

Energy-Temporal Pathways of Free-Charge Formation at Organic Bilayers: Competition of Delocalization, Disorder, and Polaronic Effects

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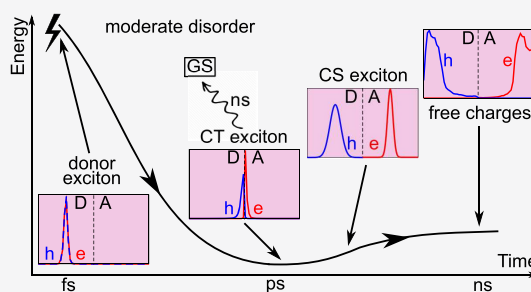
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ABSTRACT: We investigated the charge separation process in organic semiconductor bilayers from the moment of creation of a donor exciton to the time when all charge pairs have either recombined or reached external contacts. The system was modeled using a one-dimensional microscopic Hamiltonian that includes the effects of carrier delocalization, electron–hole interaction, static disorder, and carrier–phonon interaction. Transition rates between excitonic states were modeled using modified Redfield approach which takes into account polaronic effects by exact treatment of diagonal exciton–phonon interaction. An efficient numerical scheme was developed that enabled us to obtain the time dependence of energy-resolved populations of relevant exciton states on a time scale as long as 1 μ s. Our results indicated that charge separation proceeds via the so-called *cold pathway* in which donor excitons convert to relaxed charge-transfer excitons which further transform to the states of separated charges. We found that for lower disorder strengths the time scale for conversion of donor excitons to charge transfer excitons is $\sim(1\text{--}10)$ ps, while further separation to free charges takes place on the time scale reaching ~ 1 ns. These time scales are extended for larger disorder strengths because diffusion of donor excitons to the interface and transport of separated charges toward external contacts are slowed down. We also found that charge separation yield has a rather weak dependence on electron–phonon interaction strength.



INTRODUCTION

Operation of organic photovoltaic (OPV) devices is based on separation of electron–hole pairs (excitons) generated by incident sunlight into free charges. Although significant research efforts have been put in the last two decades to understand and improve the performance of OPVs, the details of charge separation mechanism are still not fully understood. The active region in OPVs typically consists of two organic semiconductor materials. The conventional picture of the charge separation process at the interface of these materials is as follows.^{1–3} Incident sunlight initially generates bound excitons in the donor material (donor excitons, XD) which then migrate to the interface of two materials into so-called charge transfer (CT) excitons, which consist of an electron in the acceptor material and a hole in the donor material that are both localized close to the interface. The next step in the separation process is transformation of CT excitons into charge separated (CS) states in which electron in the acceptor and hole in the donor are spatially separated. Electrons and holes in CS states are free to migrate toward external contacts and form current in external circuit.

The challenge to this conventional picture comes from the fact that in most efficient OPV devices almost each absorbed photon produces one electron–hole pair in external circuit, that is, internal quantum efficiency is close to one.⁴ Since

binding energy of electrons and holes in CT states is much larger than thermal energy at room temperature,¹ it remained unclear how is separation of electrons and holes from CT states possible. Along this line, there were suggestions that in the course of separation process excitons do not reach strongly bound CT states but remain in energetically higher and weakly bound CT states (so-called hot CT states) and further transform into CS states from these states.^{5,6} In such a picture, this transfer has to occur before relaxation to cold states⁷ and it was therefore believed that it takes place on very short sub-picosecond time scale. On the other hand, the conventional picture which involves separation from low energy strongly bound CT states (so-called cold CT states) was not abandoned. In particular, experimental results which show that internal quantum efficiency is nearly independent of the energy of the initial state point in favor of this picture.^{8–10}

In our previous theoretical work,^{11,12} we first investigated exciton dynamics on a sub-picosecond time scale using a fully quantum mechanical model of the heterojunction based on

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density matrix theory. Our results indicated that donor excitons generated by a pulsed photoexcitation predominantly remain in these states and that there is no significant charge transfer on this time scale.¹² To assess the possibility of charge separation on longer time scale, we used a master equation approach to find steady-state populations of relevant states and calculate the charge separation yield.¹³ Our analysis indicated that efficient separation of charges from an initial strongly bound CT state is possible. Strong binding of the electron and hole in a CT state is overcome due to a sequence of transitions to higher energy and more loosely bound CT states from which further transitions to CS states take place. We found that the separation process is most efficient at moderate values of disorder and that it is enhanced by charge carrier delocalization.¹³

However, our previous efforts did not take into account polaronic effects, which are sometimes regarded as highly important for a realistic description of exciton and charge dynamics in organic semiconductors.¹⁴ Namely, when the strength of (static) disorder is comparable to the magnitude of electronic couplings, and both of these are comparable to the coupling of electronic excitations to vibrations, there is no obvious small parameter in which a perturbation expansion can be performed. Techniques that can circumvent this problem exist, for example wave function-based methods¹⁵ or hierarchical equations of motion.¹⁶ However, their direct application to the problem of long-time charge separation, in which we necessitate an accurate description of processes occurring on time scales spanning the range from femto-seconds (nuclear dynamics) to at least nanoseconds (recombination), is computationally prohibitive. The application of these numerically exact techniques is thus typically limited to ultrafast dynamics.^{17,18} A similar situation is encountered in photosynthetic excitonic complexes, where, however, one can find various approximate approaches taking into account the competition between delocalization, disorder, and polaronic effects at least partially.^{19–21} One of these approaches, which is suited for disordered excitonic systems, is the so-called modified Redfield theory.^{22,23} In such systems, due to disorder, the overlap between different excitonic wave functions is expected to be small, so that the off-diagonal exciton–phonon couplings should be much smaller than the diagonal ones. The modified Redfield theory takes advantage of this circumstance by treating the diagonal part of the exciton–phonon interaction exactly, while its off-diagonal part is treated perturbatively.

In this work, we analyze in detail exciton dynamics on long time scales reaching $\sim 1 \mu\text{s}$, when all charge pairs have either recombined or reached external contacts. We have extended our previous model where transition rates between different exciton states were calculated assuming relatively weak electron–phonon coupling to include polaronic effects in the framework of modified Redfield approach. We obtain spectrally resolved time dependence of populations of exciton states from which we construct a full picture of charge separation process starting from generation of donor or CT exciton and ending with fully separated charges in external contacts. From the results obtained, we identify the time scales for different parts of the charge separation process and establish the effect of most relevant system parameters on these time scales. Our results point in favor of conventional cold separation mechanism.

MODEL AND METHOD

Model. The model that we use to study charge separation on an organic bilayer is essentially the same as the one we have used in our recent studies of the same phenomenon.¹³ Therefore, the model itself is presented in greater detail in section S1.1 of the Supporting Information (SI), while here we only describe its features that are relevant to the formulation of the theoretical approach. Figure 1a provides a schematic diagram of our model.

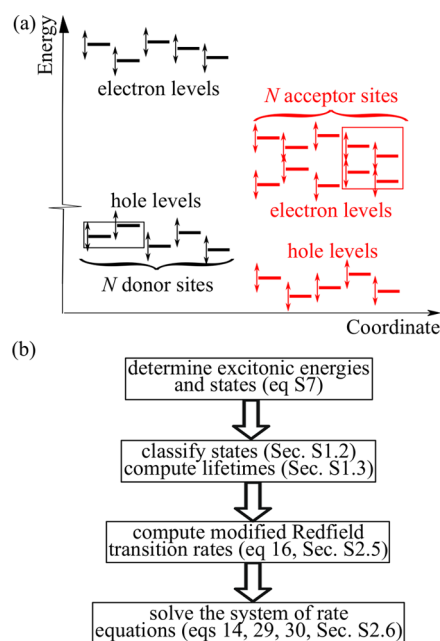


Figure 1. (a) Scheme of the one-dimensional electron–hole lattice model used to describe charge separation at the donor/acceptor interface. It consists of N donor and N acceptor sites, each of which can accommodate a number of single-electron and single-hole levels presented by horizontal lines. To mimic the existence of higher-than-LUMO orbitals that are energetically close to the LUMO level of the widely used electronic acceptor PCBM, we take two single-electron levels per acceptor site.¹³ Energies of single-carrier levels differ from site to site due to the diagonal static disorder, while two-sided vertical arrows standing on the left of each level represent its dynamical modulation by Holstein-like interaction with nuclear degrees of freedom. In a free-charge state, the electron (the hole) is mainly located in the spatial region within the rectangle in the acceptor part (the donor part) of the interface. More details can be found in ref 13 and section S1.4 of the SI. (b) Diagram outlining the main steps that have to be taken in order to compute the dynamics in a single disorder realization. Relevant equations and sections of the main text and SI are given in parentheses.

The interface between two organic semiconductors of different electronic properties is described using a one-dimensional electron–hole lattice model, in which each of the materials is modeled within the standard semiconductor model. As we have already discussed,¹³ our model takes into account on a fully quantum level all the physical effects that are regarded as relevant for the problem of charge separation in OPVs. Namely, the model includes electron and hole delocalization, attractive electron–hole interaction that binds them into excitons, static disorder, which is omnipresent in organic semiconductors, as well as the interaction of electrons and holes with nuclear degrees of freedom.

