Nonequilibrium charge dynamics in organic solar cells

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The dynamics of charge carriers after their creation at, or near, an interface play a critical role in determining the efficiency of organic solar cells as they dictate, via mechanisms that are not yet fully understood, the pathways for charge separation and recombination. Here, a combination of ultrafast transient spectroscopy and kinetic Monte Carlo simulations based on a minimalistic model are used to examine various aspects of these charge dynamics in a typical donor-acceptor copolymer:methanofullerene blend. The observed rates of charge carrier energetic relaxation and recombination for a sequence of charge densities can be all consistently described in terms of the extended Gaussian disorder model. The physical picture that arises is a) that initial charge motion is highly diffusive and boosted by energetic relaxation in the disordered density of states and b) that mobile charge carriers dissociate from and re-associate into Coulombically associated pairs faster than they recombine, especially at early times. A simple analytical calculation confirms this picture and can be used to identify sub-Langevin recombination as the cause for quantitative deviations between the Monte Carlo calculations and the measured concentration dependence of the charge recombination.

1. Introduction

Several organic photovoltaic blends can now operate with internal quantum efficiencies approaching unity,[3] meaning that they can convert almost every absorbed photon into charges that do work in an external circuit. On the other hand, many other organic material combinations, although otherwise very promising, are limited by low quantum efficiencies. In terms of the simplest approximation the lower quantum efficiencies are not surprising. A strong Coulombic attraction between geminate charge carrier pairs in low dielectric materials should mean that (undesired) geminate charge carrier recombination always competes with the (desired) charge carrier separation and therefore quantum efficiencies are always moderate. The surprising experimental observations of exceptionally high quantum efficiencies revealed that such a simplistic picture is insufficient to describe charge carrier separation in organic photovoltaics, and motivated a broad range of close physical investigations into this critical process aimed at developing an accurate mechanistic understanding of charge separation (that could be used to design high quantum efficiency materials). In this manuscript we present a rich multidimensional set of transient absorption observations which provide detailed information (on the ps to µs timescale) about the behavior of mobile, separating charge carriers in the prototypical high quantum efficiency poly[N-1′,1′,3′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole]-alt-5,5-(4′,7′-di-2-thienyl-2′-1′,3′-benzothiadiazole)] (PCDTBT): fullerene derivative blends. The measurements concurrently relax the charge carriers within the disorder density of states (DOS), and the recombination of charge carriers at a sequence of different initial charge carrier concentrations. Understood through the lens of kinetic Monte Carlo calculations, these observations reveal how mobile charge carriers hop and relax, dissociating and re-associating potentially multiple times before extraction or recombination.

The current literature regarding observations of charge carrier separation in organic bulk heterojunctions is in agreement with regards to the conclusion that charge carrier separation out of the geminate pairs occurs on the sub nanosecond timescale. A clear indication of the upper bound for the time within which charge carriers must separate was given by the precise measurement using an ultrafast pump-push-photocurrent technique of the lifetimes of geminate interfacial bound charge carrier pairs (also called interfacial charge-transfer state).[2] This work found that the lifetime for a geminate charge carrier pair which remained at the interface in relatively high quantum efficiency blends (such as P3HT:PCBM) was in general on the order of 500 ps. Thus, charge carriers which separate must certainly achieve separation in less than 500 ps. Bakulin and coworkers in this work suggest that significant charge carrier delocalization during the transient occupation of a higher lying interfacial geminate state (which would occur on the sub-picosecond timescale) is the crucial initial step towards separation.[2,3] This sub-picosecond timescale for geminate charge pair separation is supported by a wide range
of experimental results: from ultrafast measurements focusing on the mechanism of charge generation which suggest the process of initial separation is on the sub-100 fs timescale, to observations that non-geminate charge carrier recombination can start as soon as after 1 ns after geminate pair formation. Also recent measurements probing the separation of charge carriers with time from an ultrafast time-resolved observation of an upconversion signal support the picture of fast and efficient charge separation. Regarding the mechanism that drives the separation of the geminate charge carrier pairs, there is still significant discussion. The hypothesis that delocalization in a transient state on the sub-picosecond timescale is the critical step in free charge formation is supported by the pump-push-photocurrent, and ultrafast transient absorption experiments. However, recent theoretical and experimental results have suggested that the static disorder at the interfacial region combined with entropic contributions may be enough to drive efficient separation of geminate charge carrier pairs via hopping through localized states. These approaches have both used kinetic Monte Carlo simulations to model the motion of charge carriers, including their initial separation.

