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Coherent and Incoherent Contributions to Charge Separation in Multi-Chromophore Systems

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Abstract

In organic materials, exciton dissociation into free charges requires overcoming an electron-hole Coulomb interaction that exceeds the thermal energy and may still be large after charge transfer at a donor/acceptor interface. We analyze the factors affecting efficiency of charge separation and subsequent removal of electrons and holes from such a donor-acceptor interface and suggest strategies for optimizing these processes. Energy transfer, charge separation and charge transfer in the vicinity of the donor-acceptor interface are studied within a common theoretical framework based on a quantum master equation, for a model system with realistic excitation energies and electronic couplings. We find that enhancing the efficiency of both charge transfer from the donor to the acceptor and of charge removal from the donor-acceptor interface requires an intricate balance between the extent of electronic delocalization throughout the material and rates of energy dissipation. For very large exciton binding energies, cascade charge separation in systems with more than one donor and one acceptor species, such as molecular polyads, is found to greatly facilitate the dissociation of geminate pairs. Our calculations predict charge separation on sub-picosecond timescales for several parameter combinations, leading to design principles for enhancing charge separation in multi-chromophore systems.

Keywords: exciton dissociation, charge separation, bulk heterojunction

1 Introduction

The promise of cheap, eco-friendly, lightweight, and flexible organic¹⁻⁴ or hybrid^{5,6} photovoltaic cells (PVCs) that can be optimized to absorb photons with a wide range of wavelengths^{2,5} has resulted in a constant drive to improve the energy conversion efficiency (ECE) of these devices.²⁻⁴ However, although ECEs above 10% have recently been achieved for solid state organic solar cells,⁴ these efficiencies still fall far short of the theoretical limit even for single junction cells ($> 20\%$).⁷ The difficulty of enhancing the performance of organic photovoltaic devices is largely due to unique hurdles that are not present in traditional silicon technology. In silicon-based PVCs, light absorption results in the formation of free charge carriers throughout the bulk semiconductor. This is a consequence of the high dielectric constant of silicon ($\epsilon_{\text{Si}} = 11.4$ eV),⁸ which ensures effective screening of the interaction between electrons and holes even at short distances. In contrast, typical dielectric constants for organic materials are significantly smaller ($\epsilon \sim 2 - 4$),⁹ and both electron-vibration and electron-electron interactions are much stronger in these systems.¹⁰ As a result, in polymer blend¹¹ or dye-sensitized PVCs,¹² most absorbed photons produce excitons, i.e., bound electron-hole pairs that are unlikely to dissociate thermally. The Coulomb binding energy, E_b , of an exciton commonly exceeds the thermal energy $k_B T = 25$ meV at room temperature by 1 – 2 orders of magnitude and can be as high as several electronvolts.^{13,14} To dissociate into free charge carriers, the exciton must travel to a donor-acceptor heterointerface, where it is energetically favorable for one of the charges to be transferred across the interface, while the other charge remains in the original material. However, even in the resulting charge separated state the electron and the hole often experience a strong Coulomb attraction, forming a “geminate pair”: this attraction must be overcome in order for the charge carriers to escape from the interface and reach the contacts of the photovoltaic cell.¹⁵ Geminate pair recombination, as well as increased non-geminate bimolecular and trap-assisted Shockley-Reed-Hall recombination that results from lower charge carrier mobilities and higher defect concentrations than those typical for crystalline semiconductors,¹⁶ are the leading causes of

exciton loss in organic photovoltaic cells.

Theoretical descriptions of organic PVCs typically consider the following sequence of events that leads to the formation of free charges: optical absorption and exciton formation, exciton migration in the material, charge separation at a heterointerface, charge transfer away from the interface, and eventual charge extraction from the PVC (Figure 1).^{10,17} The current study focuses on the processes that occur within the donor-acceptor blend: energy transfer, charge separation, and charge transfer. It is currently well-established that spatial delocalization and coherent transfer of excitons and charges can play a significant role in the dynamics of both energy and charge transfer in organic and bioorganic systems.^{18–21} On the other hand, charge separation at donor-acceptor heterointerfaces is typically described by the Marcus rate of electron transfer from a single donor molecule to a single acceptor molecule.^{22,23} However, recent experimental studies suggest that orbital delocalization and coherent wavefunction evolution are likely responsible for the ultrafast charge separation (25 fs – 1 ps) that has been discovered in a wide variety of donor-acceptor blends.^{9,24–30} To understand this process, it is necessary to perform a combined analysis of the dynamics of charge separation together with the exciton and charge transfer dynamics in the vicinity of the heterointerface. At the level of individual charge separation complexes, such analysis can be performed very accurately using time-dependent density functional theory.³¹ However, accounting for exciton delocalization over multiple molecules is likely essential to understanding charge separation in organic PVCs.¹⁷

Figure 1: A schematic representation of the sequence of processes that leads to charge separation in organic photovoltaic cells.

In the current paper we use a common theoretical framework to investigate the combined dynamics of exciton transfer, charge separation, and charge transfer in systems that consist of multiple donor and acceptor molecules and that allow coherent evolution. Our focus here is on achieving a systematic understanding of the interplay between coherent and incoherent contributions to the dynamics. We do not attempt to quantitatively reproduce the rates of charge separation in realistic donor-acceptor blends, where a considerable amount of molecular scale structural disorder can be expected to significantly complicate and obscure charge transfer dynamics. Instead, we study a model system that is described by a relatively small number of parameters. These parameters are selected to be of the order of magnitude that is typical for common small molecule photovoltaic materials, such as porphyrins or phthalocyanines and C₆₀ derivatives (e.g., PCBM: [6, 6]-phenyl-C₆₁-butyric acid methyl ester).^{32,33} By varying the parameters in our model, we are able to observe qualitative trends that elucidate some of the factors influencing charge separation dynamics in systems consisting of multiple donor and acceptor molecules. In particular, we observe that the extent of orbital delocalization (determined by the strengths of intermolecular electronic couplings in the system) and the rate of energy dissipation affect charge separation in non-trivial ways. Understanding the complex interplay between these two factors is essential for the optimization of geminate pair formation and dissociation efficiency at the donor-acceptor interface. For very large exciton binding energies, cascade charge separation in systems with more than one donor and one acceptor species, e.g., molecular polyads, is found to greatly facilitate the dissociation of geminate pairs. Our calculations predict charge separation on sub-picosecond timescales for several parameter combinations and hence suggest design principles for enhancing charge separation in multi-chromophore systems.

2 The Model

We consider a one-dimensional system consisting of a stack of N_D electron donors (D) and a stack of N_A electron acceptors (A), separated by a single donor-acceptor interface. In the simplified model presented here, the donors are represented only by their HOMO and LUMO levels (the model can be generalized to more complex level structures). Assuming that excitations are generated in the donors and that hole transfer to acceptors is not allowed, the acceptors can be represented only by their HOMO levels. The total number of possible states for a single electron-hole pair in which both the electron and the hole are localized on individual molecules is then $N = N_D(N_D + N_A)$. All such states are shown by colored lines in Figure 2A for a system with $N_D = N_A = 3$. These states will be used as a basis in the Hilbert space of a single electron-hole pair in the system shown in Figure 2 (henceforth referred to as the “line basis”, $\{|\varphi_n\rangle\}$).

The Hamiltonian of a single electron-hole pair in the “line basis”, $\{|\varphi_n\rangle\}$, can be written as

$$\hat{H} = \sum_{n=0}^{N-1} \varepsilon_n \hat{a}_n^\dagger \hat{a}_n + \sum_{n=0}^{N-1} \sum_{m=n+1}^{N-1} J_{nm} \left(\hat{a}_n^\dagger \hat{a}_m + \hat{a}_n \hat{a}_m^\dagger \right), \quad (1)$$

where ε_n is the energy of state n and J_{nm} is the coupling between states n and m .