While the model itself is formulated in the electron–hole picture, theoretical developments are conducted in the excitonic basis, that is, in the basis of stationary states of an electron–hole pair that are compatible with our model interface. We limit our discussion to the subspace of singly excited states $\{|x\rangle\}$, in which the model Hamiltonian assumes the following form:

$$H = \sum_x \hbar\omega_x |x\rangle\langle x| + \sum_\mu \hbar\omega_\mu b_\mu^\dagger b_\mu + \sum_{\bar{x}\mu} \Gamma_{\bar{x}x}^\mu |x\rangle\langle x| (b_\mu^\dagger + b_\mu) \quad (1)$$

In eq 1, $\hbar\omega_x$ is the vertical excitation energy of exciton state $|x\rangle$, and index μ labels phonon modes whose energies are $\hbar\omega_\mu$, while $b_\mu^\dagger$ (b_μ) are the corresponding Bose creation (annihilation) operators. The third term in eq 1 is the exciton–phonon interaction, whose coupling constants $\Gamma_{\bar{x}x}^\mu$ satisfy $\Gamma_{\bar{x}x}^\mu = \Gamma_{x\bar{x}}^{\mu*}$.

The exciton–phonon interaction Hamiltonian stems from the electron–phonon and hole–phonon interaction Hamiltonians, which are taken to be of the Holstein type. Each site is assumed to be equipped with a set of phonon modes, and the relevant parameter sets on all sites (phonon frequencies and local electron–phonon and hole–phonon interaction constants) are taken to be identical. The limit of macroscopic phonon bath is taken by introducing the appropriate spectral density.

Based on their spatial properties, exciton states can be classified as donor, acceptor, CT, CS, and free-charge states. In the last three groups of states, the electron is predominantly located in the acceptor, and the hole is mainly in the donor. The discrimination between CT, CS, and free-charge states is established essentially on the basis of the mean electron–hole separation. The electron and hole in a CT state are quite close to one another and pinned to the interface. In a CS state, their mutual separation is somewhat larger. In free-charge states, charges are mainly located on the opposite edges of the interface, so that these states mimic the ones from which carrier extraction to electrodes is possible. In that spirit, we take that, once an exciton reaches a free-charge state, it permanently remains in that state. As discussed in ref 13, the disorder in on-site transition energies is crucial to identify free-charge states. Here, we introduce disorder by drawing electron and hole on-site energies from the Gaussian distribution with standard deviation σ and center at an appropriate energy. For more details, see refs 12, 13 and Section S1.2 of SI.

The model Hamiltonian is parametrized so that the values of band gaps, bandwidths, band offsets, and binding energies of the donor, acceptor, and CT exciton within our model agree with the literature values for typical OPV materials. In particular, we choose the values of model parameters to be representative of the prototypical P3HT/PCBM interface, as detailed in Section S1.4 of SI and ref 13.

METHOD

The exciton dynamics governed by Hamiltonian H is studied using the modified Redfield theory. As has been mentioned in Introduction, the essential criterion for the applicability of the modified Redfield theory is the smallness of the off-diagonal exciton–phonon couplings, which are treated perturbatively, with respect to the diagonal ones, which are treated exactly. In Results, we present numerical evidence that our model system

satisfies this criterion. Here, let us only mention that the magnitude of exciton–phonon couplings is governed by the spatial-proximity factor, which is determined by the electron and hole overlap in the two exciton states.¹³ In order to achieve high coupling between two (different) exciton states, both the electron and the hole in these states have to overlap, a condition that is difficult to meet in the presence of static disorder whose strength is comparable to electronic couplings.

The modified Redfield theory has become a standard tool in the chemical physics community,^{19,20,24} where it is commonly applied to study exciton dynamics within models containing a relatively small number of chromophores (~ 10), that is, a relatively small number of excitonic states.^{25,26} To the best of our knowledge, our work is among the first works employing the modified Redfield theory to describe excitonic dynamics in a condensed-phase system, in which the number of relevant excitonic levels is of the order of 1000. Therefore, the main steps toward the derivation of the relevant equations of motion are presented in the main body of the paper, whereas further technical details can be found in section S2 of the SI. Our presentation relies on the results of ref 27, which, in fact, in the limit of the macroscopic bath, present a lucid rederivation of the modified Redfield theory.

As the first step, the total Hamiltonian is rewritten as

$$H = H_0 + V \quad (2)$$

where the unperturbed Hamiltonian H_0 contains the diagonal part of the exciton–phonon interaction

$$H_0 = \sum_x |x\rangle \left(\hbar\omega_x + \sum_\mu \Gamma_{xx}^\mu (b_\mu^\dagger + b_\mu) \right) \langle x| + \sum_\mu \hbar\omega_\mu b_\mu^\dagger b_\mu \quad (3)$$

while the perturbation V contains its off-diagonal part

$$V = \sum_{\bar{x}\mu} \Gamma_{\bar{x}x}^\mu |x\rangle\langle x| (b_\mu^\dagger + b_\mu) \quad (4)$$

In eq 4, the prime on the sum indicates that only terms in which $\bar{x} \neq x$ are considered.

Hamiltonian H_0 can be diagonalized by performing the polaron transformation

$$U = e^{-S} \quad (5)$$

where

$$S = \sum_{\bar{x}\mu} \frac{\Gamma_{\bar{x}x}^\mu}{\hbar\omega_\mu} |x\rangle\langle x| (b_\mu^\dagger - b_\mu) \quad (6)$$

In the polaron frame, Hamiltonian H_0 becomes (an operator in the polaron frame is denoted by a tilde above its symbol)

$$\tilde{H}_0 = U^\dagger H_0 U = \sum_x \hbar\tilde{\omega}_x |x\rangle\langle x| + \sum_\mu \hbar\omega_\mu b_\mu^\dagger b_\mu \quad (7)$$

where energies of excitonic states are renormalized due to the adaptation of the nuclei to the excited-state configuration

$$\hbar\tilde{\omega}_x = \hbar\omega_x - \sum_\mu \frac{[\Gamma_{xx}^\mu]^2}{\hbar\omega_\mu} \equiv \hbar\omega_x - \lambda_x \quad (8)$$

Hamiltonian V in the polaron frame reads as

$$\tilde{V} = U^\dagger V U = \sum_{\bar{x}\mu} |\bar{x}\rangle\langle x| M_{\bar{x}\mu} \quad (9)$$

where the transition from exciton state $|x\rangle$ to exciton state $|\bar{x}\rangle$ is mediated by the dressed phonon operator

$$\sum_{\mu} M_{\bar{x}x\mu} = \sum_{\mu} \Gamma_{\bar{x}x}^{\mu} \exp \left[\sum_{\nu} \frac{\Gamma_{\bar{x}x}^{\nu} - \Gamma_{xx}^{\nu}}{\hbar\omega_{\nu}} (b_{\nu}^{\dagger} - b_{\nu}) \right] \left(b_{\mu}^{\dagger} + b_{\mu} - 2 \frac{\Gamma_{xx}^{\mu}}{\hbar\omega_{\mu}} \right) \quad (10)$$

This should be contrasted with the undressed phonon operator that mediates the same transition within the Redfield theory

$$\sum_{\mu} M_{\bar{x}x\mu}|_{\text{Red}} = \sum_{\mu} \Gamma_{\bar{x}x}^{\mu} (b_{\mu}^{\dagger} + b_{\mu}) \quad (11)$$

We see that, while the Redfield theory does not take into account neither the displacements (with respect to the ground state) of equilibrium nuclear configurations in excited states nor multiphonon processes, the modified Redfield theory takes into account both these effects.²⁸ The presence of the displaced phonon operator $b_{\mu}^{\dagger} + b_{\mu} - 2\Gamma_{xx}^{\mu}/(\hbar\omega_{\mu})$ in eq 10, which is characteristic for the equilibrium configuration of the nuclei when the electronic subsystem is in state $|x\rangle$, means that the first effect is taken into account. Processes in which an arbitrary number of vibrational quanta is exchanged with the bath to accomplish the transition $|x\rangle \rightarrow |\bar{x}\rangle$ are taken into account in eq 10 by the presence of the exponential of phonon operators.

We assume that the initial density matrix is factorized as

$$\rho(0) = |x_0\rangle\langle x_0| \otimes \frac{\exp \left[-\beta \sum_{\mu} (\hbar\omega_{\mu} b_{\mu}^{\dagger} b_{\mu} + \Gamma_{x_0x_0}^{\mu} (b_{\mu}^{\dagger} + b_{\mu})) \right]}{\text{Tr}_B \exp \left[-\beta \sum_{\mu} (\hbar\omega_{\mu} b_{\mu}^{\dagger} b_{\mu} + \Gamma_{x_0x_0}^{\mu} (b_{\mu}^{\dagger} + b_{\mu})) \right]} \quad (12)$$

so that the excitonic subsystem is taken to be in excitonic state $|x_0\rangle$, while the nuclear degrees of freedom have already adapted themselves to the displaced equilibrium configuration corresponding to the excited state $|x_0\rangle$. In eq 12, $\beta = (k_B T)^{-1}$, T is the temperature, and Tr_B denotes (partial) trace over phonon bath. Such an initial condition tacitly assumes that the adaptation of nuclear degrees of freedom to the displaced equilibrium characteristic for excited states is much faster than the population transfer between excited states. Its relevance to the problem of charge separation in OPVs can be understood from our recent investigations of the phenomenon in question.¹² Namely, we have concluded that, on a sub-picosecond time scale after photoexcitation, the majority of excitons are found in strongly bound donor or CT states, which act as traps for ultrafast charge separation. The escape from these states, therefore, occurs on time scales much longer than typical time scales for nuclear relaxation, which are of the order of 100 fs. Moreover, the fact that our origin of the time axis loosely corresponds to $t \sim 100$ fs to 1 ps after the photoexcitation is not of particular importance for our analysis, which targets processes that happen on much longer time scales. Bearing in mind that we estimate time scales (i.e., orders of magnitude), we can safely think about $t = 0$ as the moment of exciton generation. The initial condition (eq 12) in the polaron frame reads as

$$\tilde{\rho}(0) = |x_0\rangle\langle x_0| \otimes \frac{\exp \left[-\beta \sum_{\mu} \hbar\omega_{\mu} b_{\mu}^{\dagger} b_{\mu} \right]}{\text{Tr}_B \exp \left[-\beta \sum_{\mu} \hbar\omega_{\mu} b_{\mu}^{\dagger} b_{\mu} \right]} \quad (13)$$

Working in the polaron frame in this case is thus technically advantageous, since all partial traces over phonon bath are computed in its canonical equilibrium.

