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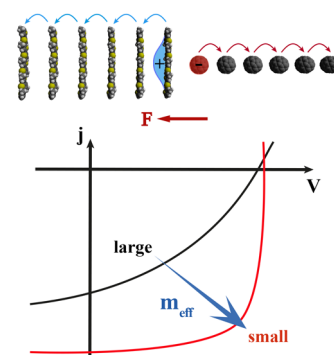
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Efficient Charge Separation of Cold Charge-Transfer States in Organic Solar Cells Through Incoherent Hopping

Stavros Athanasopoulos, Steffen Tscheuschner, Heinz Bässler, and Anna Köhler

ABSTRACT: We demonstrate that efficient and nearly field-independent charge separation of electron–hole pairs in organic planar heterojunction solar cells can be described by an incoherent hopping mechanism. Using kinetic Monte Carlo simulations that include the effect of on-chain delocalization as well as entropic contributions, we simulate the dissociation of the charge-transfer state in polymer–fullerene bilayer solar cells. The model further explains experimental results of almost field independent charge separation in bilayers of molecular systems with fullerenes and provides important guidelines at the molecular level for maximizing the efficiencies of organic solar cells. Thus, utilizing coherent phenomena is not necessarily required for highly efficient charge separation in organic solar cells.



Charge separation in solar cells is a key process for extracting carriers that contribute to a photocurrent. While in traditional inorganic solar cells the available thermal energy provides enough kinetic energy in order to overcome the Coulomb interaction between geminate electron–hole pairs, in new-generation organic solar cells, separation of charges is a cumbersome process.^{1–3} As a first step, it usually requires the presence of interfaces between an electron transporting and a hole transporting material that facilitates the transfer of the electron to the acceptor material by formation of a charge-transfer (CT) state,⁴ provided that the exciton diffusion length is large enough to reach such interfaces.^{5–7} Second, once the charges are in separate phases, they need to overcome their mutual Coulomb attraction, which is much larger than the thermal energy, due to the low dielectric constant of organic materials, which is in the range of 3–5.⁸ This charge separation process can be assisted by an electric field, although in some materials the process occurs with high efficiency even at low electric fields. A great deal of attention has been drawn recently on the mechanism of charge separation, and a number of possible scenarios have been suggested to explain the large variability in dissociation efficiencies for chemically similar molecular systems.⁹ These include dissociation via delocalized or hot states,^{10–12} ultrafast separation via band-type states,^{13,14} the presence of interfacial dipoles,^{15–19} entropic contributions,^{20–22} and coherence effects.^{23–26} Thus, there is much interest in efficiently predicting under which conditions the efficiency of separation is maximized using computer experiments.

In organic solar cells, both geminate recombination, i.e., the recombination of electron–hole carriers that trace back to the same parent exciton, and nongeminate (bimolecular) recombina-

tion, i.e., recombination of electron–hole carriers from two different parent excitons, are important loss mechanisms that reduce the quantum efficiency of the device.²⁷ It has recently been demonstrated that geminate recombination in molecule-based solar cells can be controlled by thermal annealing and chemical treatment of spin coated devices with the amount of recombination being accessible experimentally by time-delayed collection field measurements (TDCF).²⁸ Recently, we have reported that the dissociation efficiency in bilayer films of molecule donor with a C₆₀ acceptor layer can be very efficient, with the separation yield exceeding 70% at low electric fields.²⁹ Moreover, we have shown that recombination near the open circuit voltage (V_{OC}) increases with the donor layer thickness in polymer devices, and we have elaborated on the role of diffusion with Monte Carlo simulations and an analytical model. That work has also highlighted that once the limiting to efficiency contribution of geminate recombination reduces then nongeminate recombination losses are also minimized.

