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Photo-generated Carrier Mobility Significantly Exceeds Injected Carrier Mobility in Organic Solar Cells

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Abstract

Charge transport in organic photovoltaic (OPV) devices is often characterized by space-charge limited currents (SCLC). However, this technique only probes the transport of charges residing at quasi-equilibrium energies in the disorder-broadened density of states (DOS). In contrast, in an operating OPV device the photo-generated carriers are typically created at higher energies in the DOS, followed by slow thermalization. Here, by ultrafast time-resolved experiments and simulations we show that in disordered polymer/fullerene and polymer/polymer OPVs, the mobility of photo-generated carriers significantly exceeds that of injected carriers probed by SCLC. Time-resolved charge transport in a polymer/polymer OPV device is measured with exceptionally high (picosecond) time resolution. The essential physics that the method of SCLC fails to capture is that of photo-generated carrier thermalization which boosts carrier mobility. We predict that only for materials with a sufficiently low energetic disorder, thermalization effects on carrier transport can be neglected. For

a typical device thickness of 100 nm, the limiting energetic disorder is $\sigma \sim 71$ (56) meV for maximum-power point (short-circuit) conditions, depending on the error one is willing to accept. As in typical OPV materials the disorder is usually larger, our results question the validity of the SCLC method to describe operating OPVs.

1. Introduction

Organic semiconductors allow for a low-cost alternative to inorganic solar cells. Most efficient organic photovoltaic (OPV) devices are based on the concept of a bulk heterojunction (BHJ) – a disordered mixture of electron donating and electron accepting (donor/acceptor) materials. Recent developments have led to a number of donor/acceptor combinations enabling single-junction devices with power conversion efficiencies around 10%, highlighting the potential of this technology.^[1–3] To a large extent the performance of these devices is dictated by their efficiency to extract the photo-generated charge, which is related to the charge carrier mobility in the photoactive layer.

A number of time-resolved and steady-state techniques are available to estimate the charge carrier mobility in OPVs.^[4–12] However, by far the most commonly employed method is that of space-charge limited currents (SCLC).^[11,12] It can be readily understood why that is – the SCLC method has several desirable features which are often lacking in other experimental techniques: the geometry of the active layer is similar to that used in a solar cell device, sample preparation and measurements can be carried out relatively quickly, and both electron and hole mobilities can be estimated. These features have led to the widespread use of SCLC in the study of charge transport in OPVs. However, ultra-fast time-resolved experiments often give a picture that is in conflict with that from SCLC – reported photo-generated carrier mobilities on an ultra-fast timescale significantly exceed those estimated by steady-state or slow time-resolved techniques.^[13–15] As the SCLC technique only probes the quasi-equilibrium transport of injected charges, these conflicting observations suggest that in OPV devices the mobility of photo-generated charges may significantly exceed that of injected charges. Recently van der Kaap et al.^[16] have tackled this issue and concluded that photo-generated carrier transport in

organic diodes can nevertheless be described by SCLC data. However, their work was mainly based on computer simulations for a single material with little to no experimental data. In fact, detailed experimental analysis verified by modelling is not available in literature. Here, by a combination of relevant experiments and simulations, we demonstrate that for the range of energetic disorder values commonly encountered in OPVs, i.e. $\sigma \sim 70\text{-}150$ meV, the transport of photo-generated carriers cannot be described by the use of SCLC data. The initial mobility of photo-generated carriers can be orders of magnitude higher than that probed by SCLC and is in fact time-dependent.

We monitor the motion of photo-generated carriers in full solar cell devices by the use of time-resolved electric-field-induced second harmonic generation (TREFISH) technique^[9] combined with photocurrent measurements.^[13] TREFISH enables picosecond time resolution which allows us to describe photo-generated carrier transport down to single hopping events in both polymer/fullerene and polymer/polymer OPV devices. To the best of our knowledge time-resolved charge transport in a polymer/polymer OPV device is measured with such a high temporal resolution for the first time. We use low laser excitation fluences, e.g. $0.18 \mu\text{J}/\text{cm}^2$, which makes our results directly relevant to devices operating at 1 sun continuous illumination conditions. Experiments are complemented with simulations utilizing a single parameter set for both transient and steady-state experiments, thus enabling a reliable comparison of photo-generated and injected carrier mobilities, the latter of which is probed by SCLC. We show that whereas SCLC only probes the transport of injected charges residing at quasi-equilibrium energies in the density of states (DOS), photo-generated carriers in an operating OPV device temporarily reside at higher energies in the DOS and must thermalize first. Population of higher energies in the DOS increases the mobility of photo-generated carriers that can thus significantly exceed their quasi-equilibrium SCLC mobility. Concomitantly, photo-generated carriers drift a significantly larger distance than that estimated by SCLC data. We predict that in materials with a sufficiently low energetic disorder thermalization effects on carrier transport can be neglected. For a typical device thickness of 100 nm, the limiting energetic disorder is $\sigma \sim 70$ meV for

maximum-power point and $\sigma \sim 56$ meV for short-circuit conditions, depending on the error one is willing to accept.

2. Results and Discussion

2.1. Investigated Materials

We compare the motion of photo-generated and injected carriers in blends of TQ1:PC₇₁BM^[17–19] and TQ1:N2200^[20,21], full compound names are given in the Experimental section. TQ1:PC₇₁BM was deliberately chosen as the model polymer/fullerene system due to the large body of available time-resolved experimental data in literature,^[13,14,22–24] enabling us to cross-check our current results for consistency. TQ1:PC₇₁BM yields a power conversion efficiency (PCE) of 7% and displays a high internal-quantum-efficiency (IQE) of approximately 90%.^[17,19] However, TQ1:PC₇₁BM blends are known to be rather amorphous.^[18] Nevertheless, the results that follow are expected to be general and not only apply to amorphous polymers but also to those of a semi-crystalline nature. We have thus also tested blends of TQ1:N2200, where PC₇₁BM was replaced by the semi-crystalline polymer acceptor N2200,^[25] yielding reasonably well-performing polymer/polymer solar cells with a PCE of 4.4%.^[21]

2.2. Photo-generated Carrier Mobility

To obtain accurate information on photo-generated carrier transport in OPV devices, temporal resolution down to single hopping events is necessary. The use of optical probing by TREFISH in combination with electrical extraction by photocurrent measurements enables the motion of photo-generated carriers to be characterized with picosecond time resolution in complete solar cell devices.^[13,26] This is the expected timescale of charge carrier hopping in organic semiconductors, making the combination of TREFISH and photocurrent measurements the method of choice in this study.