By employing the usual second-order perturbation theory with respect to $\tilde{V}$, together with Markovian approximation, we obtain that population $f_x(t)$ of exciton state $|x\rangle$ evolves according to

$$\partial f_x(t) = - \sum_{x'(\neq x)} w_{x'x} f_x(t) + \sum_{x'(\neq x)} w_{xx'} f_{x'}(t) \quad (14)$$

where transition rates $w_{xx'}$ from state $|x'\rangle$ to state $|x\rangle$ are expressed in terms of the Fourier component of the correlation function of dressed phonon operators

$$w_{xx'} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} d\tau e^{i(\tilde{\omega}_{x'} - \tilde{\omega}_x)\tau} \sum_{\mu\nu} \langle M_{x'x\mu}^{(0)}(\tau) M_{xx'\nu} \rangle_{\text{eq}} \quad (15)$$

In the last equation, time dependence of phonon operators is with respect to the free-phonon Hamiltonian appearing in $\tilde{H}_0$ (see eq 7), whereas the averaging $\langle \dots \rangle_{\text{eq}}$ is with respect to the canonical equilibrium of the phonon bath (see eq 13). More details are provided in section S2.1 of the SI. The calculation of the phonon correlation function appearing in eq 15 is a straightforward, but rather tedious task, whose technical details are presented in section S2.2 of the SI. Here, we only quote the final result in the form that is commonly encountered in the literature

$$w_{xx'} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} d\tau e^{i(\tilde{\omega}_{x'} - \tilde{\omega}_x)\tau} \exp \left[-\frac{1}{\hbar^2} (g_{x'x',x'x'}(\tau) - 2g_{x'x',xx}(\tau) + g_{xx,xx}(\tau)) \right] \exp \left[-\frac{i}{\hbar} (\lambda_{x'x',x'x'} - 2\lambda_{x'x',xx} + \lambda_{xx,xx})\tau \right] \left[\ddot{g}_{x'x',xx}(\tau) - \left(\frac{1}{\hbar} \dot{g}_{x'x',xx}(\tau) - \frac{1}{\hbar} \dot{g}_{x'x',x'x'}(\tau) - 2i\lambda_{x'x',x'x'} \right) \left(\frac{1}{\hbar} \dot{g}_{xx,xx}(\tau) - \frac{1}{\hbar} \dot{g}_{xx,x'x'}(\tau) - 2i\lambda_{xx,x'x'} \right) \right] \quad (16)$$

Transition rates within the modified Redfield theory are entirely expressed in terms of quantity

$$\ddot{g}_{\bar{x}_2x_2,\bar{x}_1x_1}(\tau) = \sum_{\mu_2\mu_1} \langle M_{\bar{x}_2x_2\mu_2}^{(0)}(\tau) M_{\bar{x}_1x_1\mu_1} |_{\text{Red}} \rangle_{\text{eq}} \quad (17)$$

and its integrals. The quantity $\ddot{g}_{\bar{x}_2x_2,\bar{x}_1x_1}(\tau)$ represents the (equilibrium) correlation function of undressed phonon operators mediating the transition between states $|\bar{x}_2\rangle$ and $|x_2\rangle$ and the transition between states $|\bar{x}_1\rangle$ and $|x_1\rangle$, see eq 11. The function $\dot{g}_{\bar{x}_2x_2,\bar{x}_1x_1}(\tau)$ and the so-called line shape function $g_{\bar{x}_2x_2,\bar{x}_1x_1}(\tau)$ are defined as

$$\dot{g}_{\bar{x}_2x_2,\bar{x}_1x_1}(\tau) = \int_0^{\tau} ds \ddot{g}_{\bar{x}_2x_2,\bar{x}_1x_1}(s) \quad (18)$$

$$g_{\vec{x}_2, \vec{x}_1}(\tau) = \int_0^\tau ds_2 \int_0^{s_2} ds_1 \ddot{g}_{\vec{x}_2, \vec{x}_1}(s_1) \quad (19)$$

while quantity $\lambda_{\vec{x}_2, \vec{x}_1}$ represents a generalization of the expression for λ_x (see eq 8) and reads as

$$\lambda_{\vec{x}_2, \vec{x}_1} = \sum_{\mu} \frac{\Gamma_{\vec{x}_2, \vec{x}_1}^{\mu}}{\hbar \omega_{\mu}} \quad (20)$$

We note here that the derivation in section S2.1 of the SI actually results in rate eqs (eq 14) with time-dependent modified Redfield rates, $w_{xx'}(t)$, which are given by eq 16 in which the integration limits $-\infty$ and $+\infty$ are replaced by $-t$ and t , respectively. Therefore, strictly speaking, the dynamics predicted by eq 14 is not correct for times t shorter than the decay time of the phonon correlation function entering eq 15. On these time scales, non-Markovian effects become important. This circumstance, however, is not expected to affect our principal conclusions. Physically relevant treatment of short-time dynamics should proceed from an initial condition that should be appropriate for a sudden exciton photogeneration and that is different from that in eq 12. In the Discussion, we discuss why we believe the details of short-time dynamics are not particularly relevant for the long-time separation dynamics, which is of primary interest in this work.

Equation 15 nicely illustrates why this approach bears the name modified Redfield theory. Namely, population transition rates within the Redfield theory are also expressed in terms of the Fourier component of the correlation function, this time of undressed phonon operators (eq 11)¹⁹

$$w_{xx'}^{\text{Red}} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} d\tau e^{i(\omega_{x'} - \omega_x)\tau} \sum_{\mu\nu} \langle M_{x'x\mu}^{(0)}(\tau) M_{xx'\nu} |_{\text{Red}} \rangle_{\text{eq}} \quad (21)$$

Note also that, in eq 21, there is no renormalization of excitonic energies, that is, $\tilde{\omega}_x = \omega_x$. Evaluating eq 21, we obtain the familiar expression for rates in the case when only one phonon can be exchanged with the bath to perform transition $|x'\rangle \rightarrow |x\rangle$

$$w_{xx'}^{\text{Red}} = \frac{2\pi}{\hbar} \sum_{\mu} |\Gamma_{xx'}^{\mu}|^2 \delta(\hbar\omega_{x'} - \hbar\omega_x + \hbar\omega_{\mu}) n_{\text{BE}}(\hbar\omega_{\mu}) + \frac{2\pi}{\hbar} \sum_{\mu} |\Gamma_{xx'}^{\mu}|^2 \delta(\hbar\omega_{x'} - \hbar\omega_x - \hbar\omega_{\mu}) (1 + n_{\text{BE}}(\hbar\omega_{\mu})) \quad (22)$$

with $n_{\text{BE}}(E) = (e^{\beta E} - 1)^{-1}$.

As mentioned in the model description, index μ enumerating phonon modes can be understood as composite index $(i\xi)$, where i labels individual sites, while ξ counts individual phonon modes on each site. Bearing in mind our assumption that sets of phonon modes and local electron–phonon and hole–phonon interaction constants are identical on each site, the passage to the limit of macroscopic phonon bath is most conveniently done by introducing the spectral function (for $E > 0$)

$$J(E) = \sum_{\xi} g_{\xi}^2 \delta(E - \hbar\omega_{\xi}) \quad (23)$$

In eq 23, g_{ξ} are local carrier–phonon interaction constants. Under the aforementioned assumptions, correlation function $\ddot{g}_{\vec{x}_2, \vec{x}_1}(\tau)$ factorizes as follows

$$\ddot{g}_{\vec{x}_2, \vec{x}_1}(\tau) = P_{\vec{x}_2, \vec{x}_1} \ddot{g}(\tau) \quad (24)$$

where quantity $P_{\vec{x}_2, \vec{x}_1}$ depends only on spatial properties of exciton states involved, while

$$\ddot{g}(\tau) = \int_0^{+\infty} dE J(E) \left[\coth\left(\frac{\beta E}{2}\right) \cos\left(\frac{E\tau}{\hbar}\right) - i \sin\left(\frac{E\tau}{\hbar}\right) \right] \quad (25)$$

depends only on spectral density $J(E)$. Analogous factorizations also hold for $\dot{g}_{\vec{x}_2, \vec{x}_1}(\tau)$, $g_{\vec{x}_2, \vec{x}_1}(\tau)$, and $\lambda_{\vec{x}_2, \vec{x}_1}$ as detailed in section S2.3 of the SI. Here, let us only mention that quantity $P_{\vec{x}_2, \vec{x}_1}$ is a generalization of the spatial proximity factor $P_{x', xx'}$, which is the only quantity entering the Redfield population transition rates

$$w_{xx'}^{\text{Red}} = \frac{2\pi}{\hbar} P_{x', xx'} J(\hbar\omega_x - \hbar\omega_{x'}) n(\hbar\omega_x - \hbar\omega_{x'}) \quad (26)$$