The central question of this Letter is the following: Is dissociation of an optical excitation an instantaneous or a sequential process and, if so, is the rate-limiting step the creation of a charge-transfer state or its subsequent dissociation? Can we achieve efficient charge separation through incoherent hopping of Coulombically bound charges that start off from tightly bound, cold CT states, or are coherence and ultrafast separation a prerequisite for high carrier generation yields in organic solar cells? Earlier transient absorption experiments suggested that the excess energy of

vibrationally hot charge-transfer states drives charge separation.^{30,31} Meanwhile, there is growing evidence that delocalization effects are more important and they could involve delocalized states either in a polymeric donor^{15,32} or in an aggregated acceptor such as PCBM.^{14,19,33–35} There are also a number of previous Monte Carlo (MC) simulations that address this issue.^{36–38} For example, Jones et al. have investigated whether “hot” delocalized charge transfer (CT) states are responsible for the high quantum efficiency in some polymer:fullerene blend heterojunction cells. They implemented the effect of the hot CT state in a bulk heterojunction (BHJ) morphology by considering the already cooled down geminate electron–hole pair, with electron and hole separated by a certain distance r . They found that most of them collapse back to a tight bound pair at the interface, unless an unphysically large initial separation r , e.g., in excess of 10 nm, is assumed. From this they concluded that hot CT states are unlikely to be the dominant factor for high solar cell efficiencies. Rather, they speculate whether it could be that a “variation in energy levels close to the heterojunction plays a more significant role”.³⁶ Volpi and co-workers consider this implicitly by studying the effect of interfacial polarization on the dissociation of cold CT states for the case of the anthracene– C_{60} interface.³⁸ They find that, while polarization helps, the effect is not sufficient to account for the observed dissociation, so they speculate whether “charge delocalization in the polymer plays an important role”. Burke and McGehee, in contrast, consider the role of the local charge carrier mobility on the separation efficiency.³⁷ In their MC simulation for three-phase BHJ, they find that high mobility-lifetime-products are required to account for experimentally found quantum yields. This could be reconciled with experimental lifetimes if the relevant mobility is a high local one, e.g., as probed by time-resolved terahertz conductivity. In their work, the effect of delocalization is not explicitly included, though one might consider the high mobility as an incoherent delocalization effect. Also, attempts have been made to model the electron transfer dynamics by quantum mechanical models.^{13,14,24}

In order to decide whether the primary dissociation event (the creation of a CT state by charge transfer) or rather the subsequent secondary dissociation limits the overall yield of photogenerated carriers, we shall focus on the charge separation process following the electron transfer step, and we consider a “cold”, vibrationally relaxed e–h pair CT state as the initial condition.³² In so doing, we treat the dynamics of simultaneous electron and hole transport in the donor and acceptor phase, respectively, at equal grounds. In this Letter, we shed light on the mechanism of charge extraction in bilayer donor–acceptor devices by using Monte Carlo simulations^{11,39–41} to calculate the charge collection efficiency as a function of externally applied field. Entropic contributions to charge separation are naturally included within the kinetic model.²² We lay emphasis on the role of dimensionality, disorder, and bipolar transport. In addition, we examine in particular the question of delocalization, whereby the spatial extent of a charge wave function over a segment is parametrized by an effective mass of the polymer/oligomer. It is well-known that those factors have an influence on charge carrier mobility and recombination.^{41–44} Here we unravel the impact of each of those physical parameters on the JV curves and quantify their relative importance. This approach goes beyond existing one-dimensional models^{15,16,44,45} by incorporating the effect of delocalization and bipolar transport in a kinetic model that is able to quantify the separation

efficiency and relate it to device parameters under experimentally relevant conditions.

In what follows, we compute the probability that an electron–hole pair separates over a given distance of 100 nm. We use a discrete lattice of points with donor polymers as the basis with their molecular axis extending parallel to each other and to the interface with the acceptor. The hole can only make interchain hops between π -conjugated polymers. The extent of the hole wave function along the polymer chain is taken into account using an effective mass model.^{16,44,46} The main idea of the model is that the zero-point oscillations of the delocalized hole modify the potential energy of the hole by an additional kinetic energy term in the Hamiltonian. The potential energy of the hole is determined by the Coulomb potential well due to the presence of the electron and the external electric field. The more delocalized the hole is, the larger the kinetic energy term and therefore the shallower the potential. The degree of delocalization can be described by an on-chain effective mass for the hole m_{eff} given in units of the free electron rest mass. In our simulation, this is implemented by adding the associated additional kinetic energy term to the site energy (see below).⁴⁷

