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

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# S1 Details of the Model Hamiltonian

### S1.1 Formulation of the Hamiltonian

We employ a one-dimensional electron-hole lattice model, which is essentially the multiband version of the standard semiconductor model. We perform computations on the system containing 2N lattice sites which are mutually separated by lattice constant a. The sites  $0, \ldots, N - 1$  are considered to belong to the donor part of the interface, while sites  $N, \ldots, 2N - 1$  constitute the acceptor part. Single-electron levels on site i are enumerated by  $\beta_i$ , while single-hole levels on site i are counted by  $\alpha_i$ . Fermi operators  $c_{i\beta_i}^{\dagger}$  and  $c_{i\beta_i}$  $(d_{i\alpha_i}^{\dagger} \text{ and } d_{i\alpha_i})$  respectively create and annihilate an electron (a hole) in the single-electron state  $(i\beta_i)$  [single-hole state  $(i\alpha_i)$ ]. The phonon operators  $b_{i\xi}^{\dagger}$  and  $b_{i\xi}$  generate and destroy a phonon on site i belonging to mode  $\xi$ .

The total Hamiltonian is

$$H = H_{\rm c} + H_{\rm p} + H_{\rm c-p} + H_{\rm c-f}$$
(S1)

where  $H_{\rm c}$  describes interacting carriers

$$H_{c} = \sum_{\substack{i\beta_{i} \\ j\beta'_{j}}} \epsilon^{c}_{(i\beta_{i})(j\beta'_{j})} c^{\dagger}_{i\beta_{i}} c_{j\beta'_{j}} - \sum_{\substack{i\alpha_{i} \\ j\alpha'_{j}}} \epsilon^{v}_{(i\alpha_{i})(j\alpha'_{j})} d^{\dagger}_{i\alpha_{i}} d_{j\alpha'_{j}}$$

$$+ \frac{1}{2} \sum_{\substack{i\beta_{i} \\ j\beta'_{j}}} V_{ij} c^{\dagger}_{i\beta_{i}} c^{\dagger}_{j\beta'_{j}} c_{j\beta'_{j}} c_{i\beta_{i}} + \frac{1}{2} \sum_{\substack{i\alpha_{i} \\ j\alpha'_{j}}} V_{ij} d^{\dagger}_{i\alpha_{i}} d^{\dagger}_{j\alpha'_{j}} d_{j\alpha'_{j}} d_{i\alpha_{i}} - \sum_{\substack{i\beta_{i} \\ j\alpha_{j}}} V_{ij} c^{\dagger}_{i\beta_{i}} d^{\dagger}_{j\alpha_{j}} d_{j\alpha_{j}} c_{i\beta_{i}}$$

$$H_{p} = \sum \hbar \omega_{\xi} b^{\dagger}_{i\xi} b_{i\xi}$$
(S2)

describes the phonon bath,  $H_{c-p}$  accounts for the interaction of carriers with the phonon

 $i\xi$ 

bath

$$H_{\rm c-p} = \sum_{i\beta_i} \sum_{\xi} g^{\rm c}_{i\beta_i\xi} c^{\dagger}_{i\beta_i} c_{i\beta_i} (b^{\dagger}_{i\xi} + b_{i\xi}) - \sum_{i\alpha_i} \sum_{\xi} g^{\rm v}_{i\alpha_i\xi} d^{\dagger}_{i\alpha_i} d_{i\alpha_i} (b^{\dagger}_{i\xi} + b_{i\xi})$$
(S4)

whereas  $H_{c-f}$  represents the interaction of carriers with the interfacial electric field  $\mathbf{F}$  which is assumed to be uniform throughout the system

$$H_{\rm c-f} = \sum_{i\beta_i} q \mathbf{F} \cdot \mathbf{r}_i \, c_{i\beta_i}^{\dagger} c_{i\beta_i} - \sum_{i\alpha_i} q \mathbf{F} \cdot \mathbf{r}_i \, d_{i\alpha_i}^{\dagger} d_{i\alpha_i}.$$
(S5)

In eq S2, we assume that quantities  $\epsilon^{c}_{(i\beta_i)(j\beta'_j)}\left(\epsilon^{v}_{(i\alpha_i)(j\alpha'_j)}\right)$  representing electron (hole) onsite energies and transfer integrals are non-zero only for certain combinations of their indices. In greater detail, we assume that  $\epsilon^{c}_{(i\beta_i)(j\beta'_j)} \neq 0$  when it represents

- 1. on-site energy  $\epsilon_{i\beta_i}^c$  of single-electron level  $\beta_i$  on site i, for i = j and  $\beta_i = \beta'_i$ ;
- 2. negative electron transfer integral between single-electron levels on nearest-neighboring sites belonging to the same band  $\beta_i$ ,  $-J_{i\beta_i}^{c,int}$ , for i and j both belonging to the same part of the bilayer, |i j| = 1, and  $\beta_i = \beta'_j$ ;
- 3. negative electron transfer integral between single-electron levels on nearest-neighboring sites belonging to different bands,  $-J_{i\beta_i\beta'_j}^{c,ext}$ , for *i* and *j* both belonging to the same part of the bilayer, |i j| = 1, and  $\beta_i \neq \beta'_j$ ;
- 4. negative electron transfer integral between different parts of the bilayer,  $-J_{DA}^{c}$ , for i = N 1 and j = N or vice versa.