Equation 26 can be obtained from eq 22 by passing to the limit of macroscopic bath, while

$$n(E) = \begin{cases} n_{\text{BE}}(E), & E > 0 \\ 1 + n_{\text{BE}}(-E), & E < 0 \end{cases} \quad (27)$$

In this work, we assume that the spectral density is of the Drude–Lorentz form

$$J(E) = \frac{2}{\pi} \lambda \frac{E \hbar \gamma}{E^2 + (\hbar \gamma)^2} \quad (28)$$

The parameter λ , which can be interpreted as the polaron binding energy, measures the overall strength of carrier–phonon coupling. The inverse of parameter γ , γ^{-1} , is the characteristic time scale of the decay of bath correlation function $\ddot{g}(\tau)$ in eq 25. The Drude–Lorentz spectral density is widely employed in computational studies of excitonic dynamics in models of photosynthetic excitonic aggregates^{29,30} and OPVs,^{18,31,32} mainly due to the existence of relatively simple analytical expressions for $\ddot{g}(\tau)$.

The exciton recombination is taken into account on the same level as in our recent work.¹³ Equation 14 is then augmented by the following term

$$(\partial f_x(t))_{\text{rec}} = -\tau_x^{-1} f_x(t) \quad (29)$$

where lifetime τ_x of state $|x\rangle$ basically depends on the overlap of moduli of electron and hole distributions in that state. The recombination events are assumed to be unidirectional and they are tracked by following the time evolution of the ground-state (GS) population

$$\partial f_{\text{GS}}(t) = \sum_x \tau_x^{-1} f_x(t) \quad (30)$$

Further details are given in section S1.3 of the SI and in ref 13.

Our aim is to examine pathways of charge separation on time scales spanning a very broad range, from shortest time scales stemming from nuclear dynamics (~ 10 – 100 fs) all the way to time scales characteristic for recombination events (~ 100 ps to 10 ns). Computational approaches that rely on

the direct propagation of eq 14 complemented with eq 29 are thus quite expensive, especially keeping in mind that we want to follow populations of ~ 1000 excitonic levels. Rewriting eqs 14 and 29 in matrix form, we formulate an efficient algorithm to calculate exponent of a nonsymmetric matrix, which completely obviates the need for direct temporal propagation. The details of our numerical scheme are presented in sections S2.5 and S2.6 of the SI. The flow diagram summarizing the main steps in the computation of the dynamics in a single disorder realization is given in Figure 1b.

RESULTS

Calculations of the time dependence of populations of various types of exciton states were performed using the approach presented in previous section. The default parameters in the calculations were: polaron binding energy $\lambda = 80$ meV, disorder strength $\sigma = 100$ meV, temperature $T = 300$ K, $\gamma = 10$ ps $^{-1}$. Some of these parameters were varied to understand the effect of relevant factors on time scales of charge separation process. The values of the parameters that were varied will be explicitly specified in the presentation of results in this section, while for all other parameters the default values will be assumed. The transition rates were evaluated within modified Redfield theory using eq 16. Two different types of initial conditions (see eq 12) were considered. The first type assumed that initial state (state $|x_0\rangle$ in eq 12) is an XD state with energy in the range $(E - \Delta E, E + \Delta E)$ (with $\Delta E = 50$ meV) which has highest matrix element for its optical generation. The second type assumed that initial state is the lowest-energy CT state among those whose recombination lifetime is shorter than 10 ns. The first type of initial conditions is chosen to mimic the effect of external excitation by a short pulse of central frequency $E/\hbar$. We will examine the dynamics starting from initial donor states of different energies E in order to understand how excess electronic energy supplied by the excitation of high-energy donor states affects charge separation pathways and time scales. As quantitatively demonstrated in Figure S2 of the SI, higher lying donor states also display a higher degree of carrier delocalization. Whether or not the excess electronic energy or better carrier delocalization can enhance separation of initial donor excitons has been the subject of experimental studies performed both on sub-picosecond⁵ and much longer³³ time scales. The second type of initial conditions was chosen to understand the separation process once the exciton reached the lowest energy CT state. Such an initial condition is also experimentally relevant. In refs 34 and 35, it was concluded that charge separation predominantly occurs upon the fast relaxation to the bottom of the CT manifold, on time scales ranging from tens to hundreds of picoseconds.³⁵ Moreover, the authors of ref 9 succeeded in selectively exciting (from the ground state) the low energy interface-pinned CT state. The condition on the exciton recombination lifetime was introduced to avoid the possibility of selecting some state whose energy was significantly lowered due to effects of disorder, while its overlap of electron and hole wave functions is so small that it essentially does not represent the conventional CT state with both electron and hole being close to the interface. In Figure S3 of the SI, we present numerical evidence that our criterion for the choice of the initial CT state indeed gives a CT state with small electron–hole separation and quite localized carriers. In the calculation, we include all exciton states with energies lower than $E_{\text{init}} + 20k_{\text{B}}T$, where E_{init} is the energy of

initial state. All of the results presented were averaged over 256 realizations of disorder, which is sufficient to get converged results for quantities presented.¹³ In Figure 2a–d we present

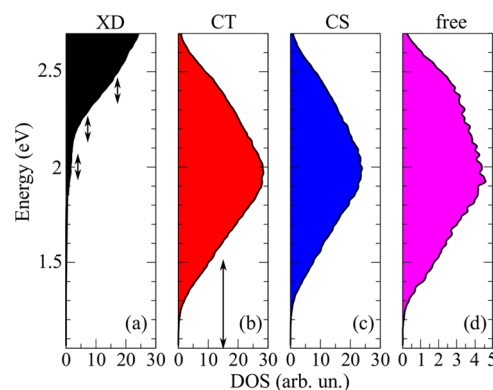


Figure 2. Disorder-averaged densities of (a) XD, (b) CT, (c) CS, and (d) free-charge states (in arbitrary units). The vertical arrows indicate energy ranges in which the initial (a) XD and (b) CT state is located. The excitonic DOS in a single disorder realization is computed by broadening each exciton level by a Gaussian with standard deviation of 5 meV.

disorder-averaged densities of XD, CT, CS, and free-charge states, respectively. The vertical arrows indicate the energy range in which the initial XD (Figure 2a) and CT (Figure 2b) state is located.

Our approach is based on the assumption that off-diagonal exciton–phonon coupling parameters (which can be quantified by the terms $P_{x_i x_j, x_f x_i}$ when $x_i \neq x_f$) are much smaller than the diagonal exciton–phonon coupling parameters (which can be quantified by the terms $P_{x_i x_i, x_i x_i}$). To check if this assumption is satisfied we present in Figure 3 the average over different disorder realizations of the quantity

$$h(E_i, E_f) = \frac{\sum_{x_i, x_g} P_{x_i x_g, x_g x_i} \exp\left(-\frac{(E_{x_i} - E_i)^2 + (E_{x_g} - E_f)^2}{2\sigma_E^2}\right)}{\sum_{x_i, x_g} \exp\left(-\frac{(E_{x_i} - E_i)^2 + (E_{x_g} - E_f)^2}{2\sigma_E^2}\right)} \quad (31)$$

which is basically the dependence of $P_{x_i x_g, x_g x_i}$ on the energies of states E_{x_i} and E_{x_g} . The results are presented for two disorder strengths, $\sigma = 50$ meV and $\sigma = 100$ meV. In each disorder realization, as well as on both axes in Figure 3, the energies $E_{i/f}$ have been rescaled to the $[0,1]$ range using the formula $e = \frac{E - E_{\text{min}}}{E_{\text{max}} - E_{\text{min}}}$, where E is the unrescaled energy, e is the rescaled energy which is shown on the axes, E_{min} and E_{max} are the minimal and maximal energy of exciton states considered for a given realization of disorder. Neither of the aforementioned energies is renormalized in the sense of eq 8. The reasons for such a rescaling will be given together with the presentation of energy–temporal pathways of charge separation, see Figure 6a–d. The results in Figure 3 point out that $h(E_i, E_f)$ is much smaller for states of different energies than for states of close energies, as can be evidenced by the fact that the off-diagonal contributions are at least an order of magnitude smaller than the diagonal contributions. Such results confirm our assumption that off-diagonal exciton–phonon coupling parameters are much smaller than the