In real systems, the parameters ε_n and J_{nm} depend on the structure and geometry of the molecules, intermolecular distances and orientations, as well as on the properties of the environment of the system. In our model we will make the following simplifying assumptions: a) only Frenkel exciton states on nearest neighbor sites, as well as those states that differ by the displacement of either the electron or the hole (but not both particles) by one site are coupled; b) the interaction between the electron and the hole affects the energies of the states m and n , ε_m and ε_n , but not the coupling between these states, J_{nm} ; c) the distance between any nearest-neighbor pair of donor molecules is a_D , the distance between any nearest-neighbor pair of acceptor molecules is a_A , and the distance between the donor and acceptor molecules at the interface is a_{DA} ; d) the relative orientations of two nearest-

Figure 2: A) The system studied consists of six molecules, numbered by Roman numerals: three electron donors (I–III) and three electron acceptors (IV–VI). Black horizontal lines represent the energy levels of isolated molecules: the HOMO and LUMO energies of a single donor are E_D^h and E_D^e , respectively; the LUMO energy of a single acceptor is E_A^e . Possible states for an electron-hole pair are shown by colored lines, with ends connecting the levels where the electron and the hole are localized. The state numbers n (Arabic numerals) are assigned as follows: $n = N_D (n_e - 1) + (n_h - 1)$, where N_D is the total number of donors in the system, n_e and n_h are the molecular site numbers at which the electron and the hole, respectively, are localized. Blue lines indicate Frenkel excitons (states 0, 4, 8), green lines – Wannier excitons (states 1–3, 5–7), magenta lines – charge transfer states (with the electron on an acceptor and the hole on a donor, states 9–17), and the red line indicates the state with maximum electron-hole separation (state 15), considered a “free-charge” state. The dotted line indicates the donor-acceptor interface. B) In two-dimensional space, each state in the “line basis” of panel A can be indicated by a dot whose x -coordinate is the position of the electron and y -coordinate is the position of the hole in real space. The states are numbered and color-coded in the same way as in panel A. States that are represented by neighboring dots along vertical lines interact via hole couplings, J_h (cyan lines). States that are represented by neighboring dots along horizontal lines interact via electron couplings: J_e^D (brown lines) if the electron is on donor molecules for both states, J_e^A (purple lines) if the electron is on acceptor molecules for both states, and J_e^{DA} (black lines) if the electron is on a donor molecule for one state and on an acceptor molecule for the other.

neighbor molecules in the stack of donors or in the stack of acceptors are the same.

With these assumptions, the coupling between states m and n that differ by the displacement of the hole by one site, e.g., states 0 and 1 (or 1 and 2, etc.) in Figure 2, is the hole transfer integral, J_h , between donor molecules. The coupling between states m and n that differ by the displacement of the electron by one site is the electron transfer integral, which can take one of three values:³⁴

- a) J_e^D between two donor molecules, if for both states m and n the electron is localized within the donor material, e.g., for states 0 and 3 (or 3 and 6, etc.) in Figure 2;
- b) J_e^A between two acceptor molecules, if for both states m and n the electron is localized within the acceptor material, e.g., for states 11 and 14 (or 14 and 17, etc.) in Figure 2;
- c) J_e^{DA} between one donor and one acceptor molecule, if for state m the electron is localized in the donor material, but for state n it is localized in the acceptor material, e.g., for states 8 and 11 (or 7 and 10, 6 and 9) in Figure 2.

The coupling between Frenkel exciton states m and n on two nearest-neighbor donor molecules, e.g. states 0 and 4 in Figure 2, is the excitonic coupling, J_{exc} . Figure 2B illustrates the couplings between states of the line basis that are included in our model Hamiltonian, Eq. (1).

The couplings J_h , J_e^D , J_e^A , J_e^{DA} , and J_{exc} can be estimated from *ab initio* electronic structure calculations on pairs of molecules. However, these couplings are highly sensitive to intermolecular distance and relative molecular orientation, and may also be affected by the molecular environment. Thus, molecular-level structural information is required for analyzing charge separation dynamics in a specific system. Since this information is typically not available for systems larger than donor-acceptor dimers, we will not explicitly calculate the couplings for the system shown in Figure 2. Instead, we will vary their values within the range that is typical for common donor-acceptor materials. For π -stacked porphyrin or phthalocyanine derivatives serving as electron donors, the electron and hole couplings, J_e^D and J_h are ~ 0.3 eV at distances $a_D \sim 3.5$ Å,³⁵ while the excitonic couplings, J_{exc} , are two

to three orders of magnitude smaller, $\sim 1 - 10$ meV.³⁶ (It should be noted, however, that J_e^D and J_h decay exponentially with the intermolecular distance a , while J_{exc} only decays as a^{-3} .) For close-packed C₆₀ fullerenes or their derivatives, such as phenyl-C₆₁-butyric acid methyl ester (PCBM), serving as electron acceptors, the electron couplings, $J_e^A \sim 0.125$ eV, and the close-packing distance is $a_A \sim 1.4$ nm.^{37,38} The electronic coupling between a porphyrin (phthalocyanine) and a fullerene molecule lies within the range $J_e^{DA} \sim 0.01 - 0.25$ eV, with the specific value depending on both their center of mass separation and relative orientation.^{39,40}

We shall define the energies, ε_n , of states in the “line basis”, $\{|\varphi_n\rangle\}$, in terms of the excitation energy, E_{exc} , of a donor molecule, the binding energy, E_b , of a Frenkel exciton on a donor molecule (with the convention $E_b > 0$), and the driving energy, ΔE , for electron transfer from a donor to an acceptor. These parameters are related to the energy levels E_D^e , E_D^h , and E_A^e in Figure 2A as follows:

$$E_{\text{exc}} = E_D^e - E_D^h - E_b, \quad (2)$$

$$E_D^e - E_A^e = \Delta E. \quad (3)$$

The excitation spectrum of porphyrins and phthalocyanines lies primarily within the visible and near infrared range,⁴¹ and these molecules are characterized by very large exciton binding energies. For instance, for Q_x excitons in free base porphyrins (excitation energy $E_{\text{exc}} = 2.04$ eV), the binding energy is $E_b = 3.08$ eV.^{13,14} We will set the energy of Frenkel excitons (states 0, 4, 8 in Figure 2) to be E_{exc} , and will estimate the energies of delocalized excited states in the donor material ($n = 1, 2, 3, 5, 6, 7$), i.e., of Wannier excitons, as

$$\varepsilon_n = E_{\text{exc}} + E_b - \frac{e^2}{4\pi\varepsilon_0\varepsilon a_D |n_e - n_h|}, \quad (4)$$

where e is the elementary charge, ε_0 is the vacuum permittivity, ε is the dielectric constant of the material into which our system is embedded, $a_D = 3.5$ Å is the lattice constant of

the donor material, n_e and n_h are molecular site numbers where the electron and the hole, respectively, are localized for state n . If the donor is tetraphenyl-porphyrin and the acceptor is C₆₀, we have $E_{\text{exc}} + E_b = 5.12$ eV.⁴²

Similarly, the energy of charge transfer states ($n=9-17$ in Figure 2) can be estimated as

$$\varepsilon_n = E_{\text{exc}} + E_b - \Delta E - \frac{e^2}{4\pi\varepsilon_0\varepsilon |(n_e - N_D - 1)a_A + a_{DA} + (N_D - n_h)a_D|}, \quad (5)$$

where a_A is the lattice constant of the acceptor material, a_{DA} is the separation between the nearest neighbor donor and acceptor molecules, and $E_{\text{exc}} + E_b - \Delta E$ is the difference between the ionization potential of a donor molecule and the electron affinity of an acceptor molecule. The absolute value term in the denominator gives the distance between the electron and the hole in the charge separated state (see Figure 2). If the donor is tetraphenyl-porphyrin and the acceptor is C₆₀, $E_{\text{exc}} + E_b - \Delta E = 3.59$ eV.⁴²

From Eqs. (2) and (3) it is evident that the approximations for the non-Coulomb terms in Eqs. (4) and (5) are equivalent to those given by Koopman's theorem for the energies of ionic states. In Eq. (4), $E_{\text{exc}} + E_b = E_D^e - E_D^h$ and in Eq. (5), $E_{\text{exc}} + E_b - \Delta E = E_A^e - E_D^h$. These terms approximate the energy of a ground state cation by removing the HOMO energy term, and the ground state anion by adding the LUMO energy term.