To make our results relevant to devices operating at 1 sun continuous illumination conditions we have used relatively low excitation fluences. TQ1:PC₇₁BM solar cell devices were excited at 550 nm with a pump fluence of 0.18 $\mu\text{J}/\text{cm}^2$, whereas TQ1:N2200 devices were excited at 810 nm with a pump fluence of 3.67 $\mu\text{J}/\text{cm}^2$. The higher pump fluence used for TQ1:N2200 is due to the fact that TQ1:N2200 absorbs rather weakly at 810 nm.^[20,21] We will show below that at such low excitation fluences the total extracted carrier density from the OPV device is comparable to that reported for other well-performing OPV systems under steady-state device operation.^[27–29]

Figure 1 shows the time-resolved extraction of photo-generated carriers at the indicated applied reverse bias in complete solar devices based on TQ1:PC₇₁BM (Figure 1a) and TQ1:N2200 (Figure 1b). Applied bias U in simulations was corrected for the approximate built-in field of the OPV device $U_{\text{bi}} = -1\text{V}$. These traces represent the cumulative collected charge at the electrodes following excitation by a laser pulse.^[9] We have previously shown that for the case of TQ1:PC₇₁BM the first half of these transients is mainly dominated by the motion of electrons, whereas the second half corresponds to the motion of holes.^[13] As in TQ1:N2200 blends only the acceptor has been replaced, the first half of the extraction kinetics is expected to be dominated by the motion of electrons in the N2200 phase. A side-by-side comparison of the extraction kinetics in both blends (Figure 1b inset) suggests that the transport of photo-generated carriers in TQ1:PC₇₁BM is faster than in TQ1:N2200. Nevertheless, the motion of holes and electrons remains convoluted, making it difficult if not impossible to make a meaningful quantitative comparison from the experimental data alone – obtaining reliable information on charge carrier mobility necessitates the use of a well-established charge transport model.

We rely on kinetic Monte Carlo simulations based on the extended Gaussian Disorder Model (eGDM),^[30] which has been successfully utilized to explain hopping carrier motion in a large variety of organic semiconductors. The basics of the GDM model are described in detail elsewhere.^[31,32] In brief, our simulations start with photo-generated excitons and take into account: exciton diffusion and electron-hole recombination; electron and hole transport; site occupation and state-filling effects; all

Coulomb interactions, including those by image charges in metal electrodes. The BHJ active layer is treated as an effective medium, meaning that local variations in active layer morphology, e.g. differences in physical properties between disordered and semi-crystalline regions, and their connectivity, are not explicitly accounted for. This is to keep the number of simulation parameters to a minimum. As such, kinetic Monte Carlo parameters represent ‘average’ values over the entire BHJ active layer. For further information regarding the model see the Experimental section and refs. [13,14,33,34].

The experimental data in Figure 1 was used to extract the simulation parameters responsible for hopping carrier motion: a_{nn} the inter-site distance, ν_0 the attempt-to-hop frequency, σ the energetic disorder. In principle, the values of these parameters do not form a unique set – a large σ can be compensated by increasing ν_0 . To avoid ambiguous fits to experiment, we have fixed a_{nn} at a reasonable value of $a_{nn} = 1.8 \text{ nm}$.^[33] This allows us to fit the experiment by a unique set of four parameters. The energetic disorder σ for holes/electrons defines dispersion,^[13] whereas hole/electron ν_0 defines the onset of charge motion. We obtain reasonably good fits to experiment (Figure 1 black dashed traces) by the use of the parameter set in **Table 1**, which is discussed at a greater length in the Supporting Information. The ability of the model to not only capture the shape of the extraction kinetics but also the field-dependence means that the simulations capture both carrier recombination and carrier transport dynamics. This enables us to predict the outcome at arbitrary field strengths. Successful model fits to experiment thereby allow us to reliably estimate the mobility of photo-generated carriers by the use of kinetic Monte Carlo simulations.

Figure 2 shows the simulated photo-generated carrier mobility for both blends at an electric field strength of 1 V/100 nm. Photo-generated carrier mobility $\mu_{\text{photo}}(t)$ is time-dependent as following the early time scales of free carrier generation the photo-generated carriers temporarily reside at higher energies in the DOS and undergo thermalization. This boosts carrier motion, as recently confirmed by time-resolved experiments.^[14] We find rather similar hole mobility kinetics in both blends – the transport of photo-generated holes in the donor phase is comparable when TQ1 is blended with either

acceptor. Comparable hole transport is expected, as in both blends the TQ1 phase remains quite amorphous.^[18,21] In contrast, the time-dependent electron mobility is significantly higher when TQ1 is blended with PC₇₁BM instead of N2200, as suggested by experiments, see the inset of Figure 1b. As such, PC₇₁BM is superior to N2200 as an electron transport material due to its higher time-dependent electron mobility. For more detailed information and how the observed difference in $\mu_{\text{photo}}(t)$ relates to the carrier hopping parameters in Table 1, see the Supporting Information.

After a sufficiently long time delay following photoexcitation, the photo-generated carriers will reach quasi-equilibrium and have a constant (time-independent) mobility. In principle, in this regime the transport of photo-generated carriers is indistinguishable from that of injected carriers, as both are transported at similar energies in the DOS. In the following we investigate the quasi-equilibrium transport of injected carriers by SCLC experiments and simulations, with the aim to compare the SCLC carrier mobility μ_{SCLC} to that of photo-generated carriers $\mu_{\text{photo}}(t)$.

2.3. Photo-generated vs SCLC Carrier Mobility

Figure 3a shows typical SCLC current-voltage characteristics for both blends. The active layers for electron- and hole-only devices were spin-cast in the same manner as for the OPV devices studied in Figure 1, ensuring a similar active layer morphology and thickness in both OPV and SCLC device experiments (detailed information on sample fabrication is described in the Experimental section).