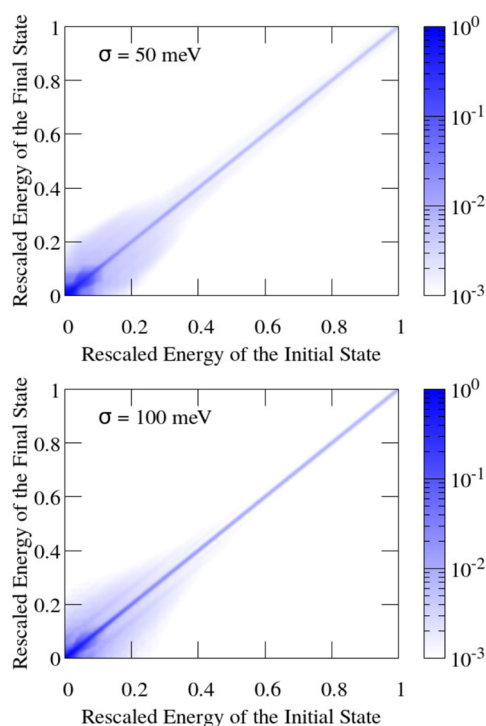


Figure 3. Dependence of spatial proximity factor $h(E_i, E_f)$ (eq 31) averaged over different disorder realizations on rescaled energy of the initial and final state for two different values of disorder strength σ . Standard deviation of the Gaussian function used to broaden the spatial proximity factor is $\sigma_E = 5$ meV. The data are shown for exciton states considered when the initial state is XD state with energy around 2200 meV.

diagonal exciton–phonon coupling parameters. We also checked the sensitivity of our results to the parameter of the spectral function γ . The results shown in Figures S7 and S8 of the SI indicate that the change of γ within reasonable limits $\gamma \in (10 - 20) \text{ ps}^{-1}$ has almost no effect on time dependence of populations.

To understand the time evolution of populations of various types of exciton states, we present in Figure 4 these dependences at four different values of disorder strength σ for initial XD state with energy of around 2200 meV, see the middle vertical arrow in Figure 2a. First step in the separation process is the transformation from the initial XD state to a CT state. In the initial XD state, electron and hole wave functions have strong overlap which means that the electron and the hole are localized around the same position in space. To transform into a CT state both electron and hole need to reach the interface and the effects of disorder slow down this process. This effect can be clearly seen from Figure 4. While for lowest disorder strength CT excitons outnumber XD excitons already at around 1 ps, for largest disorder strength this happens more than 100 ps after initial excitation. These time scales are comparable to the XD exciton recombination time and there is therefore a possibility that the XD exciton will recombine before transforming into a CT exciton. In Figure 5 (left panels) we present the time dependence of the number of excitons that have recombined from various groups of exciton states. For strong disorder the exciton remains in the donor for long time and therefore a significant portion of these excitons gets recombined (around 50% for $\sigma = 100$ meV, see bottom left panel in Figure 5). For low disorder strength a large portion of XD excitons transform into CT excitons before recombining

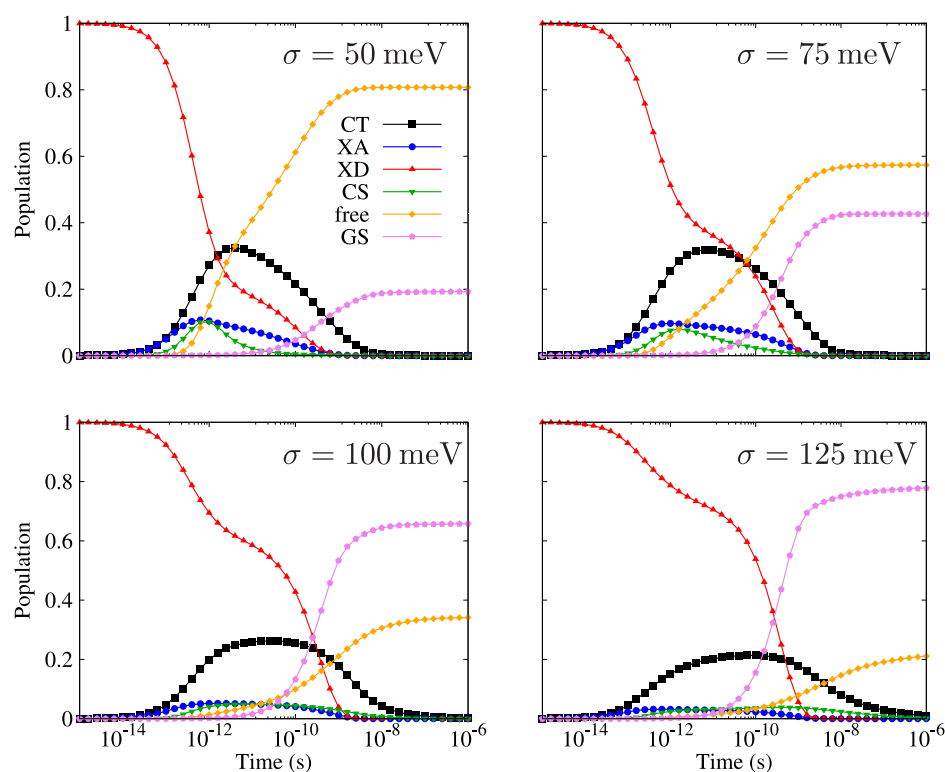


Figure 4. Time dependence of the number of CT excitons, acceptor (XA) excitons, XD excitons, CS excitons, free charges (free), and recombined pairs (GS) when initial state is XD state with energy around 2200 meV. The results are shown at four different values of disorder strength σ .

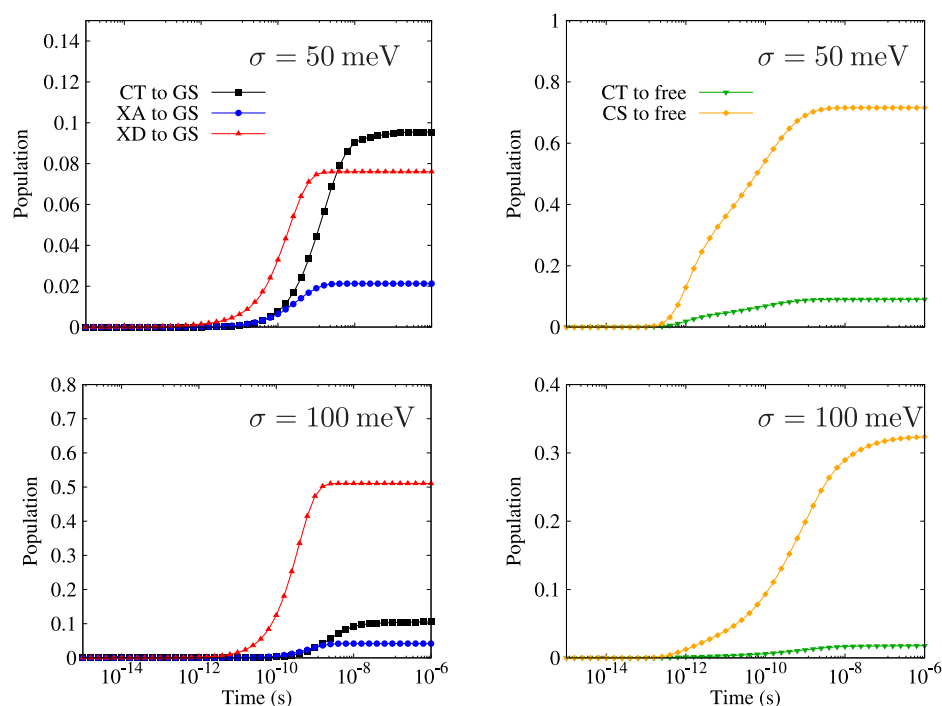


Figure 5. Left panels: Time dependence of the number of recombined pairs from CT states (CT to GS), from XA states (XA to GS) and from XD states (XD to GS). Right panels: Time dependence of the number of free charges created from CT states (CT to free) and from CS states (CS to free). The results are presented at two different values of disorder strength σ . Initial state is XD state with energy around 2200 meV.

and recombination from XD states is no longer the dominant source of recombination (see top left panel in Figure 5).

From Figure 4 we see that time scale for further separation from CT state toward free charges also strongly depends on disorder strength σ and increases as σ increases. This can be evidenced from the increase of time when free charge population reaches saturation. In our previous work,¹³ we investigated the separation from lowest CT state in detail and found that for low and moderate disorder strength it can be understood in terms of a four-state kinetic model involving the ground state, the lowest CT state, intermediate CT states and CS states. In this model an exciton that escapes from intermediate CT states to CS states reaches external contacts without any additional obstacles. For larger disorder strengths additional obstacle is caused by slow transport from CS state toward external contacts. For all disorder strengths the states from which conversion to free charges takes places are predominantly CS states. This can be seen from right panels in Figure 5. Despite the fact that almost all excitons that separate into free charges pass through CS states, their populations remain relatively small at all times. This is a consequence of the fact that no exciton remains for a long period of time in a CS state—it either makes a transition to other CS or CT states or converts into free charges. To additionally verify the statements of this paragraph regarding further evolution of an exciton that has reached a CT state, we have performed the computation where initial state is a low energy CT state chosen according to the criterion discussed in the first paragraph of this section. The results obtained are given in Figure S9 of SI and also demonstrate an increase of time scale for conversion into free charges from $\sim(1 - 10)$ ns at low and moderate disorder strength $\sigma = (50 - 75)$ meV toward $\sim 1 \mu\text{s}$ time scale at $\sigma = 125$ meV. In this case, all recombination events take place from CT states, as shown in

the left part of Figure S10 of the SI, and free states are again predominantly reached by transitions from CS states, as presented in the right part of that figure.