Typical dielectric constants of organic materials lie within the range 2 – 3. In Eqs. (4) and (5), we will assume $\varepsilon = 2.5$, the same within the donor and acceptor part of the system. This value gives reasonably good agreement for the binding energy of the lowest energy CT state (state 11 in Figure 2) for supramolecular (tetraphenyl)-porphyrin/C₆₀ dyads with the corresponding value calculated using *ab initio* methods (~ 1.82 eV for $a_{DA} = 3.5$ Å).⁴²

The electronic couplings J_h , J_e^D , J_e^A , J_e^{DA} , excitonic coupling J_{exc} , excitation energy of a donor molecule E_{exc} , binding energy for a Frenkel exciton on a donor molecule E_b , driving energy ΔE , intermolecular distances a_D , a_A , a_{DA} , and dielectric constant ε completely define the Hamiltonian of the system shown in Figure 2. One can now appreciate the complexity

of optimizing charge separation in real multi-chromophore systems. Even within the rather crude approximations that we have made, the Hamiltonian is defined by 12 parameters. In real systems consisting of molecules with more than two energy levels, with a variety of intermolecular spacings, relative molecular orientations, and local dielectric environments, the number of Hamiltonian parameters is increased dramatically.

Although charge and exciton dynamics in pigment-protein complexes are generally non-Markovian,^{20,43–45} a reasonably good description of the overall efficiency of charge and energy transfer can be achieved within the Born and Markov approximations for Hamiltonian and system-environment interaction parameters that are typically encountered in molecular systems where the electronic degrees of freedom interact with the vibrations of the molecular system and its environment.⁴⁶ This leads to a system-bath description in which the environment is described by a thermal bath without memory. Thus, we may then describe the dynamics of excitations in the system by a Lindblad master equation⁴⁷

$$\frac{d\rho}{dt} = -\frac{i}{\hbar} [\hat{H}, \rho] + \sum_{k,l} \lambda_{kl} \left(\hat{L}_{kl} \rho \hat{L}_{kl}^\dagger - \frac{1}{2} \{ \hat{L}_{kl}^\dagger \hat{L}_{kl}, \rho \} \right). \quad (6)$$

Here, ρ is the density operator of the excitation, $\hat{H}$ is its Hamiltonian defined by Eq. (1), $\{\hat{L}_{kl}\}$ may be any set of operators that form an orthonormal basis in the Liouville space of the system described by $\hat{H}$, and $\{\lambda_{kl}\}$ is a set of coefficients that describes the interaction of an excitation in the system with the bath of thermal vibrations. The operators $\{\hat{L}_{kl}\}$ describe the system-bath coupling; the coupling parameter values λ_{kl} are determined by both the properties of the thermal bath and the choice of $\hat{L}_{kl}$.⁴⁸

We write the density operator in the basis of Hamiltonian eigenstates $\{|k\rangle : \hat{H} |k\rangle = E_k |k\rangle\}$:

$$\rho = \sum_{k,l} \rho_{kl} |k\rangle \langle l| \quad (7)$$

and assign $\hat{L}_{kl}$ in Eq. (6) to be transfer operators between states of the same basis:

$$\hat{L}_{kl} = |k\rangle \langle l|, \quad \hat{L}_{kl}^\dagger = |l\rangle \langle k| = \hat{L}_{lk}. \quad (8)$$

The diagonal operators $\hat{L}_{kk}$ do not induce population redistribution among Hamiltonian eigenstates, and thus describe pure dephasing, while the off-diagonal operators $\hat{L}_{kl}, k \neq l$ describe dissipation and energy relaxation processes. Using Eqs. (7) and (8), we can now rewrite Eq. (6) as

$$\frac{d\rho}{dt} = -\frac{i}{\hbar} \sum_{k,l} \rho_{kl} (E_k - E_l) |k\rangle \langle l| + \sum_{k,l} \lambda_{kl} \left[\rho_{ll} (|k\rangle \langle k| - |l\rangle \langle l|) - \frac{1}{2} \sum_{s \neq l} (\rho_{ls} |l\rangle \langle s| + \rho_{sl} |s\rangle \langle l|) \right], \quad (9)$$

where $\rho_{kl} = \rho_{lk}^*$ are elements of the density matrix.

The first sum on the right hand side of Eq. (9) describes the unitary evolution of the system with Hamiltonian $\hat{H}$. In the basis of Hamiltonian eigenstates, this term clearly does not affect state populations, ρ_{kk} . The second sum on the right hand side of Eq. (9) describes the effects of the vibrational environment on the state populations (first term in the square brackets) and coherences (second term in the square brackets). Since $\text{Tr } \rho$ must be conserved, $0 \leq \lambda_{kl} dt \leq 1$ is the conditional probability of incoherent transfer to state $|k\rangle$ if the system is initially in state $|l\rangle$, for $l \neq k$. For $l = k$, the first term in the square brackets is zero and no redistribution of the state populations occurs: only the coherences in the density operator ρ are affected. This implies the normalization condition

$$P(l, dt) + dt \sum_{k \neq l} \lambda_{kl} = 1, \quad (10)$$

where $P(l, dt)$ is the probability that the system has not left state $|l\rangle$ within the time interval dt . By the standard definition of the the inverse lifetime ν_l of state $|l\rangle$, $P(l, dt) = \exp(-\nu_l dt) = 1 - \nu_l dt + O(\nu_l^2 dt^2)$. Since $dt \rightarrow 0$, $\nu_l dt \ll 1$ for any value of ν_l , and higher order terms in the Taylor expansion of $P(l, dt)$ can be omitted: $P(l, dt) \approx 1 - \nu_l dt$. Introducing

this expression into Eq. (10), allows us to rewrite the normalization condition, Eq. (10), in the form:

$$\sum_{k \neq l} \lambda_{kl} \approx \nu_l. \quad (11)$$

To completely define our dynamics model we must select the decoherence parameters λ_{kl} , i.e., the dissipative parameters ($k \neq l$) and the pure dephasing parameters ($k = l$). These parameters are generally determined by the spectral density of the vibrational environment.^{49–51} The requisite spectral density may be relatively complicated, especially since the states of the “line basis”, $\{|\varphi_n\rangle\}$, are delocalized, so that the electron and hole may not experience the same vibrational environment. In our simulations we will neglect the microscopic details of the thermal bath, and will only impose the requirement that at $t \rightarrow \infty$ the system should be thermalized. This can be easily achieved in the basis of Hamiltonian eigenstates, independently of the pure dephasing parameters λ_{kk} , by setting $\lambda_{kl}, l \neq k$, for the transition from state $|l\rangle$ to $|k\rangle$ to be of Miller-Abrahams form:⁵²

$$\lambda_{kl} = \begin{cases} \frac{\nu f(R_{kl})}{Z}, & E_l > E_k, \\ \frac{\nu f(R_{kl})}{Z} \exp\left(\frac{E_l - E_k}{k_B T}\right), & E_l < E_k, \end{cases} \quad (12)$$

Here, E_l and E_k are the energies of the initial and final Hamiltonian eigenstates $|l\rangle$ and $|k\rangle$, respectively, ν is the thermalization rate (the inverse lifetime ν_l of the initial state $|l\rangle$, assumed to be the same for all states), k_B is the Boltzmann constant, and T is the temperature. The function $f(R_{kl})$ imposes a spatial proximity dependence on the hopping rates between Hamiltonian eigenstates $|l\rangle$ and $|k\rangle$, and Z enforces normalization for the total probability of transfer from each initial state $|l\rangle$ to all possible final states that is required by Eq. (11). Eq. (12) uses an adaptation of the Miller-Abrahams expression for vibration-assisted tunneling to a vibration-assisted hopping between eigenstates $|k\rangle$ that is enhanced by delocalization, where the factor $\frac{\nu N f(R_{kl})}{Z}$ replaces the tunneling enhanced hopping of Ref. 52.