Here, we quantitatively connect the energetic relaxation of photogenerated charge carriers to recombination and transient mobility on the timescales relevant to the generation of free charges. In particular, the third section of this manuscript demonstrates the ability of a minimalistic-model-based kinetic Monte Carlo method to simultaneously reproduce the various dimensions (carrier relaxation in the DOS, carrier recombination, and mobility change; all for a sequence of initial carrier densities) of the rich data set described in the following section. We show that transient red shifts in photo-induced absorption spectra are an excellent measure of the relaxation of photogenerated charges in the disordered density of states by hopping to neighboring sites. In absence of electric fields a dynamic equilibrium between nearly-free and Coulombically associated charges is formed as the hopping motion is much faster than recombination. Only small electric fields are needed to shift this equilibrium to completely free charges, rationalizing the high internal quantum efficiency of this system. This sets the current manuscript apart from previous works.

2. Experimental Data

Our analysis is based on the consideration of a sequence of transient absorption surfaces of a 1:2 PCDTBT:PCBM blend taken with a broadband whitelight probe pulse at various delays with respect to a 2.33 eV excitation pulse for a sequence of different excitation pulse fluences. From previous work, we know that the excited-state population is dominated by charge carriers in the time range from 10 ps (when excitons have all been quenched by arrival at an interface) to 10 µs (when the excited state population has decayed completely due to charge carrier recombination). Using a combination of a mechanically and electronically delayed excitation pulse, we can contiguously observe the transient absorption spectrum over this time range and build up information-rich data surfaces of which an example is shown in Figure 1a (here the white line indicates the changeover from mechanically to electronically delayed excitation pulse). Examining the example surface shown in Figure 1a, we can see that the motion of charge carriers creates two distinct important features in this surface. Firstly, the bleach (1.8–2.2 eV) and PIA (below 1.6 eV) peaks decay towards zero with time as charge carriers recombine, depleting the excited-state population. Secondly, the peak of the absorption bleach shifts to lower energies with time as the charge carriers relax within the disordered DOS. The peak shift is traced by a black line as a guide to the eye. Due to its broad featureless nature the photoinduced absorption peak is not affected by the energetic relaxation, so the decrease in excited-state population caused by charge carrier recombination can be tracked by averaging the photoinduced absorption between 1.25 and 1.4 eV, (symbols, c.f. blue peak in (a)) and also from the integrated bleach peak area from the long-time data (lines, c.f. red peak in (a)). The equivalence of these two methods confirms that the shifting bleach and the PIA are both consequences of the same population.

![Figure 1a](image-url)
will then be used to appraise the adequacy with which the extended Gaussian disorder model incorporates the salient physics to describe charge carrier motion and recombination.

Figure 1b shows the position of the maximum of the absorption bleach as a function of time after excitation for a sequence of four fluences which created initial charge carrier concentrations of 0.6, 1, 2, and 5 × 10^{18} cm^{-3} respectively. Interestingly, the peak shift is seen to be independent of fluence in this range. Therefore we can conclude that the relaxation of charge carriers within the DOS broadened by static disorder occurs at the same rate irrespective of the initial charge carrier density. This intensity independence of the relaxation within the central region of the DOS makes sense when we consider that the number of charge carriers is in any practical situation relatively small compared to the total available density of states (on the order of 10^{20} cm^{-3}) so the initially created charges randomly distributed in the DOS will always have many lower energy sites available for the carriers to pass through as they relax to their equilibrium energy in the tail of the DOS.

As a technical note, the peak position was found by the following procedure: firstly, the data surface matrix was de-noised by taking a singular value decomposition of the matrix, then reconstructing the matrix using only the first four left-hand singular vectors, singular values, and right-hand singular vectors; secondly, the maximum of the bleach in these de-noised structures was found. For the lowest two fluences the poorer signal-to-noise ratio of the data means that the extraction of the peak position was somewhat less precise.

In contrast to the shift of charge carriers in the DOS, the kinetics of the charge carrier recombination is clearly fluence-dependent, as shown in Figure 1c. Comparing the timescales of the two processes we note that there is significant relaxation in the peak position of the bleach before the charge carriers start to recombine. Even at the highest fluence charge carrier recombination starts only after around 2 ns, while the red-shifting of the absorption bleach peak begins earlier, after around 100 ps. By 2 ns the peak has shifted from 2.1 eV down to roughly 1.95 eV. This accounts for the majority of the red-shifting. From 2 ns until roughly 100 nanoseconds the further red-shift is from roughly 1.95 to 1.9 eV.