Next, we would like to gain insight in time evolution of exciton energies which will unravel whether hot or cold charge separation mechanism is in place. For this reason, we calculate the time evolution of spectral distribution of excitons defined as

$$A_G(E, t) = \frac{1}{N_X(t)} \sum_{x \in G} g(E - \hbar\omega_x, \sigma_E) f_x(t) \quad (32)$$

where $N_X(t)$ is the total excitonic population at time t and $g(x, \sigma_E) = \frac{1}{\sigma_E \sqrt{2\pi}} \exp\left(-\frac{x^2}{2\sigma_E^2}\right)$ is the Gaussian function with standard deviation σ_E . The summation in eq 32 is performed over all exciton states from group G . This distribution for various exciton groups is shown in Figure 6 along with corresponding densities of states. More precisely, the quantity $a_G(e, t)$ shown in Figure 6 is $a_G(e, t) = A_G(E, t)$, where the relation between the rescaled energy e and the unrescaled energy E is presented in the discussion of Figure 3. Spectral distribution and density of states obtained in this way were then averaged over different realizations of disorder. We believe that this way of energy rescaling is excellent to gain insight into energy-temporal pathways of various groups of excitons. On the other hand, if the rescaling were not performed, lowest energy CT states would have quite different energies for various realizations of disorder, see Figure 2b. In the course of averaging over different realizations of disorder, lowest energy CT states for some configurations would be at the same energy as some high-energy states of other configurations and it would be hard to gain insight into exciton pathways in the course of charge separation. From Figure 6a we see that donor excitons that do not recombine or

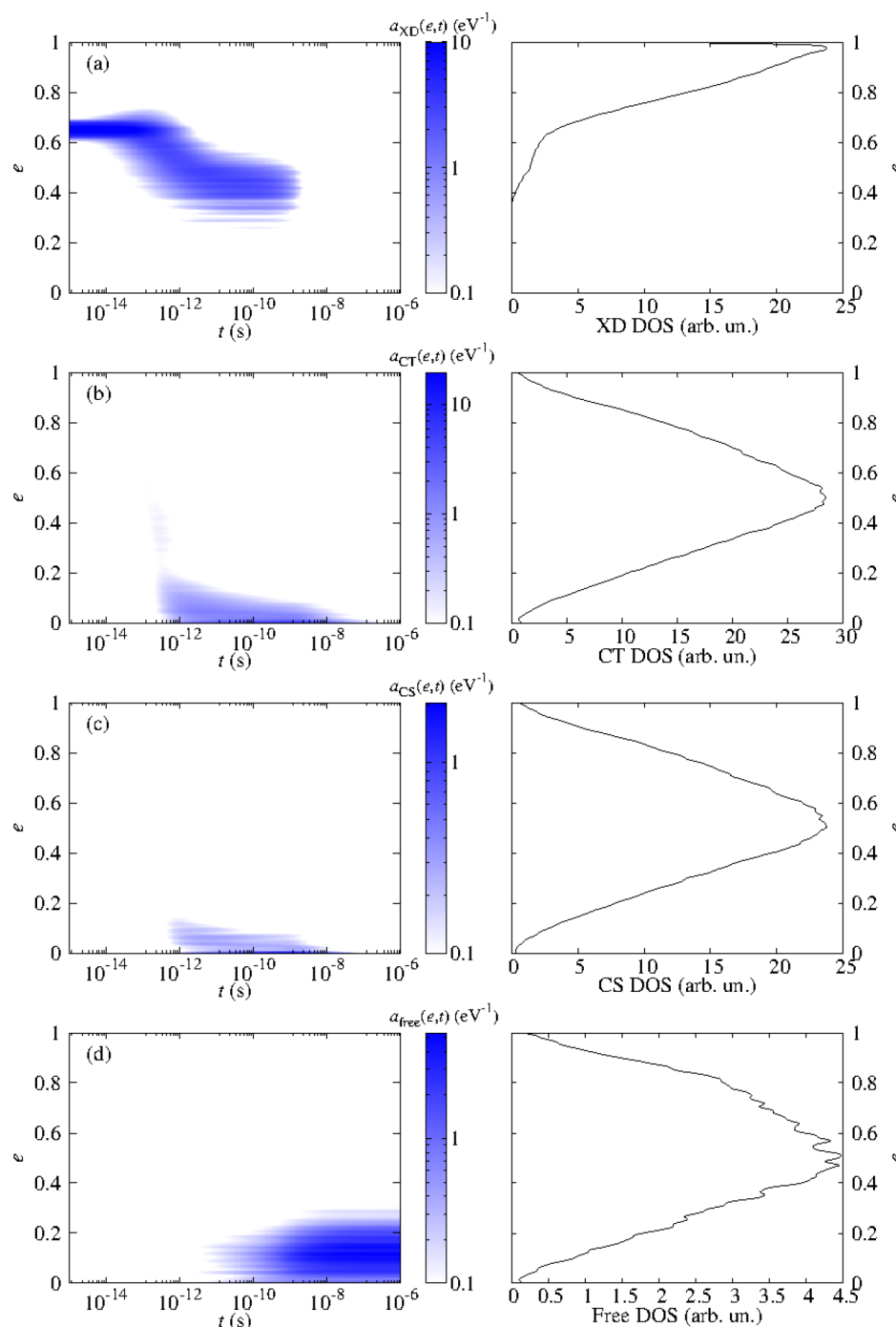


Figure 6. Energy- and time-resolved population of XD states [$a_{\text{XD}}(e, t)$], CT states [$a_{\text{CT}}(e, t)$], CS states [$a_{\text{CS}}(e, t)$], and free charges [$a_{\text{free}}(e, t)$]. Gaussian broadening of $\sigma_E = 5$ meV was used to calculate these quantities. The energy of free charges is taken at the moment of time when they are created. Initial state is XD state with energy around 2200 meV. Corresponding DOS (in arbitrary units) for each group of states is given as a reference in panels on the right. Energy axis has been rescaled in such a way that 0 corresponds to lowest energy in a certain configuration, while 1 corresponds to highest energy of that configuration.

convert to CT states relax to lower energies. Since the beginning of creation of CT states (at about 0.1–1 ps, see Figure 6b), the low energy part of CT manifold is populated, and the energy distribution is further shifted toward lower energies as the time progresses. CS states become populated at about similar times as CT states and only cold CS states are populated, as seen in Figure 6c. Figure 6d shows the distribution of energies of free charges that were created and also indicates that only low energy free charges are created.

Note that our model does not consider further evolution of free charges after their creation. Consequently, the energies of free charges in Figure 6d correspond to the moment of time when they were created. The results in Figure 6 clearly point in favor of cold separation mechanism since only low energy CT and CS excitons are present in the system and only low energy free charges are generated. We obtain the same conclusion from analogous figures obtained for different initial XD

energies (depicted by vertical arrows in Figure 2a) and for different disorder strengths, see Figures S11–S13 of the SI.

To further support the charge separation mechanism proposed, we present in Figure 7 the quantity defined as

$$N_T(t)_{G_2 G_1} = \sum_{x_1 \in G_1, x_2 \in G_2} [f_{x_1}(t)w_{x_2 x_1} - f_{x_2}(t)w_{x_1 x_2}] \quad (33)$$

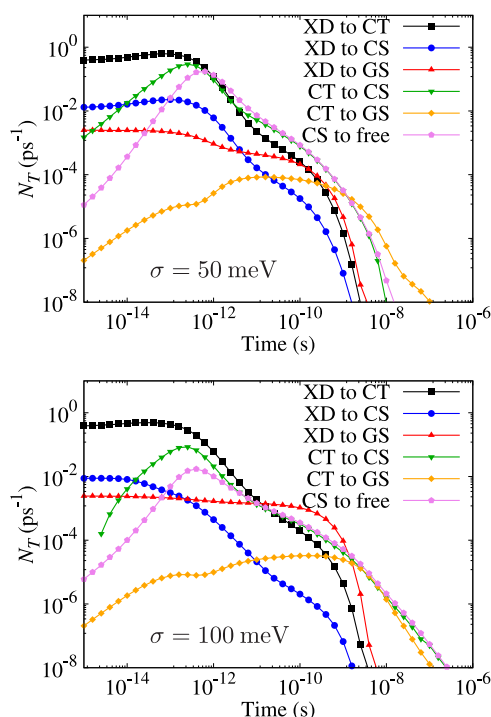


Figure 7. Time dependence of the number of transitions per unit time between most relevant groups of exciton states for disorder strengths of $\sigma = 50$ and 100 meV. Initial state is XD state with energy around 2200 meV.

This quantity represents the net number of exciton transitions per unit time from the states of group G_1 to the states of group G_2 . Figure 7 shows that dominant transitions in the system up to ~ 1 ps are the transitions from XD to CT states. After this time, for lower disorder strength of $\sigma = 50$ meV, the dominant transitions in the system are those from CT to CS states and from CS to the states of free charges. Interestingly, the value of N_T for these two groups of transitions is almost the same at those times (as can be seen in Figure 7), suggesting that almost each conversion between CT and CS states is followed by conversion from CS to free charge states. For larger times (after ~ 1 ns) recombination of a small number of remaining CT excitons dominates. For larger disorder strength of $\sigma = 100$ meV, we see that from $\sim (10 - 1000)$ ps XD recombination dominates. Nevertheless, there is again the balance between CT to CS and CS to free charge conversion, which become dominant events at times after ~ 10 ns. All these results unambiguously imply that the dominant pathway of excitons that avoid recombination is from XD, via cold CT to cold CS states, and eventually to free-charge states.