The Coulomb interaction is taken into account in the lowest monopole–monopole approximation and the interaction potential  $V_{ij}$  is taken to be of Ohno type

$$V_{ij} = \frac{U}{\sqrt{1 + \left(\frac{r_{ij}}{r_0}\right)^2}} \tag{S6}$$

where U is the on-site Coulomb interaction,  $r_{ij}$  is the distance between sites i and j,  $r_0 =$  $q^2/(4\pi\varepsilon_0\varepsilon_r U)$  is the characteristic length, and  $\varepsilon_r$  is the relative dielectric constant. Charge carriers are assumed to be locally and linearly coupled to the phonon bath (Holstein-type interaction), as given in eq S4. The sets of phonon modes are assumed to be identical on each site, that is, phonon frequency  $\omega_{\xi}$  does not depend on site index *i*. We also note that the Hamiltonian  $H_{c-p}$  fully takes into account the effect of on-site dynamic disorder, i.e. variations of on-site energies due to oscillations of phonon bath. In principle, non-local electron-phonon coupling that would introduce inter-site dynamic disorder, i.e. variations of transfer integrals due to oscillations of phonon bath, could also be added to the Hamiltonian but that would add additional parameters to the model. It is also worth mentioning that local electron-phonon coupling introduces both diagonal and off-diagonal exciton-phonon coupling, which means that both diagonal and off-diagonal dynamic disorder in exciton basis are present. In eq S5, q > 0 is the elementary charge,  $\mathbf{r}_i$  is the position vector of site i, and vector  $\mathbf{F}$  is assumed to be perpendicular to the interface and directed opposite the internal electric field of a space-separated electron-hole pair (in which the electron is primarily located in the acceptor, while the hole is mainly located in the donor).

#### S1.2 Excitonic States and Their Classification

We limit ourselves to the subspace of a single electron-hole pair and develop the description of charge separation in the excitonic basis. The most general state of an electron-hole pair can be written as the superposition

$$|x\rangle = \sum_{\substack{i\alpha_i\\j\beta_j}} \psi^x_{(i\alpha_i)(j\beta_j)} c^{\dagger}_{j\beta_j} d^{\dagger}_{i\alpha_i} |0\rangle,$$

where  $|0\rangle$  is the vacuum of electron-hole pairs. The exciton states are obtained by solving the eigenvalue problem  $(H_c + H_{c-f})|x\rangle = \hbar\omega_x |x\rangle$ , which in the basis of single-particle states localized at lattice sites reads as

$$\sum_{\substack{i'\alpha'_i\\j'\beta'_j}} \left( \delta_{ii'} \delta_{\alpha_i \alpha'_i} \epsilon^{\mathbf{c}}_{(j\beta_j)(j'\beta'_j)} - \delta_{jj'} \delta_{\beta_j \beta'_j} \epsilon^{\mathbf{v}}_{(i\alpha_i)(i'\alpha'_i)} - \delta_{j'\beta'_j} \delta_{\beta_j \beta'_j} \left( V_{ij} - q \mathbf{F} \cdot (\mathbf{r}_j - \mathbf{r}_i) \right) \right) \psi^x_{(i'\alpha'_i)(j'\beta'_j)} = \hbar \omega_x \psi^x_{(i\alpha_i)(j\beta_j)}$$
(S7)

Limiting our model Hamiltonian to the subspace of singly excited states and transforming it to the excitonic basis we obtain

$$H_{\rm c} + H_{\rm c-f} = \sum_{x} \hbar \omega_x |x\rangle \langle x|, \qquad (S8)$$

$$H_{\rm c-p} = \sum_{\bar{x}x} \sum_{i\xi} \Gamma^{i\xi}_{\bar{x}x} |\bar{x}\rangle \langle x| \left( b^{\dagger}_{i\xi} + b_{i\xi} \right), \tag{S9}$$

where the exciton–phonon interaction constants characterizing the transition between exciton state  $|\bar{x}\rangle$  and  $|x\rangle$  read as

$$\Gamma^{i\xi}_{\bar{x}x} = \sum_{\beta_i} \sum_{j\alpha_j} g^{\mathbf{c}}_{i\beta_i\xi} \psi^{\bar{x}*}_{(j\alpha_j)(i\beta_i)} \psi^{x}_{(j\alpha_j)(i\beta_i)} - \sum_{\alpha_i} \sum_{j\beta_j} g^{\mathbf{v}}_{i\alpha_i\xi} \psi^{\bar{x}*}_{(i\alpha_i)(j\beta_j)} \psi^{x}_{(i\alpha_i)(j\beta_j)}.$$
 (S10)

According to the spatial properties of stationary states obtained by solving eq S7, we can differentiate between states describing different types of excitons. In more detail, an XD state features both carriers predominantly located in the donor part of the bilayer, whereas an XA state is characterized by both carriers residing mainly in the acceptor part. In a state of space-separated electron-hole pair, the electron resides mainly in the acceptor, while the hole resides mainly in the donor. Based on the mean electron-hole separation, states of space-separated pairs can be further subdivided into CT, CS, and free-charge states. In a free-charge state, carriers are mainly localized in the so-called contact region, which consists of sites  $0, \ldots, l_c - 1$  in the donor part, and  $2N - l_c, \ldots, 2N - 1$  in the acceptor part. The

space-separated state  $|x\rangle$  is a free-charge state if

$$\sum_{i=0}^{l_c-1} \sum_{j} \sum_{\alpha_i \beta_j} |\psi^x_{(i\alpha_i)(j\beta_j)}|^2 \ge 0.7,$$
(S11)

and

$$\sum_{i} \sum_{j=2N-l_c}^{2N-1} \sum_{\alpha_i \beta_j} |\psi^x_{(i\alpha_i)(j\beta_j)}|^2 \ge 0.7.$$
(S12)