Before moving on to discuss the pure dephasing terms λ_{kk} , we first analyze the quantity $f(R_{kl})$ in more detail. This function is used to introduce a dependence of hopping rates between Hamiltonian eigenstates $|l\rangle$ and $|k\rangle$ on some measure R_{kl} of the spatial proximity between these states. If $f(R_{kl}) \equiv 1$ is assumed, the hopping rates given by Eq. (12) depend only on the energy difference $E_l - E_k$. However, the spatial localization of states $|l\rangle$ and $|k\rangle$, as well as their overlap, can also be expected to affect the transfer efficiency between them. Thus, we need some measure of the distance between a pair of states that explicitly takes the spatial extent and overlap of the states into account. We note that this distance should not be defined in terms of a distinguishability measure, since $|l\rangle$ and $|k\rangle$ are Hamiltonian eigenstates and are thus always orthogonal if they do not correspond to a degenerate eigenvalue, while they can be selected to be orthogonal if they do. Thus, $|l\rangle\langle l|$ and $|k\rangle\langle k|$ are maximally distinguishable and the trace norm distance between them is $\delta(|k\rangle\langle k|, |l\rangle\langle l|) = 0.5 \text{Tr} \, ||k\rangle\langle k| - |l\rangle\langle l|| \equiv 1$,⁵³ independent of their spatial separation. For our simulations we will instead assume that the rate of transfer between two Hamiltonian eigenstates is proportional to the pointwise density overlap between these eigenstates in the “line basis”, $\{|\varphi_n\rangle\}$:

$$f(R_{kl}) = R_{kl} = 1 - 0.5 \sum_n |c_{nk}^* c_{nk} - c_{nl}^* c_{nl}|, \quad (13)$$

where $|k\rangle = \sum_n c_{nk} |\varphi_n\rangle$, $|l\rangle = \sum_n c_{nl} |\varphi_n\rangle$. Eq. (13) satisfies $0 \leq R_{kl} \leq 1$; it becomes zero if there is no overlap between states $|k\rangle$ and $|l\rangle$ and is equal to one if these states are identical. This definition ensures that the rate of transfer between two Hamiltonian eigenstates is larger when such transfer requires less redistribution of population among states in the “line basis”. Alternative measures of the spatial proximity between states $|k\rangle$ and $|l\rangle$ can be defined;⁵⁴ simulations using such measures show the same qualitative trends and reasonably good quantitative agreement with those based on Eq. (13) (see Supporting Information).

Eqs. (12), (11), and (13) define the off-diagonal coupling parameters λ_{kl} with $l \neq k$ in

terms of a single independent parameter, ν , that characterizes the rate of energy dissipation in the system studied. The rate of energy dissipation, ν , can be selected so as to reproduce the typical timescale on which wavefunction coherence is known to survive in excitonic systems: $\sim 10^{-13} - 10^{-12}$ s.^{20,43,44} This corresponds to $\nu \sim 10^{13} - 10^{14}$. (Since simulations based on second-order Markovian master equations are known to underestimate the timescale of coherence survival,^{20,43,44} the upper bound, $\nu \sim 10^{14}$, is likely the better estimate.) We shall assume that the pure dephasing of the excited state wavefunction can be similarly characterized by a single parameter: $\lambda_l = \nu_{\text{deph}}$, for all l . In fact, our simulations show that the efficiency of charge separation is primarily determined by the rate of energy dissipation; the effect of pure dephasing is small for a wide range of ν_{deph} , including $\nu_{\text{deph}} \gg \nu$ (see Appendix). We will therefore assume $\nu_{\text{deph}} = 0$ for all simulations presented in this paper.

To ensure efficient removal of charges from the system once the “free-charge” state (state 15 in Figure 2) is reached, an imaginary constant, $-i\hbar/\tau$, is added to the energy of that state, where τ represents the free charge state lifetime. The value of τ is chosen to be small enough to remove most of the population that reaches the “free-charge” state and large enough so that the structure of the Hamiltonian eigenstates does not change significantly (i.e., $\text{Re } \hat{H} \gg \text{Im } \hat{H}$).^{55,56} This ensures that τ has little effect on the rate of charge removal from the system. In this work the value $\tau = 5$ fs was employed.

3 Results and Discussion

Using the model described in Section 2, we have simulated the dynamics of an excited state in the system shown in Figure 2. An exciton is initially created in state 0 (the Frenkel exciton state in the donor material that is furthest from the donor-acceptor interface). Exciton and hole transfer within the donor material, as well as electron transfer within the donor and acceptor materials, and across the donor-acceptor interface, are allowed and described within a common framework. The efficiency of charge separation is determined by the rate

at which the “free charge” state (state 15 in Figure 2) is reached and the charges are removed from the system. Faster decay of the total population of all states in the system, plotted in Figures 3–6 by red lines, corresponds to more efficient charge separation.

The Hamiltonian and energy dissipation parameters used for the simulations presented in this section are set to values that are typical for organic photovoltaic materials (see Section 2) and then modified so as to achieve enhanced charge separation. For all simulations in this paper, we set $a_D = 0.35$ nm, $a_A = 1.4$ nm, $E_{\text{exc}} = 2.040$ eV, $J_{\text{exc}} = 0.010$ eV, $\varepsilon = 2.5$ (see Section 2 for detailed discussion of these parameters). The remaining parameters are varied and their values are specified at the beginning of each subsection.

3.1 Role of Orbital Delocalization within the Donor and Acceptor Materials

Table 1: Hamiltonian parameters for charge separation calculations of Figure 3.

Figure	$J_h = J_e^D$ (eV)	J_e^A (eV)	a_{DA} (nm)
2A	0.300	0.125	2.200
2B	0.300	0.125	0.350
2C	0.200	0.125	0.350
2D	0.200	0.500	0.350
2E	0.200	1.000	0.350
2F	0.200	1.500	0.350

For all simulations in Section 3.1, $E_b = 3.080$ eV, $J_e^{DA} = 0.020$ eV, $\Delta E = 1.530$ eV. Parameter values that differ from those in row 2A are shown in bold.

Table 1 shows the Hamiltonian parameters that were used for the simulations presented in Section 3.1. We start with row 2A, which contains typical parameter values for systems

consisting of porphyrin or phthalocyanine donors and C₆₀ derivative acceptors, taken from the literature and discussed in Section 2. The corresponding time-dependent state populations are shown in Figure 3A.

For the parameters taken from row 2A of Table 1, the lowest energy states in the “line basis” shown in Figure 2 are Frenkel exciton states in the donor material (states 0, 4, and 8): their energy is $E_{\text{exc}} = 2.040$ eV. The energy of the lowest charge transfer state (state 11), calculated according to Eq. (5), is significantly higher: 3.328 eV. The electron and hole couplings within the donor material, J_e^D and J_h , respectively, and the electron coupling within the acceptor material, J_e^A , significantly exceed the electron coupling between the donor and acceptor molecules at the interface, $J_e^{DA} = 0.020$ eV. It is therefore expected that the eigenstates of the system will be primarily composed either of localized and delocalized excited states within the donor material (states 0–8 in Figure 2), or of charge transfer states (states 9–17 in Figure 2), with a comparatively small contribution from states of the other type. Since the energy of Frenkel exciton states in the donor material is considerably smaller than for all other states in the system, one can anticipate that after thermalization, most of the charge density will end up in one or more eigenstates with significant contributions of Frenkel exciton character. By contrast, the population of eigenstates with charge transfer character is expected to be small in thermal equilibrium. Indeed, Figure 3A shows that, although population is redistributed among excitonic states in the donor material (e.g., the population of the initial state, 0, indicated by the orange line, decreases over time, with some coherent oscillations within the first picosecond), the total population of all charge transfer states (green line) remains negligible throughout the simulation. Consequently, the probability of exciton dissociation into free charges that are subsequently extracted from the system is very small: this is reflected by the total population of all states in the system (red line) remaining close to unity at all times during the simulation of Figure 3A.

The high energy of the lowest charge transfer state (state 11 in Figure 2) relative to the Frenkel exciton states (states 0, 4, and 8) that we have found for the parameters in row

2A of Table 1 can be explained as follows. Since the binding energy, E_b , for an exciton on a single donor molecule is greater than the driving energy, ΔE , for electron transfer from the donor to the acceptor, for a sufficiently large spatial separation between the donor and the acceptor, the energy that is necessary to overcome the Coulomb attraction between the electron and hole becomes larger than ΔE . Using Eq. (5), the maximum distance at which charge separation in a donor-acceptor dimer is still favorable can be calculated as

$$a_{\text{DA}}^{\text{max}} = \frac{e^2}{4\varepsilon_0\varepsilon(E_b - \Delta E)}.$$

For $E_b = 3.080$ eV, $\Delta E = 1.530$ eV, and $\varepsilon = 2.5$, we find $a_{\text{DA}}^{\text{max}} = 1.166$ nm. Since the value $a_{\text{DA}} = 2.200$ nm that we used exceeds $a_{\text{DA}}^{\text{max}}$, charge separation is not energetically favorable.