Experimental SCLC data allows us to estimate the quasi-equilibrium carrier mobility μ_{SCLC} by the use of the Mott-Gurney law, which, in its simplest and most widely used form is

$$j = \frac{9}{8} \epsilon_r \epsilon_0 \mu_{\text{SCLC}} \frac{(U - U_{\text{bi}})^2}{d^3} \quad (1)$$

Where ϵ_0 is the vacuum permittivity, ϵ_r the dielectric constant of the active layer, d the active layer thickness, $(U - U_{\text{bi}})$ the applied voltage corrected by the built-in voltage of the device, and μ_{SCLC} the quasi-equilibrium carrier mobility. **Figure 3b** shows extracted μ_{SCLC} values by the use of Equation 1, at the expected carrier density in the single-carrier device (see the Supporting Information). The advantage of Equation 1 is its ease of use. However, note that Equation 1 provides only a single value

for the quasi-equilibrium carrier mobility and captures neither the concentration- nor the field-dependence of μ_{SCLC} , known in organic semiconductors.^[30,35] To ensure that both carrier density and field effects on μ_{SCLC} are reliably captured, necessitates the use of a more advanced charge transport model.

To ensure a reliable comparison of photo-generated and injected carrier transport, our model should be able to reproduce both the time-resolved experiment in Figure 1 and the steady-state SCLC data in Figure 3a by the same carrier hopping parameters (Table 1). Since kinetic Monte Carlo simulations with Ohmic contacts are generally very time consuming and difficult to handle correctly, we have instead used an alternative model to simulate the SCLC experiment – a one-dimensional (1D) drift-diffusion (DD) model which incorporates the eGDM formalism via a density- and field-dependent mobility.^[30,35] The advantage of the DD model is that it is computationally inexpensive and can thus be fitted to experiment by least-squares, thus ensuring that the injection properties of the contacts describe the experiment well. See the Experimental section for contact parameters that define injection and a more detailed explanation as to why an alternative model to kinetic Monte Carlo was necessary. We obtain good fits to the SCLC experiment by the use of the parameter set in Table 1 (Figure 3a black dashed traces). As now both the time-resolved and the SCLC data can be fitted by the same carrier hopping parameters, it enables us to reliably compare the mobility of photo-generated and injected charge carriers, i.e. $\mu_{\text{photo}}(t)$ and μ_{SCLC} .

Before comparing the mobility of photo-generated carriers to their quasi-equilibrium SCLC mobility, it must be noted that the comparison must be performed at a similar carrier density. This is because although the mobility of non-equilibrated (photo-generated) carriers is concentration-independent at early times,^[14] the mobility of quasi-equilibrated carriers (such as those at long time delays after photoexcitation and those probed by SCLC) is known to be concentration-dependent due DOS state-filling.^[30,35] Time-resolved measurements in Figure 1 indicate that the total extracted charge density at short-circuit and reverse bias conditions ($U < 0\text{V}$) is of the order of 10^{16} cm^{-3} , which very closely corresponds to DOS occupancies of the order of $c_0 = 10^{-4}$. The time-dependent mobility $\mu_{\text{photo}}(t)$ in

Figure 2 was therefore simulated at a DOS occupancy of $c_0 = 1 \times 10^{-4}$, corresponding to a charge carrier density of $n = 1.7 \times 10^{16} \text{ cm}^{-3}$. These values are in the range of reported carrier densities during steady-state OPV device operation for a number of BHJ systems,^[27-29] making our time-resolved data directly relevant to OPV devices operating at 1 sun continuous illumination conditions.

Figure 3b shows the estimated quasi-equilibrium μ_{SCLC} mobility from the SCLC experiment for a range of carrier densities at an electric field strength of 1V/100nm, according to the well-known parametrization by Pasveer,^[35] using the carrier hopping parameter set in Table 1. The estimated carrier density n during the SCLC experiment is of the order of $n = 1.7 \times 10^{16} - 10^{17} \text{ cm}^{-3}$, corresponding to fractional DOS occupancies of $c_0 = 10^{-4} - 10^{-3}$, comparable to those obtained in our time-resolved measurements. See the Supporting Information for how the carrier density in the SCLC experiment was estimated. The carrier density range $n = 1.7 \times 10^{16} - 10^{17} \text{ cm}^{-3}$ observed in the SCLC experiment is indicated by the shaded area in Figure 3b. State-filling at these DOS occupancies leads to only a minor increase in μ_{SCLC} , as expected.^[35] Most importantly, since now our model can capture both the field- and the concentration-dependence observed in experiments this enables us to reliably extract/compare the mobility of photo-generated carriers to their quasi-equilibrium SCLC mobility. Figure 2 compares the simulated mobility of photo-generated carriers to that of injected carriers probed by SCLC. Shaded areas indicate μ_{SCLC} mobilities in the range of carrier densities observed in the SCLC experiment $n = 1.7 \times 10^{16} - 10^{17} \text{ cm}^{-3}$ (Figure 3b). Photo-generated carrier mobilities $\mu_{\text{photo}}(t)$ are simulated at a comparable carrier density as observed in the time-resolved experiment $n = 1.7 \times 10^{16} \text{ cm}^{-3}$. We obtain excellent agreement between $\mu_{\text{photo}}(t)$ at long time delays and μ_{SCLC} . This confirms our hypothesis that at sufficiently long time delays the mobility of photo-generated carriers is indistinguishable to that of injected carriers monitored by SCLC. However, it is evident from Figure 2, that before the photo-generated carriers have fully thermalized, $\mu_{\text{photo}}(t)$ is orders of magnitude higher than μ_{SCLC} . This is because SCLC cannot capture the thermalization dynamics governing the transport of photo-generated carriers at early time scales, thus underestimating their mobility. It is thus questionable whether SCLC can be used to correctly explain photo-generated

carrier transport in disordered OPVs. In fact, our results indicate that in most cases it is invalid to do so as the associated error is substantial.

2.4. SCLC Cannot Explain Photo-generated Carrier Transport

The error in using the quasi-equilibrium μ_{SCLC} mobility can be quantified by comparing the carrier drift distance with and without thermalization

$$d_{\text{photo}}(t) = \frac{U-U_{\text{bi}}}{d} \int_0^t \mu_{\text{photo}}(t) dt \quad (2)$$

$$d_{\text{SCLC}}(t) = \frac{U-U_{\text{bi}}}{d} \mu_{\text{SCLC}} t \quad (3)$$

Equation 2 corresponds to the estimated carrier drift distance when using the time-dependent mobility of photo-generated carriers $\mu_{\text{photo}}(t)$, whereas Equation 3 corresponds to the use of the quasi-equilibrium μ_{SCLC} mobility (or $\mu_{\text{photo}}(t)$ at long time delays). Both $\mu_{\text{photo}}(t)$ and μ_{SCLC} are taken from Figure 2 at the same carrier density and electric field strength. **Figure 4a** shows the estimated hole drift distance in TQ1:PC₇₁BM at maximum-power point conditions (0.2V/70nm) using the two methods. As $\mu_{\text{photo}}(t)$ is significantly higher than μ_{SCLC} at early times, the photo-generated carriers will drift a larger distance than quasi-equilibrated carriers within the same period of time. Figure 4a thus illustrates that the use of μ_{SCLC} via Equation 3 significantly underestimates the drift distance of photo-generated carriers.