We consider a linear one-dimensional (Figure 1 top panel) and a square two-dimensional lattice (Figure 1 bottom panel)

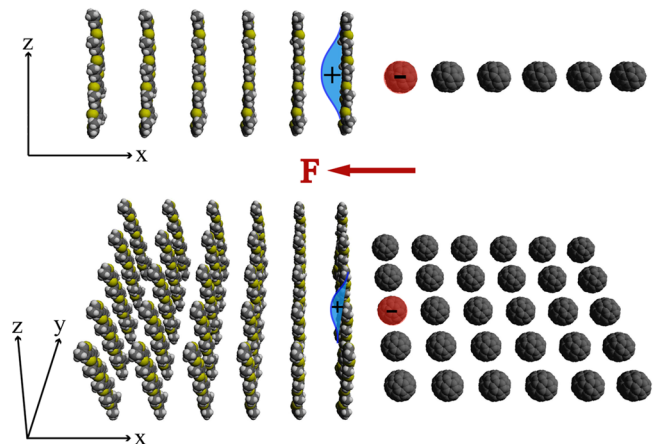


Figure 1. Schematics of the 1D (top panel) and 2D (bottom panel) bilayer lattice morphologies used for the Monte Carlo simulations. Each grid point consists of either a donor polymer chain of infinite length or a C_{60} acceptor molecule. The effect of on-chain hole delocalization is taken into account using an effective mass model.

with a constant $a = 1$ nm. For simplicity, the lattice constant remains the same for the acceptor phase, representing a fullerene based molecule, and energetic disorder is neglected. The initial condition for each independent Monte Carlo trial sets a photogenerated electron–hole pair at the interface, in a nearest neighbor charge-transfer configuration with an initial separation of 1 nm. Since we focus on geminate recombination, at every Monte Carlo trial we follow only one pair of charges. An external electric field of strength F is applied perpendicular to the DA interface with a vector direction antiparallel to the electron–hole Coulomb field.

Charge hopping rates follow the Miller–Abrahams formulation:

$$\nu_{ij} = \begin{cases} \nu_0 e^{-2\gamma r_{ij}} e^{-(\epsilon_j - \epsilon_i)/k_B T} & \text{for } \epsilon_j > \epsilon_i \\ \nu_0 e^{-2\gamma r_{ij}} & \text{for } \epsilon_j \leq \epsilon_i \end{cases} \quad (1)$$

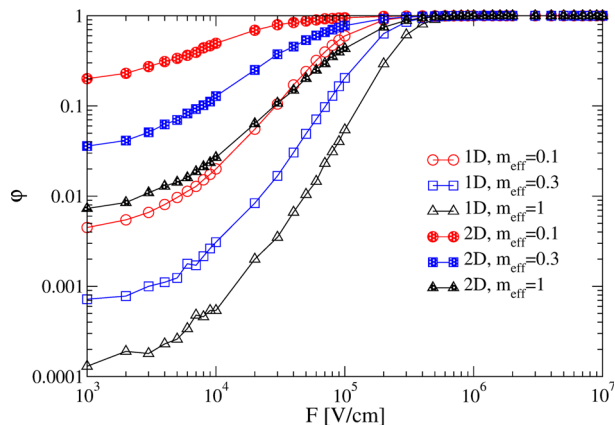


Figure 2. 1D and 2D Monte Carlo simulations for different effective mass of the donor molecules. Electron extraction efficiency φ as a function of an internal electric field F .