The van der Waals distance for a porphyrin- C_{60} dyad is 6.7 Å, but due to polarization, the effective separation of the electron and hole in a charge transfer state can be significantly smaller, e.g., ~ 3.5 Å.⁴² For our second calculation, we therefore reset a_{DA} to 3.5 Å, without modifying the other parameters (see Table 1, row 2B). The corresponding time-dependent state populations are shown in Figure 3B. Now, the energy of the lowest charge transfer state (state 11 in Figure 2), calculated according to Eq. (5), is 1.944 eV. This is the “line basis” state with the lowest energy: lower than the Frenkel exciton energy $E_{\text{exc}} = 2.040$ eV. One might expect that charge separation should now become energetically favorable. However, Figure 3B shows that at all times during the simulation most of the population remains in excitonic states (blue line). Furthermore, the only charge transfer state that acquires a non-negligible population is the lowest energy state (state 11 in Figure 2). This state describes what is known as a “geminate pair”, a charge transfer state with significant Coulomb interaction between the electron and hole.⁵⁷ Its population, shown by the cyan line in Figure 3B, accounts for nearly all of the total charge transfer state population (green line). Almost no population is transferred to the “free charge” state (state 15 in Figure 2), and thus again no charge extraction from the system occurs and the total population of all states in the system

remains close to unity (red line).

The origin of this behavior can be elucidated by diagonalization of the system Hamiltonian. The two lowest eigenstates are found to have energies $E_0 = 1.730$ and $E_1 = 1.824$ eV, respectively. When expanded in the “line basis”, the lowest energy eigenstate turns out to be composed almost exclusively (99.2%) of excitonic states in the donor material (states 0–8 in Figure 2). The second lowest eigenstate is composed predominantly (97.2%) of charge transfer states (states 9–17 in Figure 2), with 84.8% accounted for by the lowest energy charge transfer state (state 11). The ratio between the equilibrium populations of the two lowest Hamiltonian eigenstates is given by the Boltzmann factor $\exp[-(E_1 - E_0)/k_B T] \approx 2.3 \cdot 10^{-2}$ at $T = 293$ K, with higher energy eigenstates having still smaller populations. Thus, although the lowest energy state in the “line basis” is a charge transfer state (state 11 in Figure 2), the relatively small difference between its energy (1.944 eV) and the energy of the Frenkel exciton states ($E_{\text{exc}} = 2.040$ eV), as well as the large electron and hole couplings between donor molecules, lead to the lowest energy Hamiltonian eigenstate – the only state with significant equilibrium population – being composed mostly of excitonic states localized within the donor material.

Charge separation can be made energetically favorable in this system by *reducing* the electron and hole couplings between donor molecules, J_e^D and J_h . This can be achieved, for instance, by modifying saturated side chains on the donor molecules in order to change the equilibrium angle of in-plane rotation between neighboring molecules in a stack that strongly affects the electronic couplings between them.⁵⁸ (Modifying saturated side chains usually has little effect on the electronic structure of the energy levels that contribute to charge transfer, so other Hamiltonian parameters will be virtually unchanged.) In row 2C of Table 1, we reduce $J_e^D = J_h$ to 0.200 eV; the corresponding time-dependent state populations are shown in Figure 3C.

For the parameters in row 2C of Table 1, the two lowest Hamiltonian eigenvalues are $E_0 = 1.878$ and $E_1 = 1.901$ eV. In the “line basis”, the lowest energy eigenstate is composed

of 84.4% charge transfer states (states 9–17 in Figure 2) and 15.6% excitonic states in the donor material (states 0–8 in Figure 2). The second-lowest energy eigenstate is composed of 86.8% excitonic states in the donor material (states 0–8 in Figure 2) and 13.2% charge transfer states (states 9–17 in Figure 2). Figure 3C shows that in thermal equilibrium the total population of charge transfer states (green line) exceeds the total population of excitonic states in the donor material (blue line). Since the energy difference between the two lowest Hamiltonian eigenstates ($E_1 - E_0 \approx k_B T \approx 0.025$ eV at 293 K, both of these eigenstates have appreciable equilibrium populations. However, the equilibrium populations can be shifted further towards charge transfer states, e.g., by further reducing the couplings J_e^D and J_h .

Although Figure 3C shows that electron transfer from the donor to the acceptor material is achieved for the parameters in row 2C of Table 1, the electron and hole in the charge transfer state still form a geminate pair that is effectively trapped at the donor-acceptor interface. This is evident from the fact that most of the population in the charge transfer states (green line in Figure 3C) is trapped in the lowest-energy “line basis” state, state 11 in Figure 2 (cyan line in Figure 3C). The “free charge” state (state 15 in Figure 2) is not reached, and thus the efficiency of geminate pair dissociation into free charges is very small. This is reflected in the total population of all states (red line in Figure 3C) again remaining close to unity throughout the simulation.

The reason for the electron and hole becoming trapped at the donor-acceptor interface in this case, is that the single most important contribution to the lowest energy eigenstate, 78.8%, comes from the lowest energy charge transfer state in the “line basis” (state 11 in Figure 2). We have seen that the energy of this state, calculated according to Eq. (5), is 1.944 eV, significantly smaller than the energy of the “free charge” state (state 15 in Figure 2), which is 3.440 eV. Therefore, to reach the “free charge” state, an electron-hole pair in the lowest energy charge transfer state must overcome a potential barrier that significantly exceeds the thermal energy at 293 K.

Incoherent hopping of electrons and holes is not an efficient mechanism for overcoming the large Coulomb binding energy in a geminate pair. However, the efficiency of geminate pair dissociation can be enhanced by coherent charge transfer away from the donor-acceptor interface via delocalized orbitals in the acceptor material. Orbital delocalization is achieved by increasing the coupling J_e^A between acceptor molecules. Figures 3D and 3E show the results of charge transfer simulations with J_e^A increased to 0.500 eV and 1.000 eV, respectively (see rows 2D and 2E of Table 1). We find that charge extraction from the system is now enhanced for these larger coupling values, reflected in the faster decay of the total population (red line).

While orbital delocalization due to large J_e^A promotes coherent electron transfer within the acceptor material, it also has one other important consequence. This is that there is a reduction in the spatial proximity of extended orbitals that are composed primarily of charge transfer states in the “line basis” to orbitals that are composed primarily of excitonic states within the donor material. Within our model, where the rate of incoherent hopping between two orbitals $|k\rangle$ and $|l\rangle$ of the system is a function of their spatial proximity R_{kl} , this leads to less efficient energy dissipation. The result is the slower growth of the total population of all charge transfer states (green line) that is seen as J_e^A is increased from 0.125 eV (Figure 3C), to 0.500 eV (Figure 3D), to 1.000 eV (Figure 3E).⁵⁹

The fact that increasing the electron coupling J_e^A between acceptor molecules enhances population transfer between different charge transfer states, but slows down thermalization – the process that is responsible for population transfer from excitonic to charge transfer states, gives rise to an optimal balancing value that may be termed a quantum Goldilocks effect.⁶⁰ If J_e^A is too small, an electron may be transferred from the donor to the acceptor efficiently, but its Coulomb interaction with the hole that remains on the donor leads to the formation of a geminate pair (state 11 in Figure 2) that does not dissociate into free charges. On the other hand, if J_e^A is too large, coherent evolution allows the electron to escape from the donor-acceptor interface via delocalized orbitals in the acceptor material, but incoherent electron

transfer to these delocalized orbitals is hindered by their small spatial overlap with excitonic states in the donor material. Consequently, although geminate pairs dissociate quickly, electron transfer from the donor to the acceptor that leads to their formation becomes the bottleneck for charge separation. For instance, if J_e^A is increased to 1.500 eV (see row 2F of Table 1), charge separation in the system studied is effectively suppressed (Figure 3F). Thus, an optimal balance between coherent and incoherent terms in the master equation, Eq. (9), that achieves similarity of timescales for charge transfer from the donor to the acceptor and for the dissociation of geminate pairs into free charges, will allow the most efficient charge separation to be achieved. Unfortunately, for large values of the binding energy, E_b , the electron couplings, J_e^A , between acceptor molecules that are necessary to significantly enhance charge extraction may be very large. We have seen that for systems described by parameters in rows 2D–2F of Table 1, optimal charge separation is expected somewhere within the range $J_e^A = 0.5 - 1.5$ eV. Couplings of this magnitude may be difficult to achieve in molecular materials.