We quantify the error in using the quasi-equilibrium μ_{SCLC} mobility by

$$\Delta d(t) = d_{\text{photo}}(t) - d_{\text{SCLC}}(t) \quad (4)$$

$$\frac{\Delta d(t)}{d_{\text{photo}}(t)} = \frac{d_{\text{photo}}(t) - d_{\text{SCLC}}(t)}{d_{\text{photo}}(t)} \quad (5)$$

Equation 4 quantifies the loss of carrier drift distance when not accounting for thermalization. Equation 4 also quantifies the drift distance by which a quasi-equilibrated carrier is lagging behind a non-equilibrated (photo-generated) carrier. **Figure 4b** shows the resulting error for the holes versus the correct photo-generated carrier drift distance $d_{\text{photo}}(t)$ at two of the most relevant operating points of the TQ1:PC₇₁BM photovoltaic device: the maximum-power point (MPP) (0.2V/70nm) and short-

circuit (SC) (1V/70nm) conditions. The results are shown up to 500 nm as they are general and applicable to thicker samples. The error is substantial, especially at early times. For example, the average photo-generated hole is extracted from the TQ1:PC₇₁BM device at a drift distance of $d_{\text{photo}}(t) = 35$ nm (black dotted line), however, the use of a quasi-equilibrium μ_{SCLC} mobility would predict a drift distance of only 15 nm within the same period of time – an equilibrated hole is lagging behind the photo-generated hole by as much as 20 nm (Figure 4b), a significant number for a thin-film photovoltaic device. In the time domain a similarly large error is found as the mean extraction time of 12 μs predicted by the SCLC mobility overestimates the actual value of 5 μs roughly by a factor of ~ 2.5 .

For sufficiently thick samples, where the photo-generated carriers have enough time to reach quasi-equilibrium before extraction, the error should saturate. This is because at long time delays the mobility of photo-generated carriers is indistinguishable to that of injected carriers. This is indeed the case, as can be inspected from Figure 4b (solid red trace), where at large drift distances and weak electric field strengths (0.2/70nm) $\Delta d(t)$ saturates at 53 nm – the total gain in drift distance by hole thermalization in TQ1:PC₇₁BM at MPP. See the Supporting Information for data over a larger range. Figure 4b shows that the situation is worse at higher electric field strengths as the error increases substantially. For example, at short-circuit conditions $\Delta d(t)$ at $d_{\text{photo}}(t) = 35$ nm is approximately ~ 1.4 times larger than at MPP and equals $\Delta d(t) = 28.5$ nm (Figure 4b red dashed trace). Similar error values are obtained for the holes in TQ1:N2200 and for electrons in both blends. We therefore conclude that the over-simplified use of μ_{SCLC} cannot describe photo-generated carrier transport neither in TQ1:PC₇₁BM nor in TQ1:N2200 as it does not capture the effects of carrier thermalization and thus leads to substantial error in the estimated charge carrier drift distance. Note also, that due to the highly dispersive transport of photo-generated charges in actual devices, the mean mobility values discussed here are only a lowest order approximation, as in fact the majority of photo-generated charges is extracted up to orders of magnitude faster than the mean.^[13]

2.5. Other OPV Systems

The question remains whether SCLC fails to describe photo-generated carrier transport in other OPV systems, beyond those presented in this work. As the eGDM formalism employed here is general and applicable to any disordered organic semiconductor, we expect our conclusions to also apply to other material combinations: polymer/small molecule, polymer/polymer and small molecule based OPVs. In fact, a similarly high and time-dependent carrier mobility was already observed in small molecule based OPVs utilizing a merocyanine dye mixed with PC₆₁BM.^[36] In general, the smaller the energetic disorder σ of the material, the smaller the error between using a quasi-equilibrium and the photo-generated carrier mobility will be.

Figure 5 shows $\Delta d(t)$ and the $\Delta d(t)/d_{\text{photo}}(t)$ error at maximum power-point (0.2V/100nm) and at short-circuit (1V/100nm) conditions at a photo-generated carrier drift distance $d_{\text{photo}}(t) = 50$ nm in materials with different disorder. Data were obtained by kinetic Monte Carlo simulations at two ν_0 values. Simulations at the indicated disorder were carried out while keeping the rest of the parameters fixed to those obtained from experiments on TQ1:PC₇₁BM. The error in using a quasi-equilibrium μ_{SCLC} mobility is decreasing with decreasing disorder. This is due to the narrowing of the DOS distribution – with decreasing disorder $\mu_{\text{photo}}(t)$ becomes less time-dependent, making the effect of thermalization on carrier transport less important (Figure 5 inset).

The error shown in Figure 5 is independent of the attempt-to-hop frequency ν_0 – the main material parameter dictating the error is the energetic disorder σ . This is because both $\mu_{\text{photo}}(t)$ and μ_{SCLC} are linear in ν_0 , making the attempt-to-hop frequency cancel out. Therefore, if the energetic disorder of the material is known, the error in using a quasi-equilibrium μ_{SCLC} mobility can be read from Figure 5 – the result applies to any other donor or acceptor material. For a given field (1V/100nm) and carrier density ($c_0 = 1 \times 10^{-4}$, $n = 1.7 \times 10^{16} \text{ cm}^{-3}$) the result is universal. However, note that the error is carrier density dependent as the quasi-equilibrium carrier mobility μ_{SCLC} depends on carrier density.^[30,35] More concretely, if the OPV device operates at a higher carrier density, μ_{SCLC} will be higher at that density due to DOS state-filling, making it more comparable to $\mu_{\text{photo}}(t)$, thereby

reducing the error (see the Supporting Information). Nevertheless, as most highly-efficiency OPVs operate at a similar carrier density to that described here,^[27–29] the estimated error shown in Figure 5 is expected to be the most general.