The characteristics of Figure 1c, the presence of a fluence dependence and its delayed occurrence as compared to the charge relaxation transient, are, albeit somewhat more noisily, also observed in the intensity of the absorption bleach peak as shown in Figure 1c. This confirms that the transients in Figure 1b,c relate to one and the same charge population.

The mobility of a charge carrier is related to its position within the DOS. Interestingly, the fact that the distribution of charge carriers within the DOS evolves with time similarly, irrespective of the initial charge density, suggests strongly that, on the time and energy scales probed here, the charge carrier mobility and its evolution with time are also the same for each initial charge carrier density. We will use the Monte Carlo model, to be introduced below, to show that this is indeed the case.

3. Kinetic Monte Carlo Modeling

A well-known but often ignored problem in organic solar cell modeling is that a good fit with reasonable parameters to experimental data does not mean that the physics described by the model are dominant, or even relevant to the sample; it merely proves that the mathematical structure can fit the data. The idea of the minimalistic model outlined below is therefore to only include what is beyond doubt and see how far one gets. For describing transient charge dynamics and relaxation after excitation by a light pulse, the minimal ingredients are a description of exciton diffusion and of charge hopping in a disordered energy landscape while accounting for the Coulomb interactions between the many charge carriers. We find it is possible to describe very well the rich experimental data in Figure 1 with these ingredients, as will be discussed below.

This strongly suggests that on the time, length and energy scales investigated here, there is very little, if not no reason to include additional processes or mechanisms. From the results presented below it follows that the key ingredient of the model is that it captures to possibility of charges to energetically relax by moving to other sites. This does not require the inclusion of a phase-separated morphology even though this is likely to affect recombination rates. By allowing motion in 3D entropic effects are implicitly included.[6]

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[7]

\[
v_{if} = \frac{v_0}{k_B T} \left( 1 - \exp\left(-\frac{E_f - E_i \pm q \epsilon_r \mathbf{F} + \Delta E_C}{k_B T}\right) \right) = v_0 \exp\left(\frac{-\Delta E}{k_B T}\right) \left(\frac{\Delta E > 0}{\Delta E < 0}\right). \tag{1}
\]

Here \( F \) is the external electric field, \( r_{ef} \) the vector connecting initial and final sites, \( v_0 \) the attempt frequency, and \( q \) the positive elementary charge. The ± sign refers to electron (hole) hopping. The term \( \Delta E_C \) is the change in Coulomb energy. In the most general case this is calculated by explicit evaluation of the interaction of the moving charge with a) all other charges in the simulated device and b) their image charges, as well as of the interaction of the image charges of the moving particle with c) the particle itself and d) 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 the present devices metal electrodes are not present and contributions (b–d) to the Coulomb energy vanish. The Coulomb interaction between a pair of (unlike) charges is given by \( E_C = -q/(4\pi \varepsilon_0 \varepsilon r_{eh}) \) with \( \varepsilon_0 \) the dielectric constant (\( \varepsilon = 3.6 \)) and \( r_{eh} \) the electron-hole distance, and is truncated for small electron-hole distances (to avoid divergence) at minus the approximate exciton binding energy of \( E_{ex} = 0.5 \text{eV} \).

The fact that organic solar cells rely on the presence and intimate mixing of donor and acceptor materials calls for the inclusion of both materials in the MC model. The simplest way to do this, and that is chosen here, is to define an effective hopping medium with (different) electron and hole hopping parameters \( v_0 \) and \( \sigma \) that correspond to the donor highest occupied molecular orbital (HOMO) and acceptor lowest unoccupied molecular orbital (LUMO) levels, respectively. The driving force for charge transfer is implemented via an on-site electron-hole
repsone with a magnitude that equals the LUMO level offset
\[ \Delta E_{\text{LUMO}} = E_{\text{HOMO}}^\text{donor} - E_{\text{HOMO}}^\text{acceptor} \]

between donor and acceptor.

The single-particle site energies \( E_i \) are drawn from a Gaussian distribution function

\[ f(E_i) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left( -\frac{(E_i - \bar{E})^2}{2\sigma^2} \right), \]

(2)

with \( \bar{E} \), the mean energy and \( \sigma \) the broadening of the total density of states (DOS) \( N_0 \). The HOMO and LUMO energy of a single site are assumed to be uncorrelated. Charge carrier pairs sitting on the same lattice site are considered excitons and can recombine with rate \( v_{\text{ct}} \). Similarly, when sitting on neighboring sites they form a CT complex that can recombine with rate \( v_{\text{CT}} \).