where i denotes the residence site of the charge and j the target site, and the two sites are separated by a distance r_{ij} . Site energies ε_i and ε_j include contributions from the electron–hole Coulomb interaction potential including the kinetic energy term resulting from the delocalization of the hole wave function calculated by numerically solving the Schrödinger equation (see ref 16) and the voltage drop due to the applied field. Unless stated, the inverse localization length $\gamma = 2 \text{ nm}^{-1}$, the frequency prefactor $\nu_0 = 10^{12} \text{ s}^{-1}$, and $T = 300 \text{ K}$. We consider hopping events up to second nearest-neighbor distances, i.e., $r_{ij,\text{max}} = 2 \text{ nm}$, which is a sufficient cutoff distance for moderate values of temperature normalized disorder $\sigma/kT < 4$. From a simulation point of view, the parameters ν_0 and γ define the minimum hopping time, and their value does not influence the presented results since it is the relative ratio of the CT lifetime to the minimum hopping time that controls the probability for recombination (see below). In practice, these parameters determine the equilibrium charge carrier diffusion coefficient and mobility values.

At each Monte Carlo step, we calculate a waiting time for each hopping event: $\tau_{ij} = -(1/\nu_{ij}) \ln X$. In addition, we calculate a waiting time for recombination events between the electron–hole pair: $\tau_r = -\tau \ln X$, where τ is the electron–hole pair lifetime that increases exponentially with electron–hole distance r_{eh} as $\tau = \tau_{\text{CT}} e^{2\gamma(r_{\text{eh}} - a)}$, and X is a random number drawn from a box distribution between 0 and 1. The lifetime at close proximity is a parameter that we allow to vary from a minimum value of $\tau_{\text{CT}} = 35t_0$ to a maximum value of $\tau_{\text{CT}} = 3000t_0$, with t_0 being the minimum hopping time $t_0 = \frac{1}{\nu_0} e^{2\gamma a}$. The event with the smallest waiting time is selected and executed, and the interaction potential is updated. If the accepted event is a hop, then we update the site of the hole or electron and recalculate waiting times. If the chosen event is recombination, we remove the charges and start a new trial. Each trial terminates successfully when the electron–hole distance is larger or equal to 100 nm. The influence of the donor–acceptor thickness has been considered elsewhere.²⁹ The statistical quantity of interest is the separation yield

calculated as $\varphi(F) = \frac{N_{\text{sep}}(F)}{N_{\text{tot}}(F)}$, where $N_{\text{sep}}(F)$ the number of successful trials (trials with $r_{\text{eh}} \geq 100 \text{ nm}$) for an applied field F and $N_{\text{tot}}(F)$ the total number of trials of the order of 10^4 . Thus, N_{tot} is the total number of e–h pairs considered.

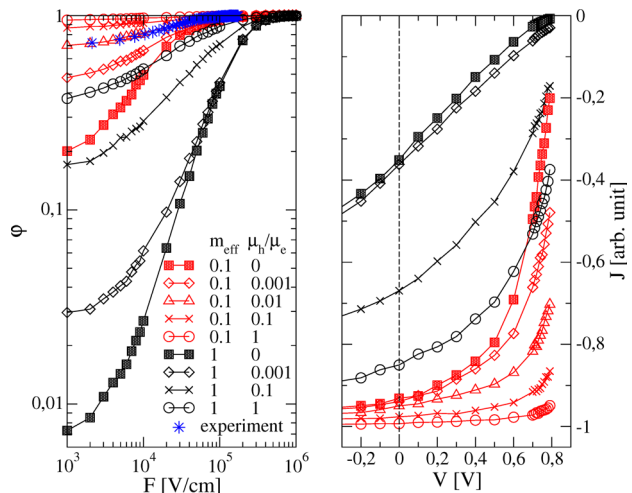


Figure 3. 2D Monte Carlo simulations, influence of imbalanced e and h mobilities. Left panel: Electron–hole separation efficiency φ as a function of an externally applied field and experimental data for a bilayer consisting of 60 nm thick layer of the T1 molecule as donor and 30 nm thick layer of C_{60} as acceptor. Right panel: resulting photocurrent JV curves for a purely geminate recombination regime.