The use of a quasi-equilibrium μ_{SCLC} mobility is only acceptable for materials with a sufficiently low energetic disorder, i.e. those leading to small error. Although it is not entirely clear what error in $d_{\text{photo}}(t)$ is acceptable, for illustrative purposes we will use 15% of the average carrier drift distance in a typical 100 nm thick active layer $15\% \times 100\text{nm} / 2 = 7.5 \text{ nm}$, i.e. $\Delta d(t)/d_{\text{photo}}(t) = 15 \%$. Figure 5 then predicts that at MPP conditions (0.2/100nm) the use of SCLC (or any other slow time-resolved or steady-state) mobility data is acceptable only for materials with $\sigma < 71 \text{ meV}$. Sufficiently low energetic disorder values are only reported for a few high-efficiency OPV systems, for example semi-crystalline donor/acceptor blends of PBDTTT-C:PC₇₁BM ($\sigma_{\text{h}} = 70 \text{ meV}$, $\sigma_{\text{e}} = 75 \text{ meV}$) and rrP3HT:PC₆₁BM ($\sigma_{\text{h}} = 33 \text{ meV}$, $\sigma_{\text{e}} = 43 \text{ meV}$).^[37,38] Such low energetic disorder values were obtained by active layer morphology control, e.g. rrP3HT:PC₆₁BM blends are typically annealed, whereas for the case of PBDTTT-C:PC₇₁BM the energetic disorder of the PC₇₁BM phase was lowered from 90 meV to 70 meV by the use of a processing additive.^[37] This illustrates that changes in active layer morphology also affect the energetic disorder of the material under investigation which may make the use of SCLC data acceptable. Nevertheless, at larger electric field strengths, such as short-circuit conditions (Figure 5 dashed traces), we can correctly describe photo-generated carrier transport only in materials with even lower disorder values $\sigma < 56 \text{ meV}$.

Blends studied in this and previous work, i.e. TQ1:PC₇₁BM, TQ1:N2200, MDMO-PPV:PC₆₁BM and PCDTBT:PC₆₁BM, are all rather amorphous and fall outside this range.^[14,33,34] This means that photo-generated carrier transport cannot be described by the use of SCLC data in amorphous blends with a large energetic disorder. Note also, that for the widely used acceptor materials such as PC₆₁BM, PC₇₁BM and N2200 we find large electron disorder values, suggesting that when these acceptors are used in amorphous blends the transport of photo-generated electrons cannot be described by SCLC data. Since most efficient-OPVs usually have an energetic disorder similar to or higher than

$\sigma > 56$ -71 meV, we suggest that the widespread use of quasi-equilibrium SCLC mobility data to describe disordered OPVs is questionable at best even at relatively weak electric fields. Quasi-equilibrium mobility data is only reliable for materials with a sufficiently low energetic disorder, and is invalid for highly disordered materials. **Figure 6** schematically summarizes the main findings of this work.

2.6. Other Experimental Techniques

The conclusions that are presented here are not limited to the method of SCLC but also apply to other techniques that probe the significantly lower mobility of the (nearly) quasi-equilibrated carriers. This includes slow time-resolved techniques with insufficient time resolution to capture photo-generated carrier thermalization, such as photo-induced charge extraction by linearly increasing voltage (photo-CELIV) and time-of-flight (TOF). Note also, that organic field-effect transistor (OFET) measurements are not very relevant either – although OFET mobilities are typically measured at very high carrier densities, making them comparable to the high photo-generated carrier mobility due to state-filling, OFET measurements neither capture the correct physics nor the dynamics of photo-generated carrier thermalization.

3. Conclusion

The essential message that we wanted to convey is that the SCLC technique cannot be used to reliably describe photo-generated carrier transport in disordered OPVs, unless the results are validated by an additional method that quantifies the presence (or the lack of) photo-generated carrier thermalization. We predict that for a typical device thickness of 100 nm, quasi-equilibrium mobility data is only valid for materials with an energetic disorder lower than $\sigma < 71$ meV at maximum-power point and $\sigma < 56$ meV at short-circuit conditions, depending on the error one is willing to accept. As in typical OPV materials the disorder is usually larger, the use of quasi-equilibrium mobility data to describe operating OPVs, predict their PCE limits and guide new material design, requires re-evaluation.

These observations make detailed studying of charge transport in OPVs a challenging task, as most techniques that allow to capture photo-generated carrier thermalization, such as the one employed here, are very time consuming and suffer from limited availability. Nevertheless, we hope that the results presented here encourage others to consider these aspects for developing a better understanding of charge transport in OPVs and organic semiconductors in general.

3. Experimental Section

Full investigated material names. poly[2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl] (TQ1), [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM), poly(N,N'-bis(2-octyldodecyl)naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl-alt-2,2'-bithiophene-5,5'-diyl) (N2200).

Investigated samples. All samples were fabricated inside a N₂-filled glovebox and encapsulated with epoxy glue, samples were measured outside the glovebox in an ambient environment. BHJ active layers were spin-coated at the same settings as for the best-performing OPV devices: active layers of TQ1:PC₇₁BM (1:2.5 ratio by weight) were spin-coated from a 25g/l (total) 1,2-dichlorobenzene (ODCB) solution yielding an active layer thickness of 70 nm, whereas active layers of TQ1:N2200 (2:1 ratio by weight) were spin-coated from a 9g/L (total) chloroform (CF) solution and then annealed for 10 mins at 120 °C before top electrode deposition, yielding an active layer thickness of 85nm. Time-resolved experiments were carried out on devices in inverted geometry: on semi-transparent ITO/PFPA-1/TQ1:PC₇₁BM/PEDOT:PSS(Clevios PH1000) devices for TQ1:PC₇₁BM, and ITO/ZnO/TQ1:N2200/MoO₃/Al for TQ1:N2200. Detailed information on OPV device preparation can be found elsewhere.^[17,21] Hole-only devices were fabricated in the following geometry ITO/PEDOT:PSS/Active layer/MoO₃/Al, electron-only devices: ITO/PEIE/TQ1:N2200/LiF/Al for TQ1:N2200 and Al/TiO_x/TQ1:PC₇₁BM/TiO_x/Al for TQ1:PC₇₁BM.