Exciton diffusion by the Förster resonant energy transfer (FRET) mechanism is explicitly accounted for. The transition rate is evaluated as

\[ v_{\text{FRET}} = \frac{R_0^6}{r_{\text{F}}} \Theta(E_{\text{F}} - E_{\text{F}}'), \]

(3)

where \( R_0 \) is the Förster radius, \( v_{\text{ct}} \), the radiative exciton decay rate, \( \Theta(\cdot) \) the Heaviside step function and \( E_{\text{F}}', E_{\text{F}} \) the exciton energies \( E_{\text{F}}' = E_{\text{F}}' - E_{\text{F}}' \), \( E_{\text{F}}' = E_{\text{F}}^\text{LUMO} - E_{\text{F}}^\text{HOMO} \) at the initial and final sites. Dexter-type exciton diffusion is implicitly accounted for as a double charge hopping process.

The waiting time before an event (hop or recombination) occurs is calculated as\[^{[7]}\]

\[ \tau = \frac{\ln(r)}{\sum v_i}, \]

(4)

where \( r \) is a random number drawn from a homogeneous distribution between 0 and 1 and \( \sum v_i \) is the sum of the rates of all possible events. The event that occurs after \( \tau \) is selected randomly, using the rates of all possible events as weight factors. Energies, rates, and waiting time are recalculated after each event.

In order to simulate the transient response to a short light pulse, each simulation is started by creating an initial concentration \( c_0 \) of excitons on an otherwise empty calculation grid. Given the high photon energy employed in the experiments an equal excitation probability is assumed for all sites, in other words excitons are generated at fully random positions. Periodic boundary conditions in the \( x,y \)-directions were applied for both charge motion and (image and direct) Coulomb interactions; (non-metallic) blocking contacts laying at \( z = 0 \) and \( z = 100 \) nm are included unless stated otherwise to create a 100 nm thick film. Independence of the results on the box size used in the calculations was assured.

This model is the minimal implementation of the extended Gaussian disorder model (EGDM) for organic solar cells.\[^{[10]}\] It is implemented on a simple cubic grid, i.e., each site is six-fold coordinated. The nearest neighbor hopping distance then equals the lattice constant and relates to the total DOS as \( a_{\text{NN}} = N_0^{1/3} \).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value and unit</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_{\text{NN}} )</td>
<td>2.6 nm</td>
<td>Ref.[^{[5]}] &amp; fit in Figure 3</td>
</tr>
<tr>
<td>( \Delta E_{\text{LUMO}} )</td>
<td>0.5 eV</td>
<td>( E_{\text{LUMO}}^\text{donor} - E_{\text{LUMO}}^\text{acceptor} )</td>
</tr>
<tr>
<td>( E_{\text{LUMO}} )</td>
<td>5.45 eV</td>
<td>Ref.[^{[10]}]</td>
</tr>
<tr>
<td>( \sigma_{\text{LUMO}} )</td>
<td>4.1 eV</td>
<td>Ref.[^{[7]}]</td>
</tr>
<tr>
<td>( \sigma_{\text{HOMO}/\text{LUMO}} )</td>
<td>0.12 eV</td>
<td>Ref.[^{[7]}]</td>
</tr>
<tr>
<td>( \sigma_{\text{HOMO}} )</td>
<td>0.08 eV</td>
<td>Fit in Figure 2</td>
</tr>
<tr>
<td>( v_{\text{LUMO}} )</td>
<td>0.11 eV</td>
<td>Fit in Figure 3</td>
</tr>
<tr>
<td>( v_{\text{HOMO}} )</td>
<td>( 3 \times 10^{12} ) s(^{-1})</td>
<td>Ref.[^{[7]}] &amp; only relevant for Figure 4</td>
</tr>
<tr>
<td>( v_{\text{CT}} )</td>
<td>( 1 \times 10^9 ) s(^{-1})</td>
<td>Fit in Figure 3</td>
</tr>
<tr>
<td>( v_{\text{m}} )</td>
<td>( 5 \times 10^8 ) s(^{-1})</td>
<td>Fit in Figure 5</td>
</tr>
<tr>
<td>( R_0/\text{NN} )</td>
<td>( 1 \times 10^8 ) s(^{-1})</td>
<td>Fit in inset of Figure 2</td>
</tr>
<tr>
<td>( R_0/\text{CT} )</td>
<td>2.4</td>
<td>Fit in Figure 2</td>
</tr>
</tbody>
</table>

Table 1. Overview of parameters used in the simulations. Parameters in grey have no effect on the results but are shown for completeness. HOMO and LUMO refer to the orbitals of the effective medium unless indicated otherwise.