At first we consider that only one of the carriers is mobile, e.g., only the electron is allowed to hop and the hole position is fixed. This situation could also be modeled analytically in one dimension,⁴⁵ and we have tested that the results for the field dependence of the separation yield are in perfect agreement with the analytical solution. Figure 2 shows that reducing the effective mass of the donor results in higher electron extraction efficiencies at intermediate and low fields. This is a straightforward result, because a lower effective mass, i.e., a longer hole delocalization along the polymer chain, translates into a smaller barrier for the e–h interaction potential (see ref 16). Let us now consider the two-dimensional case where the electron has more routes available to escape the e–h interaction potential while the hole is still stationary at the interface. Simulations reveal that φ increases by more than 1 order of magnitude for $m_{\text{eff}} = 0.1m_e$ at low fields where the driving force for electron extraction is dominated by the diffusion of the electron rather than the electric field (Figure 2). This is a remarkable result that highlights the important role of dimensionality on diffusion limited charge extraction.

Let us now lift up the restriction of immobilizing the hole and further allow for imbalanced electron and hole mobilities. Both experimental and theoretical works have indicated that this can have a significant impact on dissociation.^{48,49} Results from our Monte Carlo calculations in the 2D case depicted in Figure 3 show a striking increase in the e–h separation yield when both the hole and the electron particle are allowed to hop. For a hole effective mass $m_{\text{eff}} = 0.1$, φ becomes virtually field independent even at the diffusive regime at low electric fields. We note that there are several reports of organic solar cells with molecular oligomers as the donor material that exhibit high external quantum efficiencies^{28,50,51} and we have recently reported high separation yields in bilayer cells using the p-DTS(FBTTh₂)₂ oligomer (T1 molecule) as donor with C_{60} as acceptor.²⁹ These data are included at the left panel of Figure 3, and it is noteworthy that the field dependence can be well reproduced from the Monte Carlo simulations for $m_{\text{eff}} = 0.1$ and a mobility imbalance ratio $\mu_h/\mu_e = 10^{-2}$. Such a ratio is consistent with photo-CELIV measurements of hole mobility

$1.4 \pm 0.5 \times 10^{-4} \text{ cm}^2/(\text{V s})$ for the T1 oligomer while the electron mobility in C_{60} is of the order of $10^{-2} \text{ cm}^2/(\text{V s})$.²⁹ We can further translate the obtained Monte Carlo results to photocurrent JV curves, assuming a thickness of the active layer (electron and hole transporting material) of $d = 100 \text{ nm}$ in total, and an open-circuit voltage $V_{oc} = 0.8 \text{ V}$. The simulated JV characteristics are depicted at the right panel of Figure 3. They represent purely geminate recombination limited JV curves. These results highlight that bipolar transport dramatically increases the fill factors (FF) by lowering geminate recombination. Importantly, equal mobilities are not even required, and mobility differences of 1–2 orders of magnitude are tolerable. The geminate recombination regime can be partly accessed experimentally via time-delayed collection field measurements.²⁸ Experiments in as-cast and thermally annealed T1:PC₇₀BM film blends have shown that annealed films exhibit phases with higher crystalline domains of T1 that improve hole mobilities by an order of magnitude as measured by photocurrent and TDCF transients. Consequently, the fill factors for annealed films have been shown to improve. This is therefore in accordance with the predictions of the Monte Carlo model.

Next, we consider the influence of varying the charge-transfer state lifetime with respect to the minimum hopping time that determines the magnitude of the mobility of the particles.⁵² This can be achieved by either increasing the charge-transfer state lifetime of the pair, which corresponds to decreasing the electron–hole wave function overlap, or by decreasing the minimum hopping time, equivalent to increasing the coupling between the molecular units. When the ratio τ_{CT}/t_0 of the CT state lifetime over minimum hopping time increases, this corresponds to increasing the $\mu\tau$ product in a Braun–Onsager model.⁵³ Consequently, the separation yield increases since the electron and hole are given more chances to make hops and can get far-off in the course of their lifetime. Figure 4 shows the