We established in our previous work<sup>S1</sup> that the results are weekly sensitive to the choice of the length of contact region  $l_c$  and the exact value of the numerical factor 0.7 in the criterion for a free charge state, as long as these are changed within reasonable limits. Since the model Hamiltonian in this work is the same and only the expressions for transition rates are somewhat changed, we use the same values of these parameters in this work. The algorithm of the subdivision between CT and CS states is given in detail in ref S1. It relies on solving eq S7 with donor-acceptor transfer integrals  $J_{DA}^c \neq 0$ ,  $J_{DA}^v \neq 0$  (states  $|x\rangle$ ) and  $J_{DA}^c = J_{DA}^v = 0$  (states  $|x^{(0)}\rangle$ ). In the case  $J_{DA}^c = J_{DA}^v = 0$ , state  $|x^{(0)}\rangle$ , in which the electron is fully in the acceptor, and the hole is fully in the donor, is considered to be a CT state if its mean electron-hole separation is less or equal than N, otherwise it is considered as a CS state. In the case  $J_{DA}^c \neq 0$ ,  $J_{DA}^v \neq 0$ , if  $|x\rangle$  is a space-separated state that is not a free-charge state, we compute overlaps

$$O_{\rm CT^{(0)}}^x = \sum_{x^{(0)} \in \rm CT} \left| \langle x^{(0)} | x \rangle \right|^2, \quad O_{\rm CS^{(0)}}^x = \sum_{x^{(0)} \in \rm CS} \left| \langle x^{(0)} | x \rangle \right|^2.$$
(S13)

If  $O_{CT^{(0)}}^x > O_{CS^{(0)}}^x$ ,  $|x\rangle$  is of CT character, otherwise it is of CS character.

The degree of spatial delocalization of carriers in excitonic states can be conveniently quantified using the participation ratio (PR). The PR can be understood to measure the number of sites over which the carrier is delocalized. The participation ratio for the electron  $(PR^{x,e})$  and the hole  $(PR^{x,h})$  in exciton state  $|x\rangle$  is defined as

$$PR^{x,e} = \left(\sum_{i} |\phi_{i}^{x,e}|^{4}\right)^{-1}, \quad PR^{x,h} = \left(\sum_{i} |\phi_{i}^{x,h}|^{4}\right)^{-1}$$
(S14)

where  $|\phi_i^{x,e}|$  and  $|\phi_i^{x,h}|$  are the moduli of the wavefunction of the electron and hole in state  $|x\rangle$ , see eqs S16 and S17.

### S1.3 Exciton Recombination

The description of exciton recombination is the same as in our recent work,<sup>S2</sup> where we argued that the following expression for the lifetime  $\tau_x$  of excitonic state  $|x\rangle$ 

$$\tau_x = \tau_0 \left( \sum_{i=0}^{N-1} |\phi_i^{x,e}| \left| \phi_i^{x,h} \right| + A_{A/D} \sum_{i=N}^{2N-1} |\phi_i^{x,e}| \left| \phi_i^{x,h} \right| \right)^{-1}$$
(S15)

is plausible. The last expression basically reflects the intuitively clear fact that the smaller is the overlap between the electron and hole probability distributions, the longer is the lifetime of the exciton. In eq S15, we introduced the moduli of the wavefunction of the electron and hole in exciton state  $|x\rangle$ 

$$|\phi_i^{x,\mathbf{e}}| = \sqrt{\sum_{\beta_i} \sum_{j\alpha_j} \left| \psi_{(j\alpha_j)(i\beta_i)}^x \right|^2},\tag{S16}$$

$$\left|\phi_{i}^{x,\mathrm{h}}\right| = \sqrt{\sum_{\alpha_{i}} \sum_{j\beta_{j}} \left|\psi_{(i\alpha_{i})(j\beta_{j})}^{x}\right|^{2}},\tag{S17}$$

while  $\tau_0$  and  $A_{A/D}$  are constants which are determined so that the lifetimes of the lowest CT, XD, and XA states in the ordered system agree with the values reported in the literature.

#### S1.4 Parameterization of the Model Hamiltonian

As mentioned in the main body of the manuscript, the values of model parameters are selected so that the values of band gaps, bandwidths, band offsets, exciton binding energies, exciton recombination times, etc. within our model agree with those reported in the literature on the prototypical P3HT/PCBM blend. A detailed discussion on the parameterization of the model Hamiltonian can be found in our recent work.<sup>S2</sup> Here, let us only mention that, in order to mimic the presence of low-lying unoccupied orbitals that are close to the LUMO orbital of PCBM, we take two single-electron states per acceptor site, that is, index  $\beta_i$  for  $N \leq i \leq 2N - 1$  can take values 0 and 1. At the same time, we assume that each acceptor site is equipped with one single-hole state, while each donor site has one single-electron and one single-hole state. We also note that our model strictly describes a bilayer with layer widths Na but the model can also be of relevance for bulk heterojunctions whose characteristic dimension (typical distance between a point in the bulk heterojunction and the closest interface) is similar to bilayer width. For example, a donor (or acceptor) exciton that reaches the boundary of the system can only be reflected from it in our model. On the other hand, when it reaches the point that is at equal distance from two different interfaces in a bulk heterojunction, it can proceed to move toward a different interface. Consequently, the reflection of an exciton at the boundary in our model can be considered to be equivalent to motion toward another interface in the bulk heterojunction. More generally, the fact that an exciton is confined to a layer in our model is in some sense equivalent to the fact that the distance between an exciton and the interface in the bulk heterojunction cannot be larger than the characteristic dimension of the bulk heterojunction. The model is pictorially presented in Figure S1, while its parameters are summarized in Table S1.



Figure S1: Schematic view of the model system presenting different transfer integrals and onsite energies present in Table S1. The centers of on-site energy distributions are represented by dashed lines, while solid lines represent the actual on-site energies, which differ from site to site due to the diagonal static disorder. The probability density that the energy of the electron on donor site i  $(0 \le i \le N - 1)$  is around  $\epsilon_{i,0}^{c}$  is of the Gaussian type  $g(\epsilon_{i,0}^{c}) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(\epsilon_{i,0}^{c} - \epsilon_{D,0}^{c})^{2}}{2\sigma^{2}}\right)$ . Other on-site energies are drawn in the same manner. The contact region of the bilayer is indicated by rectangles. **F** is the vector of interfacial electric field. Adapted with permission from ref S2. Copyright 2018 American Chemical Society.