The lattice constant \( a_{\text{NN}} \) was taken from ref. \[^{[7]}\] where it was, albeit for another material system, independently determined from temperature dependent current-voltage characteristics. By lack of similar data for the present system we employ the same value (2.6 nm) here and note that this seemingly large value still leads to a CT binding energy of \( \approx 2\mathrm{eV} \) at room temperature, i.e., one would not expect appreciable free charge generation in absence of relaxation and entropic effects. Interestingly, this length scale is very similar to those recently suggested for coherent processes like charge delocalization, to which the present model is evidently “blind”.\[^{[2,11]}\] For the time (\( >10 \) ps) and length scales discussed here coherent processes are unimportant.

We note that the assumption of a single effective medium is a significant simplification of the partially de-mixed mesomorphology. Monte Carlo investigations incorporating two-phase simulated morphologies of bulk heterojunctions are possible.\[^{[14]}\] and interesting theoretical test beds for simulating how changes in morphology may affect photophysical processes.\[^{[13]}\] However, inclusion of a phase separated morphology doubles the number of unknown hopping parameters and forces one to make assumptions about the hierarchical length scales in the phase separated morphology. The minimalistic model that we present provides a tractable test case for assessing the ability of EGDM-based kinetic Monte Carlo methods to reproduce ultrafast spectroscopic experimental observations. Importantly, the energetic relaxation occurs in the levels that are explicitly times associated with many-particle MC modeling parameter values were obtained by manual fitting and should therefore be regarded as first order approximations.
accounted for in the present treatment, so valid insight into transient energetic and mobility relaxation can be gained. As discussed later, the recombination in simulations would be altered by the implementation of phase-separated morphologies. However, we will find that the current minimalistic method is sufficient to convincingly reproduce the experimental observations, and provide a self-consistent physical framework through which the fundamental physics underlying the charge dynamics can be interpreted.

4. Results and Discussion

Before turning to the modeling of the transient response of the OPV blend, we first use the kinetic MC model to fit the transient response of a thin film of the neat donor material PCDTBT, as shown in Figure 2. Given the lack of acceptor material, in this case the energetic relaxation is measured by the red-shifting with time of the excitonic emission. The relaxation of the exciton to lower energy states occurs by the Förster and Dexter mechanisms of which the former mechanism is found to dominate. The simulation is then essentially fully determined by three parameters, namely the exciton recombination rate $v_{\text{CT}}$, the ratio of the Förster radius $R_0$ and the hopping distance $a_{\text{NN}}$, and the broadening of the HOMO and LUMO levels (that are assumed to be equal for simplicity). An excellent fit, shown in Figure 2, can be reached with a unique set of physically reasonable parameters, listed in Table 1.

This fitting of the neat material allows us to determine values for $R_0/a_{\text{NN}}$ and $v_{\text{exc}}$, which are expected to remain roughly unchanged in the blend and are therefore kept fixed in the following simulations. In contrast, blending in PCBM may be expected to increase the disorder, as reported before,[9] so the disorder parameter is not held.

In the photovoltaic blend excitons are quenched by charge carrier generation by 10 ps, after which time the energy relaxation can be monitored by the red-shifting of the absorption bleach caused by the holes on the polymer while the decrease in charge carrier population can be monitored with the decay of the PIA (as was shown in Figure 1). In Figure 3 we compare this data to kinetic Monte Carlo simulations using the aforementioned parameters but increasing the disorder parameter ($\sigma_{\text{HOMO}}$) from 0.08 eV in the neat material to 0.11 eV for the blend in order to obtain good fits. In Figure 3 we see that the salient features of a fast, density independent, relaxation in energy preceding density dependent charge carrier recombination are well reproduced.

As the electron in the simulation is also transferred to the acceptor on a much shorter timescale than the relevant part of the transient in Figure 3, the shifting of the energy in the simulation is entirely due to holes relaxing in the disordered DOS. The simulation is therefore only sensitive to the hole hopping parameters $\sigma_{\text{HOMO}}$ and $v_{\text{HOMO}}$, and these can therefore be uniquely determined. Values are again listed in Table 1 and kept fixed in successive simulations. The initial charge densities in the simulations are set as the fraction of sites occupied ($n_0/N_0$), which is equivalent to the ratio of the concentration of charges to the total density of states. We calculate the initial charge density based on measurement of the photon fluence in the excitation pulse and the samples absorption,[9] while the total density of states is estimated to $a_0 = 5.7 \times 10^{19}$ be cm$^{-3}$.

