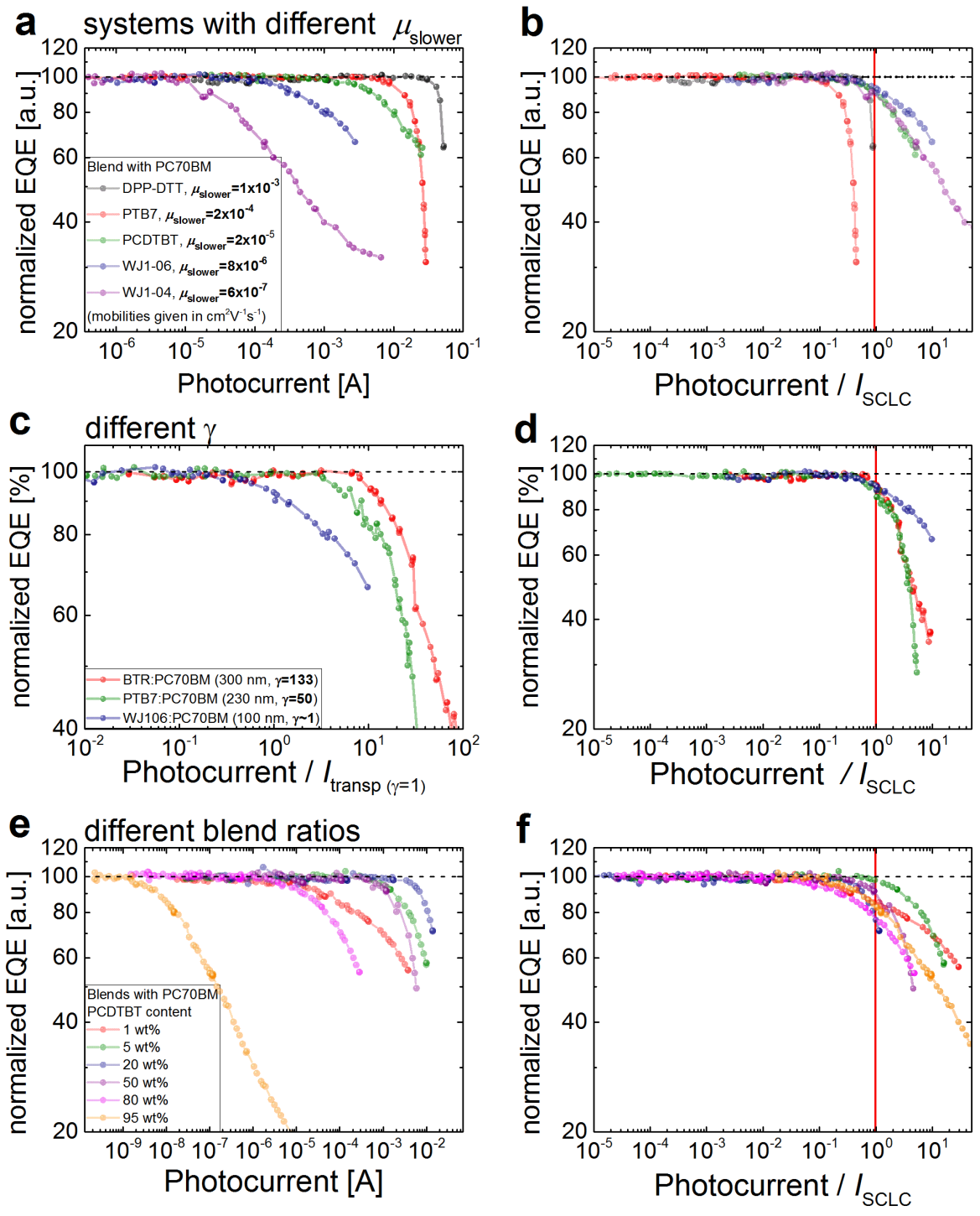


Figure 3. (a) *Experimentally measured EQEs versus the light intensity dependent external photocurrent for different electron-donors blended with PC70BM as acceptor, and similar active layer thickness of 100 nm. In these systems, the faster carriers are the electrons in the PC70BM*