Parameter (Unit)	Description	Value
N	number of sites in a single material	30
$l_c$	length of the contact region (eqs $S11$ and $S12$ )	11
a (nm)	lattice constant	1.0
U (eV)	on-site Coulomb interaction $(eq S6)$	0.65
$\varepsilon_r$	relative dielectric constant	3.0
$\epsilon_{D,0}^{\rm c} \ ({\rm eV})$	center for on-site electron energies in D	2.63
$J_{D,0}^{\mathrm{c,int}} (\mathrm{eV})$	electron transfer integral in D	0.1
$\epsilon_{D,0}^{\mathrm{v}}$ (eV)	center for on-site hole energies in D	-0.3
$J_{D,0}^{\mathrm{v,int}}$ (eV)	hole transfer integral in D	-0.15
$\epsilon_{A,0}^{c}$ (eV)	center for on-site electron energies in band 0 of A	1.565
$\epsilon_{A,1}^{\mathbf{c}}$ (eV)	center for on-site electron energies in band 1 of A	1.865
$J_{A,0}^{\mathrm{c,int}} (\mathrm{eV})$	electron transfer integral in band 0 of A	0.05
$J_{A,1}^{\mathrm{c,int}} (\mathrm{eV})$	electron transfer integral in band 1 of A	0.025
$J_{A,01}^{\mathrm{c,ext}}$ (eV)	electron transfer integral between bands 0 and 1 of A	0.02
$\epsilon_{A,0}^{\rm v}~({\rm eV})$	center for on-site hole energies in A	-1.03
$J_{A,0}^{\mathrm{v,int}}$ (eV)	hole transfer integral in A	-0.15
$J_{DA}^{c}$ (eV)	electron transfer integral between D and A	0.1
$J_{DA}^{\rm v}$ (eV)	hole transfer integral between D and A	-0.1
$ \mathbf{F} $	magnitude of the interfacial electric field	0
$\tau_0 \text{ (ps)}$	eq S15	400
$A_{A/D}$	eq S15	0.5

Table S1: Values of Model Parameters Used in Computations.

# S2 Details of the Theoretical Approach and Numerical Scheme

In the following text, we present additional details concerning the theoretical approach and numerical scheme.

## S2.1 Derivation of Rate Equations in Modified Redfield Theory

The operator  $X_{xx} = |x\rangle\langle x|$ , whose expectation value is the population of exciton state  $|x\rangle$ , is invariant under polaron transformation, i.e,  $\widetilde{X}_{xx} = X_{xx}$ . Therefore, we formulate equations of motion for excitonic populations in the polaron frame.

Time evolution of operator  $X_{xx}(t)$  in the polaron frame is governed by

$$\partial_t X_{xx}(t) = \frac{\mathrm{i}}{\hbar} [\widetilde{H}_0(t), X_{xx}(t)] + \frac{\mathrm{i}}{\hbar} [\widetilde{V}(t), X_{xx}(t)], \qquad (S18)$$

where time dependence is with respect to the full Hamiltonian  $\tilde{H}$  (we take t = 0 as the initial instant, while O is an arbitrary operator in the Schrödinger picture)

$$\widetilde{O}(t) = \widetilde{U}^{\dagger}(t)\widetilde{O}\widetilde{U}(t), \quad \widetilde{U}(t) = \exp\left(-\frac{\mathrm{i}}{\hbar}\widetilde{H}t\right).$$
 (S19)

The Dyson expansion of the full evolution operator  $\widetilde{U}(t)$  in powers of the interaction  $\widetilde{V}$  reads as (T is the chronological time-ordering sign)

$$\widetilde{U}(t) = \widetilde{U}_0(t) \times T \exp\left(-\frac{\mathrm{i}}{\hbar} \int_0^t \mathrm{d}\tau \, \widetilde{V}^{(0)}(\tau)\right),\tag{S20}$$

where

$$\widetilde{U}_0(t) = \exp\left(-\frac{\mathrm{i}}{\hbar}\widetilde{H}_0t\right), \quad \widetilde{V}^{(0)}(t) = \widetilde{U}_0^{\dagger}(t)\widetilde{V}\widetilde{U}_0(t).$$
(S21)

Therefore, up to the second order in interaction operator  $\widetilde{V}$ , the equation of motion of

operator  $X_{xx}(t)$  (eq S18) reduces to

$$\partial_t X_{xx}(t) = \frac{\mathrm{i}}{\hbar} \left[ \widetilde{V}^{(0)}(t), X_{xx} \right] - \frac{1}{\hbar^2} \int_0^t \mathrm{d}\tau \, \left[ \widetilde{V}^{(0)}(\tau), \left[ \widetilde{V}^{(0)}(t), X_{xx} \right] \right], \tag{S22}$$

where we have used  $X_{xx}^{(0)}(t) = X_{xx}$ . The equation of motion for population of excitonic state x at time t,

$$f_x(t) = \operatorname{Tr} \left\{ X_{xx}(t)\widetilde{\rho}(0) \right\}, \qquad (S23)$$

is now established using eq S22. In order to form closed equations for populations only, we disregard all contributions that are not diagonal in excitonic indices. Expectation value of the first term in eq S22 in the initial condition  $\tilde{\rho}(0)$  produces only off-diagonal contributions in excitonic indices

$$\begin{bmatrix} \widetilde{V}^{(0)}(t), X_{xx} \end{bmatrix} = \sum_{x'(\neq x)} \sum_{\mu} e^{-i(\widetilde{\omega}_x - \widetilde{\omega}_{x'})t} |x'\rangle \langle x| M^{(0)}_{x'x\mu}(t) - \sum_{x'(\neq x)} \sum_{\mu} e^{-i(\widetilde{\omega}_{x'} - \widetilde{\omega}_x)t} |x\rangle \langle x'| M^{(0)}_{xx'\mu}(t).$$
(S24)