A technical note should be made regarding the exact interpretation of the experimental relaxation traces in Figure 3. In the simulation no correlation between HOMO and LUMO levels of a single site is assumed, so the calculated shift of the bleach peak reflects solely the hole relaxation, and the extracted disorder parameter equals the broadening of the donor HOMO level. The parameter value obtained for $\sigma_{\text{HOMO}}$ (0.11 eV) is a very reasonable number in view of other EGDM parameters reported before[7,14] and suggests that this is a relatively accurate approximation of the experimental reality. Importantly, a correlation between HOMO and LUMO site energies would change
the fitted value of $E_{\text{HOMO}}^{\text{blend}}$ but not significantly affect this paper’s conclusions.

A salient feature of the data in Figure 3 is the time lag between the onset of energy relaxation (upper panel) and the onset of recombination that is shown by the decaying charge density (lower panel). Quite counter-intuitively this suggests that at these carrier densities (and certainly for the lower charge densities found in photovoltaic devices), relaxation and recombination are to a large extent independent processes before roughly 100 ns. The different pump fluence dependence of recombination and relaxation corroborates this point; a consideration of the physical rationalization for this follows in the discussion below.

As mentioned in the discussion of Figure 1b, the experimental hole relaxation traces are independent of pump fluence. This characteristic is accurately reproduced by the MC model, see Figure 3. It confirms that state filling is not important for holes in this part of the DOS at the present concentrations on the timescale of the first tens of nanoseconds (which are important for consideration of charge extraction in thin film photovoltaic devices). This is in stark contrast to steady state conditions, when charges have fully relaxed, where a very strong concentration dependence of the mobility is found at already much lower concentrations. However, for the transient, far from steady state conditions here it may therefore be expected that also the transient mobility is fairly insensitive to initial charge concentrations. For the holes, whose relaxation is experimentally followed in Figure 3, this is indeed the case. Figure 4 plots the transient electron and hole mobilities along with the corresponding transient mean energies in the DOS that are obtained from the kinetic Monte Carlo modeling. Within numerical accuracy both the hole relaxation and the hole mobility for the lowest and highest initial concentration are equal. For the electrons a small fluence dependence is observed, with higher initial concentrations giving slower energy relaxation and a slower decay of the transient mobility. This effect is attributed to state filling in the acceptor LUMO level.

For both electrons and holes these results corroborate the direct relation between the (charge's position in the) DOS and the mobility. The slight time delay between the onset of relaxation and the onset of mobility reduction that is visible in Figure 4 can be explained by the fact that the mobility is only a weak function of the carrier energy around the center of the DOS. Only when the majority of charges reach a substantially reduced DOS, does the mobility start decreasing due to a reduction in the number of available final sites that are lower in energy. The lesser availability of such sites also causes the change in the derivative of the relaxation transient that coincides with the onset of the mobility decrease at $\approx$1 ns for holes and $\approx$1 ps for electrons. The (shorter) time scale of the early relaxation is approximately $\frac{1}{6}t_0$ where 6 is the coordination number of the simple cubic lattice employed in the MC model.

The constancy of the mobilities at very short and very long time scales can be easily understood. In previous work, it was shown that at shortest time scales the vast majority of hops is energetically downward and hence occur with a rate that is close to $v_0$. This happens likewise in the present simulations. Hence, $v_0$ and the nearest neighbor hopping distance $a_{nn}$ set the mobility; its value will be discussed in relation to the rate equation model that will be presented below. At long time scales the charges reach steady state and the mobility converges to its near-equilibrium value. According to Equation (3) of ref. the used hopping parameters should give rise to zero-density mobilities of $\approx 3 \times 10^{-11}$ and $\approx 2 \times 10^{-8}$ m$^2$/V s for holes and electrons, respectively. The finite density remaining at the longest time shown explains the still somewhat higher mobility values obtained in the calculation. The noise is due to the fact that this is a computationally very inefficient way to reach significant statistics at long times due to the drastic reduction of carrier population by these longer times.

Now considering the population dynamics, we see that the dependence of the transient carrier density on initial concentration is qualitatively reproduced by the kinetic MC model, see Figure 3b. Higher initial concentrations indeed lead to faster (normalized) depopulation. The physical reason is simply that at these initial generation conditions bimolecular recombination is qualitatively reproduced by the kinetic MC model, see Figure 3b. Higher initial concentrations indeed lead to faster (normalized) depopulation. The physical reason is simply that at these initial generation conditions bimolecular recombination is significant and, as it is bimolecular, has a rate that increases with concentration. However, the strength of the $c_0$-dependence is underestimated in the MC model. The reason for this deviation will be discussed below.