Time-resolved experiments. Both TREFISH and photocurrent measurements were performed simultaneously for TQ1:PC₇₁BM – measuring the response of the OPV device from the same 550 nm

pump pulse. The working principle of the TREFISH technique is described in detail elsewhere.^[9,13] Briefly, we utilize the Electric Field-Induced Second Harmonic (EFISH) generation effect to monitor the temporal evolution of the electric field strength in the bulk of the BHJ active layer. Photo-generated charge carriers partially screen the applied electric field, leading to a reduction of the 2nd harmonic intensity, allowing for their motion to be evaluated optically with sub-picosecond time resolution. The change in the strength of the electric field can be transformed to the amount of extracted charge $Q(t) = CdE(t)$, where C is the sample capacitance per area, d is the sample thickness and $E(t)$ is the estimated E field strength. Extracted charge carrier density n can then be calculated as $n(t) = Q(t)/de$, where e is the elementary charge. Since TQ1:N2200 is only weakly absorbing at 810 nm the TREFISH part of the time-resolved experiment was measured at a higher pump fluence of $112.8 \mu\text{J}/\text{cm}^2$ to ensure an acceptable signal-to-noise ratio. Electrical extraction data for TQ1:N2200 in the 5-20 ns range are not shown as they were noisy and may be unreliable. The choice of wavelength was due to experimental limitations.

Kinetic Monte Carlo simulations. Simulations of the time-resolved experiment were carried out using a kinetic Monte Carlo model with periodic boundary conditions in the x,y direction. Metallic sink contacts were used. Active layer thickness was set to that of a real device. We use the Miller-Abrahams expression to quantify, with the least number of parameters, the nearest-neighbor hopping rate of a charge carrier in a Gaussian DOS, see the Supporting Information. The most comprehensive description of the model can be found in the Supporting Information in ref. [14] For additional information regarding the model see also refs. [13,33,34].

Drift-diffusion simulations. Drift-diffusion simulations of unipolar devices were carried out by numerically solving the coupled Poisson and drift-diffusion equations on an equidistant 1D mesh. For the drift-diffusion equations the well-known Scharfetter-Gummel interpolation scheme for the charge density was used.^[39] Boundary conditions for the charge density at the contact interfaces were calculated as simple Boltzmann factors of the effective injection barrier height, which equals the nominal injection barrier corrected for the image potential.^[40] Contact injection barrier heights

obtained by least-squares fitting to the SCLC experiment were 209 meV and 2 meV for electron-only TQ1:PC₇₁BM devices, 105 meV and 177 meV for hole-only TQ1:PC₇₁BM devices, 187 meV and 1 meV for electron-only TQ1:N2200 devices, 220 meV and 189 meV for hole-only TQ1:N2200 devices. The effect of Gaussian disorder was implemented via a density- and field-dependent mobility for which the parametrization of Pasveer was used.^[35]

Explanation for the use of 1D model instead of kinetic Monte Carlo. Attempts to simulate SCLC experiments by the kinetic Monte Carlo model were made, but these were only moderately successful – simulated current-density values overestimated those observed in the SCLC experiment by a factor of approximately 2 to 7. This was not due to a failure of the model, but due to the difficulty of simulating Ohmic contacts by the use of kinetic Monte Carlo. We are confident that by slight adjustments of contact injection barriers in the model the simulated current-density values can be corrected accordingly. Nevertheless, as kinetic Monte Carlo simulations are very time consuming and thus do not allow for least-squares fitting we did not pursue this attempt. We have however made sure that the one-dimensional DD model used in the main text is consistent with kinetic Monte Carlo.

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Figure 1. Time-resolved extraction of photo-generated carriers. **(a)** TQ1:PC₇₁BM solar cell device excited at 550 nm with a pump fluence of $0.18 \mu\text{J}/\text{cm}^2$. Due to limitations of electrical extraction measurements the initial 5-20 ns are prone to error and are marked by thinner lines. **(b)** TQ1:N2200 solar cell device excited at 810 nm with a pump fluence of $3.67 \mu\text{J}/\text{cm}^2$ (TQ1:N2200 absorbs weakly at this wavelength). Colored traces indicate experimental data, black dashed traces indicate kinetic Monte Carlo simulations. Applied bias U in simulations was corrected for the approximate built-in field of the OPV device $U_{\text{bi}} = -1\text{V}$. The inset in Figure 1b shows that photo-generated carrier extraction in TQ1:PC₇₁BM is significantly faster than in TQ1:N2200. Experimental data for TQ1:PC₇₁BM are taken from ref. [13].

Figure 2. Simulated photo-generated carrier mobility comparison to SCLC mobility. Simulated time-dependent photo-generated carrier mobility $\mu_{\text{photo}}(t)$ at an electric field strength of 1V/100nm for TQ1:PC₇₁BM (solid lines) and TQ1:N2200 (dashed lines) at a carrier density of $n = 1.7 \times 10^{16} \text{ cm}^{-3}$, corresponding to a DOS occupancy of $c_0 = 10^{-4}$. Blue corresponds to electrons, red corresponds to holes. Shaded areas indicate the estimated SCLC mobility μ_{SCLC} for TQ1:PC₇₁BM (solid fill) and TQ1:N2200 (patterned fill). The lower/upper bounds correspond to μ_{SCLC} values for the range of carrier densities observed in the SCLC experiment $n = 1.7 \times 10^{16} - 10^{17} \text{ cm}^{-3}$, corresponding to a DOS occupancy range of $c_0 = 10^{-4} - 10^{-3}$, see Figure 3b.

Figure 3. SCLC experiment and estimated SCLC carrier mobility dependence on carrier density. **(a)** Typical SCLC current-voltage characteristics of TQ1:PC₇₁BM (filled symbols) and TQ1:N2200 (empty symbols) for electron-only (blue) and hole-only (red) devices. Active layer thickness is the same as for the OPV devices in Figure 1: 70 nm for TQ1:PC₇₁BM and 85 nm for TQ1:N2200 devices. Black dashed lines are fits according to the 1D drift-diffusion model using the same hopping parameters as for the time-resolved data in Figure 1. **(b)** Shows the estimated SCLC carrier mobility μ_{SCLC} dependence on carrier density at an electric field strength of 1V/100nm, according to the well-known parameterization by Pasveer^[35] (lines). Quasi-equilibrium mobility μ_{SCLC} values estimated by fits of the data in (a) to the Mott-Gurney law (Equation 1) are marked by symbols. The carrier density range $n = 1.7 \times 10^{16} - 10^{17} \text{ cm}^{-3}$ observed in the SCLC experiment (see the Supporting Information) is indicated by the shaded area.