phase (except holes in DPP-DTT phase), and electron mobilities are similar in these systems (varying from 10^{-4} - 10^{-3} $cm^2V^{-1}s^{-1}$). In contrast, the hole mobility is very different (varying from $5x10^{-7}$ - 10^{-3} $cm^2V^{-1}s^{-1}$), leading to large differences in the limiting photocurrent (and fill factor, which varies from 30%-72%).[36] ***(b)*** *The EQE of the same systems plotted versus the figure of merit (FOM_{SCLC}) demonstrates that the theory can successfully describe the collection efficiency of bulk heterojunctions with large differences in their transport properties. (**c**) The EQE as a function of the photocurrent normalized to the transport limited current I_{transp} with γ set equal to 1 to highlight the effect of the actual γ for a Langevin (WJ1-06:PC70BM) and two efficient non-Langevin systems PTB7:PC70BM (PCE ~ 6.5%) and BTR:PC70BM (PCE ~ 9.5%).[21,31] Both systems exhibit a strongly reduced recombination coefficient ($\gamma \sim 50$ for PTB7:PC70BM,[21] and $\gamma \sim 133$ for BTR:PC70BM).[31] (**d**) confirms that FOM_{SCLC} can correctly describe the recombination onset in these efficient systems with strongly supressed recombination. (**e**) EQE versus photocurrent for the PCDTBT:PC70BM system with different blend compositions varying from 1wt% PCDTBT to 95wt% PCDTBT with similar active layer thickness of 75 nm. Changing the blend ratio allows to effectively vary the slower carrier mobility and the onset of bimolecular recombination. (**f**) Confirms that the model can successfully explain bimolecular recombination in systems with varying blend compositions.*

Lastly, we note that we also tested the impact of several experimental parameters on the I_{SCLC}, such as the active layer thickness (as demonstrated in ref.[21] and replotted in **Supplementary Figure 4** for PCDTBT:PC70BM and PTB7:PC70BM blends over a wide range of film thicknesses), different photon energies - resulting in different carrier distribution profiles. While most experimental results in this work were obtained under short-circuit conditions, in ref.[21] we

also investigated the impact of changing the applied voltage and we found a good agreement according to the theory.

In conclusion we have shown how the charge transport parameter mediate the interplay between bimolecular recombination and charge extraction in organic photovoltaics under the influence of space charge effects by discussing different approaches that have been proposed in the literature. We find that figures of merit derived under neglect of space charge effects may apply to Langevin-systems, but they fail in the case of strongly non-Langevin devices. The important conclusion is that strongly Non-Langevin systems are space charge limited, while Langevin systems are transport limited. In all cases, the slower carrier mobility defines the photocurrent at which bimolecular recombination becomes significant or comparable to the extraction rate. In contrast, increasing the faster carrier mobility in the BHJs organic solar cells does not lead to performance improvements for either transport- and space charge limited conditions. Lastly we have verified the theoretical/numerical predictions for a large number of BHJ systems (25) with different slower carrier mobilities, active layer thicknesses, blend ratios, reduction factors. The results are critical for device engineering as they allow for minimised charge collection losses for given system parameters, such as capacitance, film thickness, built-in voltage and dielectric constant.

Experimental Methods

Simulations: The numerical simulations were performed using one dimensional continuity equations for electron and hole densities considering uniform charge generation, no-charge injection and no capacitance-resistance (RC) limitations. The film absorption was set to unity therefore the EQE equals the Internal Quantum Efficiency (IQE). Details of the code can be found in the Supplementary Information.

Experiments: Details of the method of plotting the EQE in arbitrary units, which is obtained from the ratio of the photocurrent and laser power, as a function of the photocurrent can be found in previous publications.[21,30] The I_{SCLC} has been calculated based on the measured individual parameters. The capacitance was measured using dark charge extraction by linearly increasing voltage)[21,39] and assumed to be independent on the light-intensity. The built-in voltage was estimated from the maximum produced photovoltage at highest laser powers.[37] The slower carrier transit time using resistance dependent photovoltage,[21] and the reduction factor was obtained from the extracted charge using transient photovoltage at high laser fluences that saturate the photovoltage.[37] The electrode area of the studied devices was 0.2 cm^2 which allows to calculate the photocurrent density.

ASSOCIATED CONTENT

AUTHOR INFORMATION

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

Supporting Information. The Supporting Information includes:

Numerical intensity dependent photocurrent simulations; Molecular Structures; EQE vs. photocurrent and I/I_{SCLC} of PTB7:PC70BM blends with varying blend compositions; EQE vs. photocurrent and I/I_{SCLC} of PCDTBT:PC70BM and PTB7:PC70BM blends with different film thicknesses; Details of Numerical Methods.

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