Inspecting the parameters in Table 1 that are used to reproduce the experimental data with the minimalistic MC model, it can be noted that the downward hopping rate $v_0$ for especially the electron is substantially higher than the exciton and CT recombination rates. As discussed above, at short time scales the vast majority of hops are energetically downward and thus occur with a rate that is close to $v_0$. An important consequence of the strongly different time scales of hopping and recombination is that CT complexes continuously dissociate and re-associate and only occasionally recombine. Moreover, at the relatively large initial charge concentrations used in these experiments the re-formation of CT complexes is very often a non-geminate process. In the MC simulations the fraction of charges that dissociate but then re-associate and recombine with their geminate partner is 0.13-0.03 for lowest to highest
pump fluence, respectively. Thus, recombination is mostly bimolecular and non-geminate.

In holding with our minimalistic approach, we have assumed for simplicity that the initial optically-created CT states are indistinguishable from the CT states recreated by the association of mobile oppositely charged carriers over an interface. This assumption leads to an inverse CT lifetime of 20 ns, which is quite a lot longer than typically sub-nanosecond lifetime for optical CT states observed in typical polymer:PCBM blends.\cite{2,5} This assumption leads to an inverse CT lifetime of 20 ns, which is quite a lot longer than typically sub-nanosecond lifetime for optical CT states observed in typical polymer:PCBM blends.\cite{2,5}

In light of this discrepancy, it is possible if not probable that initial optically-created CT states and electrically reformed CT states have distinct dynamics. In this case, the CT lifetimes presented in this work are weighted towards those perhaps more loosely bound (or precursor) CT states which influence non-geminate recombination and are formed through the electronic re-association of charge carriers. Rumbles and coworkers have discussed such a CT or CT precursor state using the nomenclature \{D+...A\}.\cite{15}

The inset to Figure 5 captures the above in a simplified energy diagram with only three (labeled) transitions that matter. On the time scales of Figure 5 the charge separation is complete, i.e., the concentration of excitons has dropped to 0. This leads to the following set of differential equations can be easily solved by forward integration:

\[
\frac{dn_{\text{CT}}}{dt} = - (v_{\text{CT}} + v_0)n_{\text{CT}} + k_{\text{bi}}n^2,
\]

\[
\frac{dn}{dt} = v_0n_{\text{CT}} - k_{\text{bi}}n^2.
\]

Here, \(n\) and \(n_{\text{CT}}\) are the concentrations of free charges and CT complexes, respectively, while \(k_{\text{bi}}\) is the bimolecular recombination rate. We have used the fact that the electron and hole mobilities in reasonable agreement with the short-time plateaus in Figure 4.

More importantly, it follows from the discussion above that the decay of the total charge density is independent of \(v_0\) provided \(v_0\) is much higher than \(v_{\text{CT}}\); the populations of CT complexes and free charges may be considered communicating vessels in constant (dynamic) equilibrium; the position of this equilibrium is independent of \(v_0\) as both the dissociation and association rates depend linearly on \(v_0\). This makes the model essentially a single-parameter \((v_{\text{CT}})\) model.

Figure 5 compares the MC results (symbols) to the predictions of the rate equation model when \(\gamma_{\text{pre}}\) is assumed to be 1. Note that \(\gamma_{\text{pre}}\) is the only unknown parameter in the rate equation model, all the other parameters are taken from the MC input data in Table 1. As seen in Figure 5 the agreement is good at short times for all initial concentrations. The rate equation model breaks down at longer times, as expected, when the majority of hops are no longer downward in energy and \(v_0\) becomes a poor measure of the kinetics. In passing we note that these results imply that the present minimalistic MC model yields a simulated rate of bimolecular recombination that is close to the Langevin rate. This in line with earlier literature on kinetic Monte Carlo simulations.\cite{16}

Having established that the simplified rate equation model captures the essential physics of the transient recombination process, it may next be used to investigate possible reasons for the quantitative difference between the pump fluence dependence predicted by the MC model and the experimental data seen in Figure 3b.

In many cases a bimolecular recombination rate below the value expected on basis of the Langevin model has been found for organic photovoltaics.\cite{15,17} In the rate equation model this is readily incorporated by setting \(\gamma_{\text{pre}} < 1\). The result of fitting this rate equation to the experimental data is shown as dashed lines on Figure 6. We used \(\gamma_{\text{pre}} = 0.03\) and set \(v_{\text{CT}} = 4 \times 10^8\) s\(^{-1}\) in order to keep the correct position on the time axis. The strong fluence dependence of the recombination rate in the experiments is now captured. The increased dispersion in lifetime for sub-unity \(\gamma_{\text{pre}}\) is the result of an increased dependency of the bimolecular recombination lifetime, that is proportional to \(1/(k_{\text{bi}}n)\), on \(n\). The physical reason for sub-Langevin recombination is subject of ongoing discussion,\cite{15,16,17b,18} and mostly beyond the scope of the present work. We should, however, stress that Langevin recombination with \(\gamma_{\text{pre}} < 1\) is an emergent property of the present MC model. In view of the (deliberate) neglect of phase separation in the minimalistic MC model a likely explanation for a sub-unity \(\gamma_{\text{pre}}\) is the presence of an aggregated PCBM phase (and/or pure polymer phases) with lower-lying energy levels that act almost as charge carrier sinks within the experimental devices.\cite{15,19}