3.2 Decreasing the Binding Energy

We now consider possible strategies for optimizing charge separation in the system shown in Figure 2, given the features displayed in Figure 3 and discussed above. Since a large binding energy, E_b , for excitons in the donor material hinders charge separation, reducing this parameter is one straightforward solution. Figure 4 shows the results of a charge separation simulation with the same Hamiltonian parameters that have been used for the simulation whose results are shown in Figure 3C, except for the binding energy, E_b , that has been reduced from 3.080 to 0.600 eV (approximately fivefold). It is evident that as the energy dissipation rate, ν , is increased from 0 (Figure 4A), to 10^{13} s^{-1} (Figure 4B), to the realistic value of 10^{14} s^{-1} (Figure 4C), charge extraction from the system quickly becomes significantly more efficient than that seen in Figure 3C. Because increasing ν accelerates energy dissipation in the system, we can conclude that the rate of charge extraction is limited in the present case

Figure 3: The results of charge separation simulations with Hamiltonian parameters taken from rows 2A–2F of Table 1 and energy dissipation rate $\nu = 10^{14} \text{ s}^{-1}$. Panel labels in the figure correspond to row labels in the table. Red line – total population of all sites in the system, blue line – total population of all excitonic states in the donor material (states 0–8 in the “line basis” of Figure 2), green line – total population of all charge transfer states (states 9–17 in the “line basis” of Figure 2), cyan line – population of the lowest energy charge transfer state (state 11 in the “line basis” of Figure 2), orange line – population of the initial excitonic state (state 0 in the “line basis” of Figure 2).

by the rate of charge transfer state formation, rather than by the rate of charge removal from the donor-acceptor interface (geminate pair dissociation). This conclusion is confirmed by considering the total population of all excitonic states within the donor material (states 0–8 in Figure 2), shown by the blue lines. For Figures 4A–C, most of the population in the system resides in the excitonic states within the donor materials throughout the simulation (blue line), with only a relatively small fraction of the population (green line) residing in charge transfer states. Thus, the bound electron-hole pair quickly dissociates into free charges once charge transfer states are formed. Only for very large ν values does the rate of geminate pair dissociation become the limiting factor for charge separation. For $\nu = 10^{15} \text{ s}^{-1}$ (Figure 4D), most of the population quickly moves into charge transfer states (states 9–17 in Figure 2), and the rate of charge extraction from the system is thereafter determined by the rate at which the “free charge” state (state 15 in Figure 2) is reached. We have seen above that the escape of charges from the donor-acceptor interface is achieved primarily by means of coherent evolution of the system density operator. Thus, further accelerating thermalization (increasing ν beyond 10^{-15} s^{-1}) would suppress, rather than enhance, charge extraction from the system.

Lower binding energies can be achieved by using materials with extended molecular orbitals. For instance, the exciton binding energy for an ethylene-bridged porphyrin dimer is 2.10 eV, down from 3.08 eV for a monomer.¹³ In fact, extremely low binding energies could be achieved by using highly polarizable “giant orbital materials”, such as highly conjugated polymers.⁶¹ Yet, increasing intramolecular electronic couplings also reduces the material’s bandgap, pushing the LUMO energy down and the HOMO energy up. This means that the driving energy for electron transfer from a porphyrin dimer to a C_{60} molecule is smaller than for electron transfer from a porphyrin monomer by approximately 0.8 eV.¹³ Enhanced absorption intensity to the Q-band for dimers relative to monomers¹³ could partially compensate for lower exciton dissociation efficiency. However, we have seen above that too much orbital delocalization in the donor material can lead to charge separation becoming ener-

getically unfavorable because of the reduced bandgap of that material (see Figure 3B). The lower bandgap can disqualify some dimers or higher oligomers from use as electron donors, although this is by no means a universal concern: after all, conjugated polymers are among the most popular materials encountered in organic photovoltaics.⁶² In fact, for polymers that consist of small monomer units with absorption shifted towards the ultraviolet range of the spectrum (such as phenylene or thiophene), the lower bandgap of the polymer is essential, since it ensures absorption of visible light while also reducing the exciton binding energy.

Figure 4: The results of charge separation simulations with the same Hamiltonian parameters as for Figure 3C, except for the binding energy, E_b , that has been reduced from 3.080 to 0.600 eV. The energy dissipation rates are $\nu = 0$ (A), $\nu = 10^{13}$ s⁻¹ (B), $\nu = 10^{14}$ s⁻¹ (C), and $\nu = 10^{15}$ s⁻¹ (D). Red line – total population of all sites in the system, blue line – total population of all excitonic states in the donor material (states 0–8 in the “line basis” of Figure 2), green line – total population of all charge transfer states (states 9–17 in the “line basis” of Figure 2), cyan line – population of the lowest energy charge transfer state (state 11 in the “line basis” of Figure 2), orange line – population of the initial excitonic state (state 0 in the “line basis” of Figure 2).

3.3 Increasing the Coupling between Excitonic and Charge Transfer States

Another possible strategy for enhancing charge separation in multi-chromophore donor-acceptor systems would be to design the system in such a way that an exciton in the donor material could be converted to free charges by coherent evolution of the system density operator alone, with little need for energy dissipation. For this to happen, electrons and holes in such materials would need to quickly delocalize within spatially extended orbitals before recombination can occur. In terms of the model system studied (Figure 2), this would require excitonic states in the donor material, particularly the initial state (state 0 in Figure 2), to be directly coupled to the “free-charge” state (state 15 in Figure 2). To ensure this, it is necessary to increase the electron coupling J_e^{DA} between the donor and acceptor molecules at the interface, as well as the couplings within the donor and acceptor materials.

Figure 5A shows the results of a charge separation simulation with the same parameters that were used for Figure 3D, except for the coupling J_e^{DA} , which was increased from 0.02 to 0.2 eV. Note that J_e^{DA} only couples excitonic states in the “line basis” with the electron localized on site III (states 6–8 in Figure 2) to states with unchanged localization of the hole, but with the electron transferred to site IV (states 9–11 in Figure 2). Thus, to ensure that the states 0 and 15 in Figure 2 are directly coupled (i.e., that there is at least one Hamiltonian eigenstate to which both of these states contribute non-negligibly), relatively large electron and hole couplings within the donor and acceptor materials are also required. When the electron couplings within the acceptor material is $J_e^{\text{A}} = 0.5$ eV (Figure 5A), a tenfold increase in the donor-acceptor coupling, J_e^{DA} , results in only a small enhancement for the efficiency of exciton dissociation into free charges: compare the total population of all states (red line) in Figures 3D and 5A. This is because excitonic states in the donor material are directly coupled to bound charge transfer states, but not to the “free charge” state (state 15 in Figure 2). Thus, the increased coupling J_e^{DA} does not significantly enhance exciton dissociation: in fact, for some combinations of coupling J_e^{D} and J_e^{A} values it could

even make charge separation less efficient by facilitating coherent back transfer of electrons from the acceptor to the donor material.

Increasing the electron coupling between a donor and an acceptor molecule, J_e^{DA} , from 0.02 to 0.2 eV for larger values of the electron coupling within the acceptor material, e.g. $J_e^{\text{A}} = 1.000$ eV, changes the characteristics of the charge separation process significantly. The results of simulations with the same Hamiltonian parameters that were used for Figure 3E, except for a tenfold increased coupling $J_e^{\text{DA}} = 0.2$ eV, are shown in Figures 5B–D. From these figures it is evident that the decay of the total population in all system states as a function of time acquires a pronounced dependence on the energy dissipation rate ν . When $\nu = 0$ (Figure 5B), the total population of all states (red line) decays quickly within the first picosecond following the creation of an excitation in state 0 (Figure 2), but then reaches a constant non-zero value. As ν is increased to 10^{13} s^{-1} (Figure 5C), and then to 10^{14} s^{-1} (Figure 5D), the duration of the initial fast decrease of the total population of all states (red line) is reduced, but a slower non-zero decrease is observed at longer times. For all three ν values, the efficiency of charge separation in the first few picoseconds significantly exceeds that seen for $J_e^{\text{DA}} = 0.02$ eV with all other parameters unchanged that is shown in Figure 3E.

To understand this behavior, recall that the eigenstates $|k\rangle$ and $|l\rangle$ of the system Hamiltonian are orthogonal for $k \neq l$. Thus, in the absence of energy dissipation, the populations of these eigenstates evolve independently,

$$\rho_{kk}(t) = \rho_{kk}(0) \exp\left(2\frac{\text{Im } E_k}{\hbar}t\right), \quad (14)$$

where ρ_{kk} is the population of state $|k\rangle$ (see Eq. 7) and E_k is the Hamiltonian eigenvalue that corresponds to eigenvector $|k\rangle$. The imaginary component of the eigenstate energy, $\text{Im } E_k$, derives from the small imaginary constant, $-i\hbar/\tau$, that was added to the diagonal Hamiltonian term corresponding to the energy of the “free charge” state $|\varphi_{15}\rangle$ (state 15 in Figure 2), as described in Section 2. This term ensures efficient removal of charges

from the system once the state $|\varphi_{15}\rangle$ is reached.⁵⁶ Since the non-Hermitian character of the Hamiltonian arises from a single term corresponding to $|\varphi_{15}\rangle$, the Hamiltonian eigenvectors with the largest contributions of that state to their “line basis” expansion correspond to the largest $|\text{Im } E_k|$ values. Since for $\tau > 0$, $\text{Im } E_k < 0$, according to Eq. (14), the population decay for the eigenstates with the largest $|\text{Im } E_k|$ values (largest contribution of the “free charge” state $|\varphi_{15}\rangle$) occurs with the highest rate.