Figure 4. Carrier drift distance and error in using a quasi-equilibrium mobility. **(a)** Compares the estimated hole drift distance when either using the photo-generated $\mu_{\text{photo}}(t)$ (red trace) or quasi-equilibrium μ_{SCLC} carrier mobility (blue trace) in a TQ1:PC₇₁BM photovoltaic device at maximum-power point conditions. The black trace shows the corresponding $\Delta d(t)/d_{\text{photo}}(t)$ error in using μ_{SCLC} , as defined in Equation 5. **(b)** Shows the $\Delta d(t)$ (red) and the $\Delta d(t)/d_{\text{photo}}(t)$ error (black) in using μ_{SCLC} for the holes in a TQ1:PC₇₁BM photovoltaic device at short-circuit (dashed line) and at maximum-power point (solid line) conditions. $\Delta d(t)$ corresponds to the drift distance by which a quasi-equilibrated carrier is lagging behind a photo-generated carrier. The black dotted line in both Figures marks the average drift distance to the extracting electrode (~ 35 nm) for a photo-generated carrier in a TQ1:PC₇₁BM OPV device.

Figure 5. Predicted error in carrier drift distance for other materials. Estimated $\Delta d(t)$ and $\Delta d(t)/d_{\text{photo}}(t)$ error at short-circuit (1V/100nm) (dashed lines with squares) and at maximum-power point (0.2V/100nm) (solid lines with circles) conditions at a photo-generated carrier drift distance $d_{\text{photo}}(t) = 50$ nm in a hypothetical material with the indicated disorder. The estimated error is independent of the attempt-to-hop frequency $\nu_0 = 1.8 \times 10^{13} \text{ s}^{-1}$ (solid symbols), $\nu_0 = 5 \times 10^{10} \text{ s}^{-1}$ (open symbols). The inset shows that $\mu_{\text{photo}}(t)$ becomes less time-dependent with decreasing energetic disorder. The shaded green area in both panels marks the suggested range of acceptable error described in the main text.

Figure 6. Schematic description of the different charge transport scenarios. **(a)** In materials with a large energetic disorder σ , the photo-generated carriers temporarily occupy higher energies in the DOS which substantially increases their mobility at early times. This allows them to drift faster than quasi-equilibrated carriers, as indicated by the photo-generated carrier hopping arrows (red) extending further in the device than for quasi-equilibrated carriers (black arrows). The amount by which a quasi-equilibrated carrier is lagging behind a photo-generated carrier $\Delta d(t)$ is indicated in the Figure (Equation 4 in the main text). **(b)** In materials with a sufficiently low energetic disorder, the effect of photo-generated carrier thermalization on carrier transport becomes negligible, which is due to the narrowing of the DOS distribution. Photo-generated carrier transport is then comparable/indistinguishable to that of quasi-equilibrated carriers.

Table 1. Carrier hopping parameters.

	Electrons		Holes	
	TQ1:PC ₇₁ B M	TQ1:N2200	TQ1:PC ₇₁ B M	TQ1:N2200
Energetic disorder, σ [meV]	125	141	113	127
Attempt-to-hop frequency, ν_0 [s ⁻¹]	1.8×10^{13}	1.2×10^{13}	5×10^{10}	1×10^{11}

Supporting Information

Photo-generated Carrier Mobility Significantly Exceeds Injected Carrier Mobility in Organic Solar Cells

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1. Miller-Abrahams expression

We use the Miller-Abrahams expression to quantify, with the least number of parameters, the nearest-neighbor hopping rate of a charge carrier from an initial state i with energy E_i to a final state f with energy E_f as

$$v_{if} = \begin{cases} v_0 \exp\left(-\frac{E_f - E_i \pm q \mathbf{r}_{if} \cdot \mathbf{F} + \Delta E_C}{k_B T}\right), & \Delta E > 0 \\ v_0, & \Delta E \leq 0 \end{cases} \quad (S1)$$

Here $\mathbf{F}$ is the electric field, $\mathbf{r}_{if}$ the vector connecting initial and final sites, v_0 the attempt-to-hop frequency, and q the positive elementary charge. Note that v_0 contains both the charge transfer integral and the localization radius which are only implicitly, i.e. via v_0 , but not explicitly accounted for. The $+$ ($-$) sign refers to electron (hole) hopping. The term ΔE_C is the change in Coulomb energy and is calculated by explicit evaluation of the interaction of the moving charge with all other charges in the simulated device and their image charges, as well as of the interaction of the image charges of the moving particle with the particle itself and all other particles. Image charges arise when metallic contacts are present, the number of image charges accounted for in the simulations is increased till the resulting effective Coulomb potential no longer changes. In order to avoid divergences at zero separation, the Coulomb interaction between a pair of (unlike) charges $E_C = -q/4\pi\epsilon_0\epsilon_r r_{eh}$ with $\epsilon_0\epsilon_r$ the dielectric constant ($\epsilon_r = 3.6$) and r_{eh} the electron-hole distance is truncated at minus the approximate exciton binding energy of $E_b = 0.5$ eV. The single-particle site energies E_i are drawn from a Gaussian broadened DOS.

2. Carrier hopping parameters define the magnitude of $\mu_{\text{photo}}(t)$

Table S1. Carrier hopping parameters.

	Electrons		Holes	
	TQ1:PC ₇₁ B M	TQ1:N2200	TQ1:PC ₇₁ B M	TQ1:N2200
Energetic disorder, σ [meV]	125	141	113	127
Attempt-to-hop frequency, ν_0 [s ⁻¹]	1.8×10^{13}	1.2×10^{13}	5×10^{10}	1×10^{11}

The observed difference in the magnitude of $\mu_{\text{photo}}(t)$ can be better understood by inspecting the extracted carrier hopping parameters, listed in Table S1. The combination of the energetic disorder σ and the attempt-to-hop frequency ν_0 defines the magnitude of carrier mobility. The time-dependent hole mobility in TQ1 is substantially lower than that of electrons in both blends. The substantially higher time-dependent electron mobility in PC₇₁BM and N2200 originates from the two orders of magnitude higher ν_0 compared to TQ1. Such a large difference in ν_0 between the donor and the acceptor phase has been previously observed between pristine MDMO-PPV and pristine PC₆₁BM,^[1] and also in blends of MDMO-PPV:PC₆₁BM and PCDTBT:PC₆₁BM.^[1,2] Since these materials have somewhat similar carbon-carbon bonds and ν_0 is generally understood to be related to a characteristic phonon frequency in the material, it is not entirely clear why the different materials show substantial differences in ν_0 , and thus different electron and hole mobilities. However, in the simplified Miller-Abrahams formalism that we employ here also the charge transfer integral and the localization radius are contained in ν_0 , see the section discussing the Miller-Abrahams expression. We speculate that in TQ1:PC₇₁BM blends, the origin of the increase in ν_0 for electrons is due to the spherical/rigid core of the PC₇₁BM molecule. For the case of TQ1:N2200, we tentatively attribute the increase in ν_0 for N2200 to its semi-crystalline nature. Similar arguments likely hold for other donor/acceptor combinations.