On the other hand, the second term in eq S22

$$\begin{split} \left[\widetilde{V}^{(0)}(\tau), \left[\widetilde{V}^{(0)}(t), X_{xx}\right]\right] &= \sum_{x'(\neq x)} \sum_{x''(\neq x')} \sum_{\nu\mu} e^{-i(\widetilde{\omega}_{x'} - \widetilde{\omega}_{x''})\tau} e^{-i(\widetilde{\omega}_{x} - \widetilde{\omega}_{x'})t} |x''\rangle \langle x| M_{x''x'\nu}^{(0)}(\tau) M_{x'x\mu}^{(0)}(t) \\ &+ \sum_{x'(\neq x)} \sum_{x''(\neq x')} \sum_{\nu\mu} e^{-i(\widetilde{\omega}_{x''} - \widetilde{\omega}_{x'})\tau} e^{-i(\widetilde{\omega}_{x'} - \widetilde{\omega}_{x'})t} |x\rangle \langle x''| M_{xx'\mu}^{(0)}(t) M_{x'x'\nu}^{(0)}(\tau) \\ &- \sum_{x'(\neq x)} \sum_{x''(\neq x)} \sum_{\nu\mu} e^{-i(\widetilde{\omega}_{x'} - \widetilde{\omega}_{x''})\tau} e^{-i(\widetilde{\omega}_{x'} - \widetilde{\omega}_{x'})t} |x'\rangle \langle x''| M_{x'x\mu}^{(0)}(t) M_{xx'\nu}^{(0)}(\tau) \\ &- \sum_{x'(\neq x)} \sum_{x''(\neq x)} \sum_{\nu\mu} e^{-i(\widetilde{\omega}_{x} - \widetilde{\omega}_{x''})\tau} e^{-i(\widetilde{\omega}_{x'} - \widetilde{\omega}_{x})t} |x''\rangle \langle x'| M_{x''x\nu}^{(0)}(\tau) M_{xx'\mu}^{(0)}(t) \end{split}$$
(S25)

eventually produces some population-like terms. Isolating such terms and taking their ex-

pectation values in the initial condition  $\tilde{\rho}(0)$ , we obtain

$$\partial_t f_x(t) = -\sum_{x'(\neq x)} w_{x'x}(t) f_x(t) + \sum_{x'(\neq x)} w_{xx'}(t) f_{x'}(t),$$
(S26)

where time dependent transition rates from state  $|x'\rangle$  to state  $|x\rangle$  are given as

$$w_{xx'}(t) = \frac{2}{\hbar^2} \int_0^t \mathrm{d}\tau \operatorname{Re} \left\{ \mathrm{e}^{\mathrm{i}(\widetilde{\omega}_{x'} - \widetilde{\omega}_x)(t-\tau)} \sum_{\mu\nu} \left\langle M_{x'x\mu}^{(0)}(t) M_{xx'\nu}^{(0)}(\tau) \right\rangle_{\mathrm{eq}} \right\}$$
$$= \frac{2}{\hbar^2} \int_0^t \mathrm{d}\tau \operatorname{Re} \left\{ \mathrm{e}^{\mathrm{i}(\widetilde{\omega}_{x'} - \widetilde{\omega}_x)\tau} \sum_{\mu\nu} \left\langle M_{x'x\mu}^{(0)}(\tau) M_{xx'\nu} \right\rangle_{\mathrm{eq}} \right\}.$$
(S27)

We made use of the stationarity of the phonon correlation function

$$\left\langle M_{x'x\mu}^{(0)}(t)M_{xx'\nu}^{(0)}(\tau)\right\rangle_{\rm eq} = \left\langle M_{x'x\mu}^{(0)}(t-\tau)M_{xx'\nu}\right\rangle_{\rm eq},$$
 (S28)

which is guaranteed because we perform canonical averaging over nuclear degrees of freedom. If time scales on which we study excitonic dynamics are much longer than the time scale on which the phonon correlation function decays, we may perform the Markovian approximation and set  $t \to +\infty$  in Eq. (S27) to obtain time-independent transition rates<sup>S3</sup> that are presented in the main body of the manuscript

$$w_{xx'} = \frac{2}{\hbar^2} \int_0^{+\infty} \mathrm{d}\tau \operatorname{Re} \left\{ \operatorname{e}^{\mathrm{i}(\widetilde{\omega}_{x'} - \widetilde{\omega}_x)(t-\tau)} \sum_{\mu\nu} \left\langle M_{x'x\mu}^{(0)}(t) M_{xx'\nu}^{(0)}(\tau) \right\rangle_{\mathrm{eq}} \right\}$$

$$= \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} \mathrm{d}\tau \operatorname{e}^{\mathrm{i}(\widetilde{\omega}_{x'} - \widetilde{\omega}_x)\tau} \sum_{\mu\nu} \left\langle M_{x'x\mu}^{(0)}(\tau) M_{xx'\nu} \right\rangle_{\mathrm{eq}}.$$
(S29)

These modified Redfield transition rates satisfy the condition of the detailed balance<sup>S4</sup>

$$\frac{w_{xx'}}{w_{x'x}} = e^{\beta(\hbar\tilde{\omega}_{x'} - \hbar\tilde{\omega}_x)}.$$
(S30)

In the next section, we present the calculation of the phonon correlation function appear-

ing in the modified Redfield rates.