We further study the impact of polaron binding energy on exciton dynamics in general and charge separation yield in particular. Similarly as in ref 13, the separation yield is defined as the long-time limit of the total free-charge population. In

Figure 8 we present the dependence of separation yield from initial XD state on polaron binding energy at two different

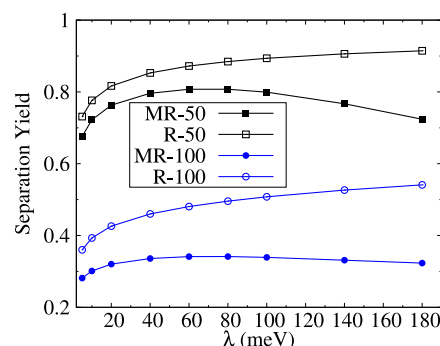


Figure 8. Dependence of separation yield on polaron binding energy λ when transition rates are modeled within modified Redfield theory for disorder strength of $\sigma = 50$ meV (label MR-50) and $\sigma = 100$ meV (label MR-100) and when transition rates are modeled within Redfield theory for disorder strength of $\sigma = 50$ meV (label R-50) and $\sigma = 100$ meV (label R-100). Initial state is XD state with energy around 2200 meV.

values of disorder strength in cases where transition rates were modeled using modified Redfield (eq 16) and Redfield (eq 26) approaches. The effect of electron–phonon interaction, whose strength is in our model quantified by polaron binding energy, on exciton transport is twofold. On the one hand, the increase in electron–phonon interaction increases the phonon-assisted scattering between exciton states and hence the transition rates between the states. This effect is included both in Redfield and modified Redfield rates. On the other hand, the increase in electron–phonon interaction tends to “dress” the carriers by the respective phonon cloud, which leads to a decrease in the transition rates between the states. This effect is captured only within the modified Redfield approach. As a consequence of previous facts, the transition rates always increase with increase in electron–phonon interaction strength within Redfield approach. For this reason, the separation yield is a monotonously increasing function of λ within Redfield approach. On the other hand, within modified Redfield approach, the transition rates and the separation yield are not monotonous functions of λ , which can be seen in Figure 8. The maximum in the dependence of the yield on λ is more pronounced for smaller disorder strength. In this case, relative role of localization induced due to polaron effects in comparison to localization induced by disorder is larger, leading to a more pronounced dependence of yield on λ . Nevertheless, we see from Figure 8 that in practice the separation yield depends only weakly on λ . This is true in particular in the range from 10 to 100 meV, which is the range of realistic values of λ .^{14,36} Some quantitative differences between separation yield from Redfield and modified Redfield approach exist, as can be seen in Figure 8. The separation yield is consistently smaller in the modified Redfield than in the Redfield approach, and the difference between the two yields increases as the magnitude of the carrier–phonon interaction is increased. Nevertheless, the overall conclusions regarding the time scales for conversion between different exciton types and separation mechanism are not expected to be affected by the choice between the two models for transition rates. This is confirmed by the results presented in Figure S5 of the SI, which compares the dynamics of excitonic populations and

recombination events produced by modified Redfield and Redfield transition rates. Since the excitonic dynamics in the two cases is similar, see Figure S5a,c,e, the correlation between the values of the respective transition rates is expected, as evidenced by Figure S6 of the SI, which shows pairs (w_R , w_{MR}) of transition rates predicted by Redfield (w_R) and modified Redfield (w_{MR}) approaches. For most transitions, the two models predict transition rates that are of the same order of magnitude. However, the difference in the separation yields presented in Figure 8 means that the most important transitions for the full charge separation (from XD to CT and from CT to CS states), which involve a significant spatial transfer of charge, are somewhat slower in the modified Redfield than in the Redfield approach. The effect is more pronounced for stronger couplings to vibrations and is also reflected in recombination data in Figure S5b,d,f. Higher recombination probabilities from both XD and CT states within the modified Redfield approach (with respect to the Redfield approach) reflect smaller escape rates from XD toward CT and from CT toward CS states. The preceding discussion clearly demonstrates that the approach adopted in this work takes into account (at least partially) the “dressing” of electronic excitations by phonons. For completeness, we present in Figure S14 of the SI the dependence of separation yield from initial CT state on λ . This dependence exhibits the same features as in the case of initial XD state, with a slight difference that it is somewhat more pronounced.

In our previous work,¹³ we used the transition rates which are equivalent to Redfield rates, with somewhat different spectral function (Ohmic with exponential cutoff instead of Drude–Lorentz). Since we have established that exciton dynamics and separation mechanism are expected to be similar both within Redfield and modified Redfield approach and we have previously shown¹³ that the choice between Drude–Lorentz and Ohmic (with exponential cutoff) spectral function does not strongly affect the separation yield from initial XD state, it is expected that all the trends obtained when a particular parameter of the Hamiltonian is changed (such as transfer integrals, band offsets, on-site Coulomb interaction, temperature, energy of initial donor state, electric field strength) will remain qualitatively similar as in our previous study. For example, we found in our previous work¹³ (in agreement with other studies^{17,32}) that the dependence of charge separation yield on electric field is a monotonously increasing function that is nearly constant at fields below $\sim 10^6$ – 10^7 V/m, which then increases and eventually reaches one at fields on the order $\sim 10^7$ – 10^8 V/m and we expect overall similar behavior here. Because of these expectations and the fact that the evaluation of modified Redfield rates is significantly more computationally prohibitive than the evaluation of Redfield rates, we do not repeat the analysis of these dependences from our previous work here.

DISCUSSION

Connection to Experimental Results. We now discuss the connection of our results to available experimental results from the literature. The most common experimental technique for investigating the time dependence of populations is pump–probe transient absorption spectroscopy. Within this technique, one initially excites the system by the pump pulse that creates excitons and then probes the system by another optical pulse. Optical response to the second pulse gives information about populations of certain groups of exciton states. Two time

scales were typically identified in the signals obtained from the application of this technique to polymer/fullerene blends: a very short ~ 100 fs time scale and a longer ~ 10 ps time scale.^{34,37–40} The longer ~ 10 ps time scale originates from conversion of XD to CT excitons. On the other hand, the short time scale may originate from ultrafast transfer of excitons generated very close to the interface which do not need to diffuse to the interface to convert into CT excitons. We will discuss in particular the results on P3HT/PCBM blend since the parameters of our model were chosen to mimic this system. In ref 41, the authors analyzed exciton and charge dynamics in P3HT/PCBM blends of varying degree of disorder: (i) regiorandom P3HT; (ii) regioregular P3HT; (iii) annealed regioregular P3HT. They found that in cases (i) and (ii) recombination from CT states occurs with a time constant of 2 ns with more recombination events in case (i). Such results are in overall agreement with our results regarding the time scale for recombination (see Figure 5) and its independence on disorder strength. The time scale for conversion of XD to CT states is less than 100 fs in cases (i) and (ii) in ref 41; however, one should note that these samples consist of a blend where there is a PCBM molecule close to each P3HT chain and therefore XD excitons do not need to diffuse to the interface to transform to CT states. On the other hand, our model mimics the P3HT/PCBM bilayer and predicted XD to CT conversion time scales should be compared to annealed samples [case (iii) in ref 41] where regions of pure P3HT are formed. The time scale for XD to CT conversion in case (iii) in ref 41 was reported to be approximately 9 ps and is comparable to our results, see Figure 6a,b, or Figure 4.

Since excitons in different states may respond to the same probe, it is difficult to reliably distinguish between different groups of states in a typical transient absorption experiment. It turns out in practice that XD excitons can be reliably identified but that it is quite difficult to distinguish between CT and CS states.¹¹ These difficulties can be circumvented in a time-delayed collection-field experiment, which exclusively measures free (extractable) charges.⁴² Charge generation by an energy-selective photoexcitation is followed by application of a high reverse bias voltage to extract free charges. In a recent study employing this experimental technique,³³ it is shown that the relaxation to the bottom of the CT manifold cannot be avoided, no matter how large the excess energy stemming from the excitation of high-energy donor states is. Moreover, the authors demonstrate that the majority of recombination, as well as the separation events occur starting from CT manifold, and that most photogenerated species either recombine or transform into free carriers within a couple of nanoseconds following the photoexcitation. The results we present in this work, in particular the energy- and time-resolved pathways summarized in Figures 6 and S7–S9, and the resolution of separation and recombination events performed in Figure 5 are thus in agreement with the central conclusions of ref 33.

Dynamics of excitons in polymer/fullerene blends was also studied using several other time-resolved techniques. In ref 40, interpretation of polarization-sensitive transient absorption measurement of P3HT/PCBM blends implied the time-scale of $\sim (0.1 - 20)$ ps for the formation of CT states and up to ~ 100 ps time scale for further conversion into free charges. In ref 43 time-resolved electric field-induced second harmonic method was used to monitor the charge separation process. It was shown that the charges separate by several nanometers during the first several picoseconds, while further separation

and formation of free carriers takes place on a subnanosecond time scale. In ref 7 the authors used time-resolved two-photon photoemission technique to visualize the time dependence of spectral distribution of excitons in a phthalocyanine/fullerene blend. They found that formation of CT states and their further relaxation occurs on a picosecond time scale. Time scales in these experiments are comparable with what we obtain for lower values of disorder strength.