We now consider the expansion of the system Hamiltonian eigenstates in the “line basis”, $\{|\varphi_n\rangle\}$: $|k\rangle = \sum_n c_{n,k} |\varphi_n\rangle$. For the Hamiltonian parameters used for the simulations presented in Figures 5B–D, the initial excitonic state, $|\varphi_0\rangle$ (state 0 in Figure 2), contributes significantly (more than 1%) to the expansions of the second ($|c_{0,2}|^2 = 0.150$), third ($|c_{0,3}|^2 = 0.439$), fourth ($|c_{0,4}|^2 = 0.304$), fifth ($|c_{0,5}|^2 = 0.074$), and eleventh ($|c_{0,11}|^2 = 0.031$) excited eigenstates of the system Hamiltonian. At $t = 0$, 99.8% of the total population in the system resides in these five eigenstates. Three of them also have a sizable contribution (more than 1%) from the “free charge” state, $|\varphi_{15}\rangle$ (state 15 in Figure 2): the third ($|c_{15,3}|^2 = 0.017$), fourth ($|c_{15,4}|^2 = 0.061$), and fifth ($|c_{15,5}|^2 = 0.036$) excited eigenstates. Together, these three eigenstates account for 81.7% of the system’s total population at $t = 0$, but their populations decay rapidly due to the relatively large contributions of the “free charge” state.

For $\nu = 0$, no population redistribution among eigenstates occurs. At times $t > 1$ ps, after the population of the third, fourth, and fifth excited Hamiltonian eigenstates has decayed almost completely (and thus the total population has decayed by $> 80\%$), most of the remaining population resides in the second ($|c_{0,2}|^2 = 0.150$) and eleventh ($|c_{0,11}|^2 = 0.031$) excited eigenstates. These eigenstates have a considerably smaller contribution of the “free charge” state, $|\varphi_{15}\rangle$, in their “line basis” expansion: particularly the second excited eigenstate, for which $|c_{15,2}|^2 = 9.5 \cdot 10^{-6}$. Consequently, for $\nu = 0$ there is very little charge extraction from the system at longer times (Figure 5B). As ν is increased to 10^{13} and then to 10^{14} s^{-1} , population redistribution among Hamiltonian eigenstates becomes allowed. We

observe that even the lowest excited eigenstate of the system Hamiltonian is higher in energy than the Hamiltonian ground state by $0.468 \text{ eV} \gg k_B T = 0.025 \text{ eV}$ at $T = 293 \text{ K}$. Thus, in thermal equilibrium, the population is overwhelmingly found in the ground state. Since the contribution of the “free charge” state to the Hamiltonian ground state is relatively small ($|c_{15,0}|^2 = 1.68 \cdot 10^{-3}$), if the population is moved here from the third, fourth, and fifth excited states before it is extracted from the system, the rate of charge extraction is reduced. We see this effect in Figures 5C and 5D for $t < 1 \text{ ps}$. However, at longer times, population transfer from states that show very little decay, primarily from the second excited state, to the ground state leads to enhanced charge extraction from the system. This can be seen in Figures 5C and 5D for $t > 1 \text{ ps}$. We thus conclude that energy dissipation may hinder charge separation across long distances on short timescales, but enhance it on longer timescales.

The simulations discussed in this section show that if the electron coupling between the donor and acceptor molecules at the interface, as well as the electron and hole couplings within the donor and acceptor materials, are sufficiently large, charge separation can be enhanced due to coherent electron and hole delocalization within the Hamiltonian eigenstates (orbitals) of the system. However, only some of the system orbitals effectively couple the initial excitonic state (state 0 in Figure 2) to the “free charge” state (state 15 in Figure 2). Consequently, energy dissipation suppresses exciton dissociation that results from coherent charge delocalization if the contribution of the “free charge” state to the system orbitals with the highest thermal populations is smaller than to the orbitals into which the exciton is placed initially, and enhances exciton dissociation otherwise. For our initial excitonic state that is a coherent superposition of Hamiltonian eigenstates, the increase of the energy dissipation rate, ν , leads to the suppression of ultrafast exciton dissociation and the enhancement of exciton dissociation on timescales above 1 ps that is seen in Figures 5B–D.

Figure 5: The results of charge separation simulations with the same Hamiltonian parameters as for Figure 3D (A) or 3E (B–D), except for the donor-acceptor electronic coupling, J_e^{DA} , that has been increased from 0.020 to 0.200 eV. The energy dissipation rates are $\nu = 10^{14} \text{ s}^{-1}$ (A), $\nu = 0$ (B), $\nu = 10^{13} \text{ s}^{-1}$ (C), and $\nu = 10^{14} \text{ s}^{-1}$ (D). Red line – total population of all sites in the system, blue line – total population of all excitonic states in the donor material (states 0–8 in the “line basis” of Figure 2), green line – total population of all charge transfer states (states 9–17 in the “line basis” of Figure 2), cyan line – population of the lowest energy charge transfer state (state 11 in the “line basis” of Figure 2), orange line – population of the initial excitonic state (state 0 in the “line basis” of Figure 2).

3.4 Cascade Charge Separation in Molecular Triads

For some of the Hamiltonian parameter sets considered in Sections 3.1–3.3 we have seen relatively efficient long-distance charge separation (see Figures 3E, 4C–D, 5C–D). This occurred for cases where some of the couplings (particularly J_e^A) have values comparable with the exciton binding energy, E_b . Thus, to optimize charge separation in the system shown in Figure 2, it is necessary to either increase the intermolecular couplings to very large values (Figures 3E, 5C–D) or significantly reduce the exciton binding energy (Figures 4C–D). In practice, achieving these parameter values may not be easy. Therefore, we now consider how the system studied can be modified so that charge separation becomes efficient for typical parameter values, such as those in rows 2A–2C of Table 1.

One possible modification involves using two acceptor materials with different LUMO levels in the arrangement shown in Figure 6A. This ensures that the electron is always moving downhill in energy, or at least that the energy barrier that it has to overcome in order to leave the interface between the donor and the acceptor A_1 is reduced. Assume that the two acceptor species, A_1 and A_2 , are identical in all respects, except for their LUMO energies. Then, we can calculate the Hamiltonian as described in Section 2 using the same parameters as for Figure 3C, with no distinction between the two acceptor species, except for keeping the driving energy $\Delta E = 1.530$ eV for material A_1 , but increasing it to, e.g., 2.530 eV, for material A_2 . Figures 6B and 6C show the results of charge transfer simulations with this parameter set, for $\nu = 10^{13}$ and $\nu = 10^{14}$ s $^{-1}$, respectively. It is evident that the efficiency of charge extraction from the system significantly exceeds that found when all acceptor molecules are identical (Figure 3C). We also see that increasing the energy dissipation rate, ν , reduces the rate of charge separation at short times, but increases it at long times, for the same reasons that we discussed when considering Figures 5B–D.

Introducing a second acceptor material into the system is significantly more effective than simply increasing the driving energy ΔE . In the latter case, the electron-hole distance in the geminate pair is unaffected, and the charges still need to climb a high potential barrier

to escape from the donor-acceptor interface. On the other hand, in the former case, the driving energy difference between the two acceptor species makes it energetically favorable for the electron in the geminate pair to move further away from the donor. Geminate pair dissociation can also be enhanced by introducing a hole acceptor that provides the driving energy for the removal of the hole from the donor-acceptor interface, instead of an additional electron acceptor.^{63,64} A drawback of introducing a second electron or hole acceptor material is that energy is irreversibly lost when electrons are transferred to it, and the maximum theoretically possible energy conversion efficiency is reduced. Despite this, cascade charge separation is one of the most viable options for achieving efficient exciton dissociation when large binding energies are involved. Covalently bound molecular triads or higher polyads (tetrads, pentads, etc.) are particularly attractive for charge separation due to their well-defined electronic structure and the possibility of controlling their spatial organization.⁶³⁻⁶⁷

It is interesting to note that cascade charge separation may not necessarily require using more than two molecular species, since charge and exciton localization energies on identical molecular units may vary considerably due to their different polar or polarizable environments.^{20,21,44} Variations of the electrostatic potential in the vicinity of a donor-acceptor interface due to the environment could provide the additional driving energy for geminate pair dissociation. Molecular scale structure of the donor-acceptor interface can thus significantly influence the efficiency of charge separation.