# **S2.2** Calculation of the Correlation Function $\left\langle M_{x'x\mu}^{(0)}(\tau)M_{xx'\nu}\right\rangle_{\rm eq}$

The correlation function of interest is

$$\left\langle M_{x'x\mu}^{(0)}(\tau)M_{xx'\nu}\right\rangle_{\rm eq} = \Gamma_{xx'}^{\nu}\Gamma_{x'x}^{\mu} \times \\ \times \left\langle \left(b_{\mu}^{\dagger}(\tau) + b_{\mu}(\tau) - 2\frac{\Gamma_{x'x'}^{\mu}}{\hbar\omega_{\mu}}\right)U_{x'}^{\dagger}(\tau)U_{x}(\tau)U_{x}^{\dagger}U_{x'}\left(b_{\nu}^{\dagger} + b_{\nu} - 2\frac{\Gamma_{x'x'}^{\nu}}{\hbar\omega_{\nu}}\right)\right\rangle_{\rm eq}$$
(S31)

where, for simplicity of notation, we omit subscript (0) on time-dependent operators, and we define

$$U_x = \exp\left(-\sum_{\rho} \frac{\Gamma_{xx}^{\rho}}{\hbar\omega_{\rho}} \left(b_{\rho}^{\dagger} - b_{\rho}\right)\right)$$
(S32)

Using the operator identity

$$\exp(A)\exp(B) = \exp(A+B)\exp\left(\frac{1}{2}[A,B]\right), \text{ for } [A,[A,B]] = [B,[A,B]] = 0$$
 (S33)

we transform the product of four U operator as follows

$$U_{x'}^{\dagger}(\tau)U_{x}(\tau)U_{x}^{\dagger}U_{x'} = \exp\left[-i\sum_{\rho}\Delta_{x'x\rho}^{2}\sin\left(\omega_{\rho}t\right)\right] \times \\ \times \exp\left[\sum_{\rho}\Delta_{x'x\rho}\left(\left(1 - e^{-i\omega_{\rho}\tau}\right)b_{\rho} - \left(1 - e^{i\omega_{\rho}\tau}\right)b_{\rho}^{\dagger}\right)\right]$$
(S34)

where we introduced

$$\Delta_{x'x\rho} = \frac{\Gamma^{\rho}_{x'x'} - \Gamma^{\rho}_{xx}}{\hbar\omega_{\rho}} \tag{S35}$$

The averaging over equilibrium phonon distribution can then be performed separately for each mode

$$\left\langle M_{x'x\mu}^{(0)}(\tau)M_{xx'\nu}\right\rangle_{\rm eq} = \Gamma_{x'x}^{\mu}\Gamma_{xx'}^{\nu}\exp\left[-i\sum_{\rho}\Delta_{x'x\rho}^{2}\sin\left(\omega_{\rho}t\right)\right] \times \prod_{\rho} \operatorname{Tr}_{\rho}\left\{ \left(b_{\mu}^{\dagger}\mathrm{e}^{\mathrm{i}\omega_{\mu}\tau} + b_{\mu}\mathrm{e}^{-\mathrm{i}\omega_{\mu}\tau} - 2\frac{\Gamma_{x'x'}^{\mu}}{\hbar\omega_{\mu}}\right)\exp\left[\Delta_{x'x\rho}\left(\left(1 - \mathrm{e}^{-\mathrm{i}\omega_{\rho}\tau}\right)b_{\rho} - \left(1 - \mathrm{e}^{\mathrm{i}\omega_{\rho}\tau}\right)b_{\rho}^{\dagger}\right)\right] \times \left(b_{\nu}^{\dagger} + b_{\nu} - 2\frac{\Gamma_{x'x'}^{\nu}}{\hbar\omega_{\nu}}\right)\widetilde{\rho}_{B,\rho}^{\mathrm{eq}}\right\}$$
(S36)

where  $\operatorname{Tr}_{\rho}$  denotes averaging over the subspace of mode  $\rho$ , while

$$\widetilde{\rho}_{B,\rho}^{\mathrm{eq}} = \frac{\exp\left[-\beta\hbar\omega_{\rho}b_{\rho}^{\dagger}b_{\rho}\right]}{\mathrm{Tr}_{\rho}\exp\left[-\beta\hbar\omega_{\rho}b_{\rho}^{\dagger}b_{\rho}\right]}$$

Further calculations are most conveniently performed by separately considering a number of cases that can arise. Identities that are used to calculate traces are summarized in Section S3. We introduce the phonon number  $n_{\mu}^{\rm ph} = (e^{\beta\hbar\omega_{\mu}} - 1)^{-1}$ .

Case 1.  $\rho \neq \mu$  and  $\rho \neq \nu$ 

$$\left\langle \exp\left[\Delta_{x'x\rho}\left(\left(1-\mathrm{e}^{-\mathrm{i}\omega_{\rho}\tau}\right)b_{\rho}-\left(1-\mathrm{e}^{\mathrm{i}\omega_{\rho}\tau}\right)b_{\rho}^{\dagger}\right)\right]\right\rangle_{\mathrm{eq},\rho}=\\=\exp\left[-2\Delta_{x'x\rho}^{2}\left(1-\cos\left(\omega_{\rho}\tau\right)\right)\left(n_{\rho}^{\mathrm{ph}}+\frac{1}{2}\right)\right]$$
(S37)

Case 2.  $\rho = \mu$  and  $\mu \neq \nu$ 

$$\left\langle \left( b_{\mu}^{\dagger} \mathrm{e}^{\mathrm{i}\omega_{\mu}\tau} + b_{\mu} \mathrm{e}^{-\mathrm{i}\omega_{\mu}\tau} - 2\frac{\Gamma_{x'x'}^{\mu}}{\hbar\omega_{\mu}} \right) \exp\left[ \Delta_{x'x\mu} \left( \left( 1 - \mathrm{e}^{-\mathrm{i}\omega_{\mu}\tau} \right) b_{\mu} - \left( 1 - \mathrm{e}^{\mathrm{i}\omega_{\mu}\tau} \right) b_{\mu}^{\dagger} \right) \right] \right\rangle_{\mathrm{eq},\mu} = \left[ \Delta_{x'x\mu} \left( \mathrm{e}^{\mathrm{i}\omega_{\mu}\tau} - 1 \right) n_{\mu}^{\mathrm{ph}} + \Delta_{x'x\mu} \left( 1 - \mathrm{e}^{-\mathrm{i}\omega_{\mu}\tau} \right) \left( 1 + n_{\mu}^{\mathrm{ph}} \right) - 2\frac{\Gamma_{x'x'}^{\mu}}{\hbar\omega_{\mu}} \right] \times \\ \times \exp\left[ -2\Delta_{x'x\mu}^{2} \left( 1 - \cos\left(\omega_{\mu}\tau\right) \right) \left( n_{\mu}^{\mathrm{ph}} + \frac{1}{2} \right) \right]$$
(S38)