Discussion on Theoretical Approach and Model.

Theoretical and simulation studies that investigated time dependence of exciton populations in organic heterojunctions were certainly performed in the past. Nevertheless, the studies based on model Hamiltonians were restricted to short (sub-picosecond) time scales.^{17,18,32,44–49} Consequently, these studies could capture at most the process of XD to CT conversion and could not capture further charge separation. Some of these studies also included polaronic effects to a certain extent.^{17,18,32,44,45,49} The studies on longer time scales were exclusively based on the assumption that electrons and holes are hopping between a predefined set of sites and relevant properties are typically extracted from a kinetic Monte Carlo simulation.^{50–56} Such studies typically do not include polaronic and delocalization effects, while in some cases delocalization is added through its effect on site energies⁵⁶ and polaronic effects are sometimes added if hopping rates are calculated using the Marcus expression.⁵² On the other hand, our study starts from a model Hamiltonian whose parameters were chosen to mimic a particular bilayer and includes both the effects of delocalization and polaronic effects in the same approach.

The modified Redfield theory interpolates between widely used theories of exciton/charge transport to which it reduces in appropriate limits.²⁵ Standard Redfield rates (eq 26) are obtained from eq 16 by neglecting all terms $\dot{g}_{\bar{x}_2x_2,\bar{x}_1x_1}$, $\dot{g}_{\bar{x}_2x_2,\bar{x}_1x_1'}$, $\dot{g}_{\bar{x}_2x_2,\bar{x}_1x_1}$ in which $\bar{x}_2 = x_2$ or $\bar{x}_1 = x_1$. In this limit, electronic couplings are treated in all orders, while the interaction with phonons is considered in the second order. The path toward the Förster and Marcus transition rates is presented in section S2.4 of the SI. In these limits, the interaction with phonons is treated in all orders, while electronic couplings are considered in the second order. The modified Redfield theory can thus be regarded as a viable route to go beyond all conventional limits and include both delocalization and the most important part of the couplings to vibrations in a nonperturbative manner. It is applicable to transitions in which the spatial overlap between the carriers in the excitonic states involved is relatively small. In our model, the disorder strength is comparable to electronic couplings, so that the carriers in excitonic states are only partially delocalized. This is shown in Figure S4, which presents data on the participation ratio of the electron and hole in various excitonic states. We see in Figure S4 that in the XD, CT, and CS states that are mainly involved in the separation process (see blue traces in Figure 6), the carriers are localized on only a couple of neighboring units. Full charge separation is achieved by transitions (from XD to CT, from CT to CS, and to CS to free-charge states) in which the spatial positions of the electron and hole are significantly changed. Therefore, the spatial overlap of the initial and final states in transitions that are crucial to reach free-charge states is expected to be small, and the rates predicted by the modified Redfield theory are expected to be reliable.

As already mentioned, the initial condition embodied in eq 12 is appropriate to describe the dynamics starting on time scales ~ 100 fs to 1 ps after a sudden photoexcitation event. Our approach is not intended to capture ultrafast dynamics right after exciton photogeneration. Should one want to examine such dynamics, and still treat polaronic effects on the level presented in our study, one should resort to the so-called nonequilibrium modified Redfield theory.^{28,57} The appropriate initial condition to describe sudden photogeneration in excitonic state $|x_0\rangle$ is of the form given on the right-hand side of eq 13, where nuclear degrees of freedom have not had time to accommodate themselves to the displaced equilibrium characteristic for $|x_0\rangle$, but are in their canonical equilibrium (which is associated with the ground state). A derivation that is similar to (but somewhat more involved than) that presented in section S2.1 of the SI produces rate equations (eq 14) with time-dependent nonequilibrium modified Redfield rates, which capture non-Markovian effects and dynamical interplay between nuclear relaxation toward equilibrium in electronically excited state and population transfer. It is shown that, already after a couple of γ^{-1} (in our case, a couple of hundreds of femtoseconds) after exciton photogeneration, time-dependent nonequilibrium modified Redfield rates reach their asymptotic values, which coincide with the modified Redfield rates given in eq 16.⁵⁷ In other words, nuclear relaxation toward nuclear equilibrium in excited states (see phonon factor of the initial condition in eq 12) is completed a couple of hundreds of femtoseconds after a sudden photogeneration. Our recent analysis¹² of ultrafast exciton dynamics triggered by a short photoexcitation suggests that, on sub-picosecond time scales following exciton photogeneration, population transfer mainly occurs within the manifold of donor states, while transitions toward states of spatially separated charges predominantly take place on much longer time scales. These conclusions are not expected to change when polaronic effects are taken into account. We thus believe that, in order to gain insight into time scales and pathways of long-time charge separation, it is reasonable to use time-independent modified Redfield rates (eq 16) along with the initial condition in eq 12.

Next, we comment on the possible influence of the dimensionality of the model on the results. Our main conclusion is that the main path of charge separation includes the transition from XD states to low energy CT states (step 1), followed by conversion of CT states to CS states (step 2) and eventual transport from CS states to free charge states (step 3). We will discuss next how the effect of dimensionality could affect the transport over these routes. Step 2 involves the transition from low energy CT state to intermediate CT state with somewhat larger energy and larger electron–hole separation and the transition from that state to some CS state. Since only a few transitions constitute this step, the effect of dimensionality is not expected to play any role on this step. On the other hand, the effect of dimensionality might be important when charge (or exciton) transport over larger distance takes place. In this case, additional dimensions might help the charge to find additional routes if direct one-dimensional route is not accessible. As a consequence, one might expect that higher dimensionality might accelerate steps 1 and 3. The results of our previous work¹⁵ suggest that step 2 is actually the rate limiting step for low and moderate disorder strengths (say up to $\sigma \sim 80$ meV). Therefore, for these disorder strengths, steps 1 and 3 are already fast enough and their further acceleration will not enhance the separation yield.

On the other hand, steps 1 and 3 do become rate limiting for larger disorder strengths and it is possible that higher dimensionality will accelerate these steps and increase the separation yield.

Next, we comment on the extent by which dimensionality affects the efficiency of steps 1 and 3 and consequently the separation yield. An important point to note in this regard is that the exciton states in our model exhibit a certain degree of delocalization. As a consequence, a donor exciton in step 1 can reach a CT state after making only a few transitions—it does not need to travel slowly site by site. In a similar manner, an electron and a hole in step 3 can also reach the free charge state in a few steps only and not by passing each site. It is therefore important to note that our model is different than frequently used hopping models in which an exciton (or a charge) is localized at a site and can usually hop only to nearest neighbor sites. In such models, the transport can be very slow in one dimension in the presence of disorder and adding new dimensions strongly accelerates the transport. For example, in ref 56 the authors showed that separation yield at low electric fields in one dimension is rather low (between 10^{-4} and 10^{-2} depending on the parameters) and that the separation yield in 2D model can be 2 orders of magnitude larger than in 1D model. In our model, the transport is already relatively efficient in 1D as can be evidenced by reasonably large separation yields of at least 20% even at highest disorder strength (see Figure 4d). Therefore, we expect that additional dimension will only slightly increase the separation yield at large disorder strength, while it will hardly affect it at low and moderate disorder strengths.

This expectation can rigorously be confirmed only by extending the model to higher dimensions which is at present a significant challenge both from computational and conceptual side. On the computational side, higher dimension introduces a significantly larger number of relevant exciton states, which then introduces the need for a much larger number of transition rates that need to be calculated and a larger eigenvalue problem and the system of linear equations that need to be solved to obtain time dependence of populations. On the conceptual side, real morphology of the materials near the interface is not well-known. Ideally, one would like to start in the simulation from the atomic structure of the materials near the interface, then parametrize an effective model similar to ours and use that model further. However, in the case of P3HT/PCBM several questions arise regarding for example the orientation of P3HT chains with respect to the interface, the sharpness of the interface, the amount of order/disorder in each of the materials near the interface, etc.

CONCLUSIONS

In conclusion, we presented the method for simulation of charge separation process in organic semiconductor bilayers from the creation of exciton in the donor to the final time (which can be as long as 1 μ s later), when there are no more charge pairs present in the system. In the course of separation process, donor excitons first relax to lower energies and eventually transform into a CT state. Charge transfer excitons then convert into CS and free-charge states via intermediate CT states which have higher energies and larger electron–hole separation. In more disordered systems the processes of conversion between XD and CT states and the conversion from CT toward free carrier states are slowed down and charge separation yield is lowered since some XD or CT excitons

recombine before they convert to other exciton types. Polaronic effects were included in the computations and it turned out that in relevant range of electron–phonon interaction parameters charge separation yield rather weakly depends on electron–phonon interaction strength. Computation results indicate that it is the conventional cold charge separation mechanism that takes place in organic heterojunctions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.9b10862>.

Detailed description of the model, theoretical approach, and numerical scheme, together with additional figures complementing the discussion in the main text (PDF)

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Notes

The authors declare no competing financial interest.

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