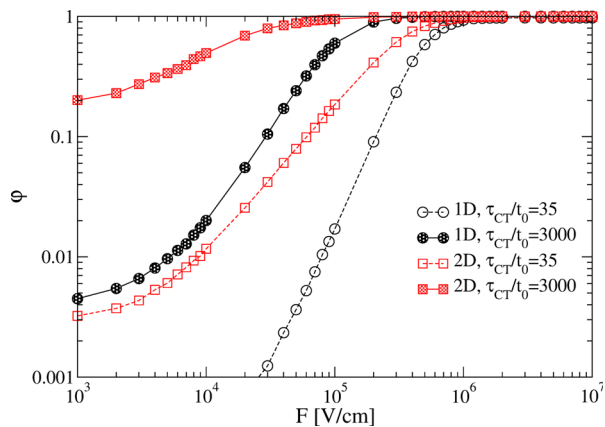


Figure 4. 1D and 2D Monte Carlo simulations of electron–hole separation efficiency ϕ as a function of an internal electric field F for $m_{eff} = 0.1$ and different CT state lifetime over minimum hopping time ratios.

changes in ϕ for the 1D and 2D cases. At the low field regime, ϕ increases by the same order of magnitude that τ_{CT}/t_0 increases. The role of energetic disorder has also been investigated, and we find that the inclusion of Gaussian disorder does not alter the conclusions presented here. A detailed study on the influence of disorder will be presented elsewhere.

We are now in a position to answer the pertinent question of whether we can achieve efficient charge separation of cold CT states through incoherent hopping of Coulombically bound charges. Based upon the main results obtained in this Letter, we are not only able to simulate experimental photocurrent JV curves dominated by geminate recombination by considering only incoherent hopping processes, but we can also quantify the contribution of important parameters, which independently lead to higher charge separation yields with weaker field dependence. These parameters include transport dimensionality, bipolar transport, effective mass, and the ratio of minimum hopping time over CT state lifetime, i.e., the $\mu\tau$ product. Given that typically CT state lifetimes do not vary dramatically in most organic blends, overall increase in transport dimensionality has the strongest effect following by bipolar transport and lowering the effective mass. Although bipolar transport is crucial, we find that fully balanced mobilities is less important.⁵⁴ Given that typically electron mobilities can be one or 2 orders of magnitude higher than hole mobilities this is a favorable result. The value of the effective mass is mainly controlled by molecular design with m_{eff} varying from about 0.1 in well-conjugated polymers^{55,56} to values on the order of 1 in disordered molecules exhibiting strong hole localization. We stress that our results are also relevant to recent experiments showing that both delocalized hole states as well as fullerene aggregation improve charge separation.^{13,32} In comparison with published experimental results, our simulations explain the increase of fill factors with increased crystallinity obtained by thermal annealing or chemical treatment. Paradoxically, the delocalization of the *hole* wave function also assists the transport of the *electron* in the acceptor phase by lowering the Coulomb interaction potential, whereas fullerene aggregation is expected to increase the hopping rates of the electron. It is also gratifying that our results consistently confirm and further complement previous MC calculations that focused, e.g., on the role of mobility or polarization.^{37,38} Moreover, the implementation of the delocalization through a (site-specific) additional kinetic energy term corresponds, in a way, to the suggestion made by Jones et al. that the variation in energy levels close to the interface might be crucial.³⁶ Our findings also have the following consequences for optimizing organic solar cell devices: First, for the design of organic solar cells, it is not sufficient to focus on only one material in which the transport states are efficiently delocalized. Rather, both materials need to display either high charge delocalization or high carrier mobilities, ideally both. Second, morphologies that promote filamentary 1D transport are detrimental for charge separation, whereas architectures that favor transport with increased dimensionality (even at the expense of localization) are superior. It is also important to highlight that our results were obtained within an incoherent hopping formalism of vibrationally relaxed CT states³² where the initial electron–hole pair has a close proximity of only 1 nm. Therewithal, we find that an incoherent transport model can describe efficient charge separation without the need to invoke “hot” processes, in agreement with ref 57. Coherence is therefore not the only route toward improving the efficiencies of organic solar cells. More consideration should be given to the fact that optimally efficient devices can be realized with simple material architectures that utilize incoherent hopping.

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