Case 3.  $\rho = \nu$  and  $\mu \neq \nu$ 

$$\left\langle \exp\left[\Delta_{x'x\nu}\left(\left(1-\mathrm{e}^{-\mathrm{i}\omega_{\nu}\tau}\right)b_{\nu}-\left(1-\mathrm{e}^{\mathrm{i}\omega_{\nu}\tau}\right)b_{\nu}^{\dagger}\right)\right]\left(b_{\nu}^{\dagger}+b_{\nu}-2\frac{\Gamma_{x'x'}^{\nu}}{\hbar\omega_{\nu}}\right)\right\rangle_{\mathrm{eq},\nu}=\left[\Delta_{x'x\nu}\left(1-\mathrm{e}^{-\mathrm{i}\omega_{\mu}\tau}\right)\left(1+n_{\nu}^{\mathrm{ph}}\right)+\Delta_{x'x\nu}\left(\mathrm{e}^{\mathrm{i}\omega_{\nu}\tau}-1\right)n_{\nu}^{\mathrm{ph}}-2\frac{\Gamma_{x'x'}^{\nu}}{\hbar\omega_{\nu}}\right]\times\right]\times\left(\mathrm{S39}\right]\times\exp\left[-2\Delta_{x'x\nu}^{2}\left(1-\cos\left(\omega_{\nu}\tau\right)\right)\left(n_{\nu}^{\mathrm{ph}}+\frac{1}{2}\right)\right]$$

Case 4.  $\rho = \mu = \nu$ 

$$\left\langle \left( b_{\mu}^{\dagger} \mathrm{e}^{\mathrm{i}\omega_{\mu}\tau} + b_{\mu} \mathrm{e}^{-\mathrm{i}\omega_{\mu}\tau} - 2\frac{\Gamma_{x'x'}^{\mu}}{\hbar\omega_{\mu}} \right) \exp\left[ \Delta_{x'x\mu} \left( (1 - \mathrm{e}^{-\mathrm{i}\omega_{\mu}\tau}) b_{\mu} - (1 - \mathrm{e}^{\mathrm{i}\omega_{\mu}\tau}) b_{\mu}^{\dagger} \right) \right] \left( b_{\mu}^{\dagger} + b_{\mu} - 2\frac{\Gamma_{x'x'}^{\mu}}{\hbar\omega_{\mu}} \right) \right\rangle_{\mathrm{eq},\mu} = \left\{ \left[ \Delta_{x'x\mu} \left( \mathrm{e}^{\mathrm{i}\omega_{\mu}\tau} - 1 \right) n_{\mu}^{\mathrm{ph}} + \Delta_{x'x\mu} \left( 1 - \mathrm{e}^{-\mathrm{i}\omega_{\mu}\tau} \right) \left( 1 + n_{\mu}^{\mathrm{ph}} \right) - 2\frac{\Gamma_{x'x'}^{\mu}}{\hbar\omega_{\mu}} \right]^{2} + \left( n_{\mu}^{\mathrm{ph}} \mathrm{e}^{\mathrm{i}\omega_{\mu}\tau} + (1 + n_{\mu}^{\mathrm{ph}}) \mathrm{e}^{-\mathrm{i}\omega_{\mu}\tau} \right) \right\} \times \exp\left[ -2\Delta_{x'x\mu}^{2} \left( 1 - \cos(\omega_{\mu}\tau) \right) \left( n_{\mu}^{\mathrm{ph}} + \frac{1}{2} \right) \right]$$

$$(S40)$$

Combining all these results together, we finally obtain

$$\left\langle M_{x'x\mu}^{(0)}(\tau)M_{xx'\nu}\right\rangle_{\rm eq} = \Gamma_{xx'}^{\nu}\Gamma_{x'x}^{\mu}\exp\left[-i\sum_{\rho}\Delta_{x'x\rho}^{2}\sin\left(\omega_{\rho}\tau\right) - \sum_{\rho}\Delta_{x'x\rho}^{2}\left(1-\cos(\omega_{\rho}\tau)\right)\coth\left(\frac{\beta\hbar\omega_{\rho}}{2}\right)\right] \times \left[\left(\Delta_{x'x\nu}\left({\rm e}^{{\rm i}\omega_{\nu}\tau}-1\right)n_{\nu}^{\rm ph}+\Delta_{x'x\nu}\left(1-{\rm e}^{-{\rm i}\omega_{\nu}\tau}\right)\left(1+n_{\nu}^{\rm ph}\right)-2\frac{\Gamma_{x'x'}^{\nu}}{\hbar\omega_{\nu}}\right)\times \left(\Delta_{x'x\mu}\left({\rm e}^{{\rm i}\omega_{\mu}\tau}-1\right)n_{\mu}^{\rm ph}+\Delta_{x'x\mu}\left(1-{\rm e}^{-{\rm i}\omega_{\mu}\tau}\right)\left(1+n_{\mu}^{\rm ph}\right)-2\frac{\Gamma_{x'x'}^{\mu}}{\hbar\omega_{\mu}}\right)+\delta_{\mu\nu}\left(n_{\mu}^{\rm ph}\,{\rm e}^{{\rm i}\omega_{\mu}\tau}+\left(1+n_{\mu}^{\rm ph}\right){\rm e}^{-{\rm i}\omega_{\mu}\tau}\right)\right]$$

$$(S41)$$

# S2.3 Introducing the Spectral Function

We now demonstrate how to rewrite the results obtained in previous sections in terms of the correlation function of undressed bath operators that mediate population transfer between different excitonic states. In other words, we firstly calculate

$$C_{\bar{x}_{2}x_{2},\bar{x}_{1}x_{1}}(t) = \sum_{\mu\nu} \left\langle M_{\bar{x}_{2}x_{2}\mu} |_{\text{Red}}^{(0)}(\tau) M_{\bar{x}_{1}x_{1}\nu} |_{\text{Red}} \right\rangle$$
$$= \sum_{\mu} \Gamma^{\mu}_{\bar{x}_{2}x_{2}} \Gamma^{\mu}_{\bar{x}_{1}x_{1}} \left[ \coth\left(\frac{\beta\hbar\omega_{\mu}}{2}\right) \cos\left(\omega_{\mu}t\right) - i\sin\left(\omega_{\mu}t\right) \right]$$
(S42)