4 Possible Extensions of the Charge Transfer Model

A major limitation of the system studied in this paper is the inclusion of only two energy levels per donor molecule and of a single level per acceptor molecule. Including additional electronic states offers additional possibilities for optimizing electron transfer. For instance, it has been suggested that charge separation involves three close-lying states in a PCBM acceptor.⁶⁸ “Hot” charge transfer states (i.e., charge transfer states where the electron is not

Figure 6: (A) A modification of the system shown in Figure 2 that uses two acceptor species, A_1 and A_2 , with different LUMO energies, $E_{A_1}^e$ and $E_{A_2}^e$, respectively. (B) and (C): The results of charge separation simulations with the same Hamiltonian parameters as for Figure 3C, except for a larger driving energy, $\Delta E = 2.530 \text{ eV}$, for charge transfer from the donor to the acceptor A_2 . The driving energy for charge transfer from the donor to the acceptor A_1 is 1.530 eV , like for the simulations in Figure 3C. The energy dissipation rates are $\nu = 10^{13} \text{ s}^{-1}$ (B) and $\nu = 10^{14} \text{ s}^{-1}$ (C). Red line – total population of all sites in the system, blue line – total population of all excitonic states in the donor material (states 0–8 in the “line basis” of Figure 2), green line – total population of all charge transfer states (states 9–17 in the “line basis” of Figure 2), cyan line – population of the lowest energy charge transfer state (state 11 in the “line basis” of Figure 2), orange line – population of the initial excitonic state (state 0 in the “line basis” of Figure 2).

in the acceptor LUMO, but in a higher molecular orbital) may have stronger coupling to donor excitonic states than the “cold” charge transfer states considered in this paper.^{26,30} They are also likely to show fast relaxation to “cold” charge transfer states, since the electron in these states is localized on the same molecule. Thus, the presence of “hot” excitonic states could enhance electron transfer to the acceptor material, significantly increasing the efficiency of charge extraction from the system.^{26,30} The introduction of additional electronic states into the model could also give rise to complications that are not considered in this paper. For instance, in many cases, photosensitization occurs via a triplet state of the donor.⁶⁹ If the multiplicity of excited states is taken into account, the rate of charge separation could be limited by intersystem crossing.

The calculations presented in this paper were performed with only energy dissipation included in the dynamical model: the pure dephasing terms in the master equation, Eq. (9), were set to zero. Additional simulations suggest that adding pure dephasing and varying its rate over several orders of magnitude, up to values that significantly exceed the rate of energy dissipation, has little effect on the charge separation efficiency (see Supporting Information). This is likely because pure dephasing does not induce the “localization” of the electron-hole pair in the “line basis”, and thus it does not disrupt charge transfer through delocalized orbitals.⁷⁰ It also does not affect population transfer between Hamiltonian eigenstates. Thus, the introduction of pure dephasing into the simulation is of no consequence for the two major factors that determine the efficiency of charge separation: the rate of charge transfer state formation (determined by the energy dissipation rate), and the ability of the charge transfer state to delocalize and reach the “free charge” state (determined by the extent of orbital delocalization). Spatial coherence (orbital delocalization) is significantly more important for efficient charge separation than temporal coherence (the survival of relative phases in the wave function over time).

Although the simulations presented in this paper qualitatively reproduce many of the features of charge separation in real organic photovoltaic systems, an accurate quantitative

description requires more precise estimates for the Hamiltonian and decoherence parameters than those described in Section 2. The energies of excitonic and charge transfer states, as well as the couplings between these states for various intermolecular distances and orientations, can be found from DFT/TDDFT calculations.^{13,42} A detailed analysis of the effects of intermolecular and intramolecular vibrational modes on charge and exciton transfer may also be necessary for calculations on specific systems of interest.⁴⁹⁻⁵¹

5 Conclusions

In this paper we presented a simple model that treats the processes of exciton transfer, charge transfer, and charge separation in multichromophore donor-acceptor systems within a consistent common framework. The electron-hole pair is described as a single quasiparticle, and its dynamics is simulated using a Lindblad master equation with a tight-binding Hamiltonian and decoherence due to interaction with vibrations introduced by pure dephasing and Miller-Abrahams energy dissipation terms. Incoherent hopping terms between any pair of states in the system are assumed to depend on both the spatial separation between and overlap of these states. The model is parametrized using values of electronic excitation energy, exciton binding energy, electronic and excitonic couplings, driving energy for charge separation, permittivity, and intermolecular distances that are typical for organic photovoltaic materials. Simulations based on the proposed model allowed us to observe several qualitative trends for charge separation in molecular materials that imply possible strategies for optimizing this process.

We found that two processes largely govern charge separation in donor-acceptor materials: charge delocalization within extended orbitals and energy dissipation upon transition from an excitonic state to a charge transfer state. These processes are not independent and may both be affected by the same alteration to the system. To achieve efficient charge separation, an optimum balance between the charge delocalization and energy dissipation must be sought.

When the binding energy significantly exceeds the electronic couplings within the system, as is common for organic materials, charge separation occurs in two steps. First, one of the charges that composes the exciton is transferred to the electron(hole) acceptor material, while the other charge remains in the donor material. This results in the formation of a geminate pair in which the electron and the hole are in different materials but experience significant Coulomb attraction. Second, the geminate pair dissociates, with the electron and the hole leaving the donor-acceptor interface and becoming free charges. The formation of the geminate pair must be energetically favorable and is driven by energy dissipation. We found that charge delocalization within the donor or acceptor material hinders this process, since it reduces the spatial overlap between the orbitals that the transferred charge occupies in the excitonic and charge transfer states. On the other hand, we observed that once a geminate pair is formed, charge delocalization enhances its dissociation into free electrons and holes. Thus, to achieve optimum long-distance charge separation, the degree of orbital delocalization within the donor and acceptor materials should be chosen so as to achieve equal rates of geminate pair formation and dissociation.

In highly polarizable materials with π -conjugated systems that extend over both the donor and acceptor materials, spatially extended charge transfer states can be formed purely by means of coherent wavefunction delocalization. The Coulomb attraction between the electron and the hole in such states is very weak, and the charges can be treated as essentially free. This situation occurs when electronic couplings throughout the system are comparable to or greater than the exciton binding energy. Our simulations show that this is conducive to charge separation, since the electron and the hole can independently travel through the material and be removed from it at external contacts, similarly to the situation in common inorganic crystalline semiconductors such as Si, Ge, and GaAs, where the exciton binding energy is smaller than the thermal energy at room temperature and is commonly neglected.⁷¹ It should be noted, however, that purely coherent wavefunction evolution can only facilitate the removal of population from eigenstates of the system Hamiltonian that are completely

delocalized. Population transfer from localized to delocalized eigenstates requires an incoherent process (see Section 3.3). This incoherent contribution was found to hinder charge separation on ultrashort timescales (< 1 ps), but to enhance it on longer timescales.

We have also seen that one of the most practical approaches to facilitating geminate pair dissociation is cascade charge separation. In this scheme, an additional electron(hole) acceptor is added to the system in order to provide the driving energy for overcoming the Coulomb attraction between the electron and the hole in a geminate pair. Cascade charge separation can be realized in molecular triads or higher polyads. Alternatively, the environment in the vicinity of a donor-acceptor interface can be engineered so that its electrostatic potential provides the additional driving energy for charge removal from the interface. To minimize energy losses in a charge separation cascade, the driving energy for each charge separation step can be tuned so as to precisely compensate for the energy gain due to the weaker Coulomb interaction between the electron and the hole at progressively larger distances.

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Supporting Information Available:

Results pertaining to the effect of pure dephasing on charge separation and results of all simulations presented in this paper for an alternative measure of spatial separation R_{kl} between Hamiltonian eigenstates.⁵⁴ This material is available free of charge via the Internet at <http://pubs.acs.org>.

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