Let us finally discuss the implications of the physical picture sketched in Figure 6b for OPV operation at normal light intensity, i.e., around 1 sun steady-state illumination.
multiple dissociation and re-association of CT complexes at short time scales remains at low light levels as this is a direct consequence of the diffusive relaxation in the disordered DOS. Driven by diffusion the electron and hole can still become nearly free, i.e. separated by multiple sites. However, in absence of collecting contacts and fields the very weak Coulomb attraction between a nearly free electron-hole pair will lead to the eventual re-association and recombination of the (nearly) relaxed charges. The lower charge concentration will render the chances for finding a non-geminate recombination partner small and recombination will mostly be geminate, though not necessarily at the site of formation of the initial CT complex. This picture is changed dramatically by the presence of a small electric field. Rather than having to overcome the still substantial electron-hole binding energy in a CT complex, the field only needs to compete with the much weaker Coulomb attraction in a nearly free electron-hole pair. Hence, the energetic relaxation at short times, allowing the electron and hole to independently diffuse to a nearly free state, enables the experimentally observed efficient generation of free charges at very low fields.

The connection between relaxation and repeated partial dissociation on one hand and facile full dissociation into free charges, i.e., a high quantum efficiency of the operating solar cell on the other is reflected in device calculations with the same parameters as used above. In these simulations metal contacts, assumed to be perfect sinks, were placed at $z = 0$ and $z = 100$ nm, sandwiching a single donor-acceptor interface at $z = 50$ nm. Excitons were generated with a rate $5 \times 10^{11}$ cm$^{-3}$ s$^{-1}$, corresponding to $\approx 1$ Sun white light illumination. The dissociation quantum efficiency for excitons reaching the DA-interface is $0.95$ at $F_z = 2 \times 10^6$ V m$^{-1}$ ($\approx$maximum power point) and $0.99$ at $F_z = 1 \times 10^7$ V m$^{-1}$ ($\approx$short circuit) in good agreement with the reported near-unity quantum efficiency of optimized PCDTBT:PCBM cells.\textsuperscript{[14]}

Let us finally mention some implications of the present findings. First, as the energetic relaxation acts as an energy reservoir for charge separation only a weak temperature dependence of the quantum yield is predicted; a more extensive discussion of this matter is given in ref. [7]. Interestingly, materials having less disorder then needed to overcome the remaining CT binding energy, may be expected to show reduced quantum efficiencies. Second, these results highlight that on the time scale at which charges hop under nonequilibrium conditions, $50$ fs and $200$ ps ($\approx 1/6\nu_e$) for electrons and holes respectively, the corresponding absorption bleaching in transient absorption will not remain constant.\textsuperscript{[11]} This enables estimating initial, downward hopping rates from the onset of spectral shifts.

5. Conclusion

We have investigated experimentally and numerically the dynamic charge relaxation and recombination in a typical donor-acceptor copolymer:methanofullerene blend as used in the active layer of state-of-the-art organic photovoltaic cells. We find that a minimalistic kinetic Monte Carlo model, incorporating only exciton and charge motion in a disordered but otherwise homogeneous medium, gives an accurate description of the experimental data. The present findings prove the relevance of the extended Gaussian disorder model, that was developed to describe charge transport in near-equilibrium situations, for gaining insight in the very-far-from-equilibrium processes governing charge generation in organic solar cells. In particular, the initial motion of photogenerated charges is highly diffusive and driven by relaxation in the disordered density of states, explaining the transient red shifts in photoinduced absorption spectra. The underlying charge (hopping) motion is much faster than the recombination. Therefore a dynamic equilibrium between nearly-free and Coulombically-associated charges is formed. Therefore only small electric fields are needed to overcome the remaining Coulomb interaction between the nearly-free charges and to efficiently generate completely free charges. A simple analytical calculation confirms this picture and hints at sub-Langevin recombination as the cause for quantitative
deviations between the Monte Carlo calculations and the measured concentration dependence of the charge recombination.

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