The origin of the higher time-dependent electron mobility in TQ1:PC₇₁BM compared to TQ1:N2200 is the ~ 15 meV lower electron energetic disorder of PC₇₁BM compared to N2200. Since ν_0 values for electrons for TQ1:PC₇₁BM and TQ1:N2200 are similar, the higher time-dependent electron

mobility in TQ1:PC₇₁BM is related to ~15 meV lower electron energetic disorder of PC₇₁BM compared to N2200. As such, PC₇₁BM is superior to N2200 as an electron transport material due to its lower energetic disorder. In contrast, we find rather similar time-dependent hole mobilities in both blends, despite a ~ 15 meV lower energetic disorder for the holes in TQ1:PC₇₁BM. This is because the effect of energetic disorder on the magnitude of the carrier mobility strongly depends on v_0 , which is 3 orders of magnitude lower for the holes. Comparable hole $\mu_{\text{photo}}(t)$ is expected, as in both blends the TQ1 phase remains quite amorphous.^[3,4]

3. SCLC carrier mobility dependence on carrier density from experiment

Figure S1. Estimated SCLC mobility dependence on carrier density. Blue corresponds to electrons, red corresponds to holes. Lines correspond to the estimated SCLC carrier mobility μ_{SCLC} dependence on carrier density at an electric field strength of 1V/100nm, according to the well-known parameterization by Pasveer.^[5] Symbols correspond to μ_{SCLC} values estimated by fits of experimental data (Figure 3a in the main text) to the Mott-Gurney law (equation S1 and equation S2 below). Shaded area marks the carrier density range $n = 1.7 \times 10^{16} - 10^{17} \text{ cm}^{-3}$ referred to in the main text.

The carrier density during the SCLC experiment can be estimated from the commonly employed Mott-Gurney law, which, in its simplest and most widely used form is

$$j = \frac{9}{8} \epsilon_r \epsilon_0 \mu_{\text{SCLC}} \frac{(U - U_{\text{bi}})^2}{d^3} \quad (\text{S2})$$

Where ϵ_0 is the vacuum permittivity, ϵ_r the dielectric constant of the active layer, d the active layer thickness, $(U - U_{\text{bi}})$ the applied voltage corrected by the built-in voltage of the device, and μ_{SCLC} the quasi-equilibrium carrier mobility. The carrier density n in the SCLC device can be approximated by

$$n \approx \frac{9}{8} \epsilon_r \epsilon_0 \frac{(U - U_{\text{bi}})}{d^2} \quad (\text{S3})$$

Using equation (2) one can approximately estimate the quasi-equilibrium carrier mobility μ_{SCLC} dependence on carrier density directly from the SCLC experiment, as is shown in Figure S1. However, note that equation (1) does not accurately capture neither the concentration- nor the field-dependence of μ_{SCLC} , the method used in the main text is more reliable.

4. Predicted error depends on carrier density due to DOS state-filling

Figure S2. Predicted error dependence on carrier density. (a) Estimated $\Delta d(t)$ error for the holes in TQ1:PC₇₁BM at short-circuit (SC) (1V/100nm) (dashed lines) and at maximum-power point (MPP) (0.2V/100nm) (solid lines) conditions at a DOS occupancy of $c_0 = 1 \times 10^{-4}$ (black) and $c_0 = 4 \times 10^{-4}$ (red), corresponding to a carrier density range of $n = 1.7 \times 10^{16} - 6.8 \times 10^{17} \text{ cm}^{-3}$. This corresponds to the typical carrier density range found in high-efficiency OPV devices.^[6–8] At these carrier densities the error is decreasing with increasing carrier density as the quasi-equilibrium (long time) carrier mobility is increasing due to DOS state-filling, see the inset of Figure S2a, making it more comparable to the mobility of photo-generated carriers at early times. (b) Shows the estimated $\Delta d(t)$ and $\Delta d(t)/d_{\text{photo}}(t)$ error at SC (squares) and at MPP (circles) conditions at a photo-generated carrier drift distance $d_{\text{photo}}(t) = 50$ nm for a hypothetical material with the indicated disorder and at the same DOS occupancy range as in Figure S2a. The attempt-to-hop frequency ν_0 was set to that of holes in TQ1:PC₇₁BM $\nu_0 = 5 \times 10^{10} \text{ s}^{-1}$. This illustrates that for OPV devices operating at higher carrier densities, the use of SCLC (and other slow time-resolved and steady-state techniques) is acceptable for materials with a higher energetic disorder σ . Nevertheless, the result shown in the main text for $c_0 = 1 \times 10^{-4}$ ($n = 1.7 \times 10^{16} \text{ cm}^{-3}$) is expected to be the most general, as most high-efficiency OPV devices are operating at a comparably carrier density.^[6–8]

We point out that the quasi-equilibrium carrier mobility μ_{SCLC} is also field-dependent, thereby making the estimated error field-dependent. However, for electric field strengths relevant to operating OPV devices this effect is less important than the carrier density dependence of μ_{SCLC} , and is thus not shown. All mobilities in this work were simulated at an electric field strength of 1V/100nm unless indicated otherwise.

4. Figure 4b data over a larger range

Figure S3. Shows the $\Delta d(t)$ (red) and the $\Delta d(t)/d_{\text{photo}}(t)$ error (black) in using μ_{SCLC} for the holes in a TQ1:PC₇₁BM photovoltaic device at short-circuit (dashed line) and at maximum-power point (solid line) conditions. $\Delta d(t)$ corresponds to the drift distance by which a quasi-equilibrated carrier is lagging behind a photo-generated carrier.

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