This correlation function has the following properties under time reversal and exchange of indices

$$C_{\bar{x}_2 x_2, \bar{x}_1 x_1}(-t) = C^*_{\bar{x}_2 x_2, \bar{x}_1 x_1}(t)$$
(S43)

$$C_{\bar{x}_1x_1,\bar{x}_2x_2}(t) = C_{\bar{x}_2x_2,\bar{x}_1x_1}(t), \quad C_{x_1\bar{x}_1,\bar{x}_2x_2}(t) = C^*_{\bar{x}_1x_1,x_2\bar{x}_2}(t) = C_{\bar{x}_2x_2,\bar{x}_1x_1}(t)$$
(S44)

The integral of the correlation function  $C_{\bar{x}_2x_2,\bar{x}_1x_1}(t)$  is usually denoted as  $\dot{g}_{\bar{x}_2x_2,\bar{x}_1x_1}(t)$ 

$$\dot{g}_{\bar{x}_{2}x_{2},\bar{x}_{1}x_{1}}(t) = \int_{0}^{t} \mathrm{d}\tau \, C_{\bar{x}_{2}x_{2},\bar{x}_{1}x_{1}}(\tau) \\
= \sum_{\mu} \frac{\Gamma^{\mu}_{\bar{x}_{2}x_{2}}\Gamma^{\mu}_{\bar{x}_{1}x_{1}}}{\omega_{\mu}} \left( \coth\left(\frac{\beta\hbar\omega_{\mu}}{2}\right)\sin\left(\omega_{\mu}t\right) - \mathrm{i}\left(1 - \cos\left(\omega_{\mu}t\right)\right) \right)$$
(S45)

while double integral of the correlation function  $C_{\bar{x}_2x_2,\bar{x}_1x_1}(t)$  is commonly known under the name of lineshape function  $g_{\bar{x}_2x_2,\bar{x}_1x_1}(t)$ 

$$g_{\bar{x}_{2}x_{2},\bar{x}_{1}x_{1}}(t) = \int_{0}^{t} \mathrm{d}\tau \, \int_{0}^{\tau} \mathrm{d}\tau' \, C_{\bar{x}_{2}x_{2},\bar{x}_{1}x_{1}}(\tau') = \sum_{\mu} \frac{\Gamma_{\bar{x}_{2}x_{2}}^{\mu} \Gamma_{\bar{x}_{1}x_{1}}^{\mu}}{\omega_{\mu}^{2}} \left( \coth\left(\frac{\beta\hbar\omega_{\mu}}{2}\right) (1 - \cos\left(\omega_{\mu}t\right)) + \mathrm{i}\sin\left(\omega_{\mu}t\right) - \mathrm{i}\omega_{\mu}t \right)$$
(S46)

We may, therefore, write  $C_{\bar{x}_2x_2,\bar{x}_1x_1}(t) \equiv \ddot{g}_{\bar{x}_2x_2,\bar{x}_1x_1}(t)$ . Formally, the above definitions of  $\dot{g}$  and g are valid for t > 0, while for t < 0 we can use their properties under time reversal

$$\dot{g}_{\bar{x}_2 x_2, \bar{x}_1 x_1}(t) = -\dot{g}^*_{\bar{x}_2 x_2, \bar{x}_1 x_1}(-t), \quad g_{\bar{x}_2 x_2, \bar{x}_1 x_1}(t) = g^*_{\bar{x}_2 x_2, \bar{x}_1 x_1}(-t)$$
(S47)

In addition to quantities  $\ddot{g}, \dot{g}$ , and g, we also introduce

$$\lambda_{\bar{x}_2 x_2, \bar{x}_1 x_1} = \sum_{\mu} \frac{\Gamma^{\mu}_{\bar{x}_2 x_2} \Gamma^{\mu}_{\bar{x}_1 x_1}}{\hbar \omega_{\mu}} \tag{S48}$$

One may now rewrite eq S29, in which the result embodied in eq S41 is inserted, in terms of  $\ddot{g}, \dot{g}, g$ , and  $\lambda$  to obtain the expression for the rate of populaton transfer within the modified Redfield theory that is given in the main text.

In our model, phonon modes are counted by site index i and mode index  $\xi$ . If we now assume that the electron-phonon and hole-phonon coupling constants are independent of the site index i and the band index  $\beta_i, \alpha_i$  and are both equal to  $g_{\xi}$ , we can rewrite the exciton-phonon coupling constants (eq S10) as

$$\Gamma^{i\xi}_{\bar{x}x} = g_{\xi} P^i_{\bar{x}x}, \quad P^i_{\bar{x}x} = \sum_{\beta_i} \sum_{j\alpha_j} \psi^{\bar{x}*}_{(j\alpha_j)(i\beta_i)} \psi^x_{(j\alpha_j)(i\beta_i)} - \sum_{\alpha_i} \sum_{j\beta_j} \psi^{\bar{x}*}_{(i\alpha_i)(j\beta_j)} \psi^x_{(i\alpha_i)(j\beta_j)}$$
(S49)

The spectral function J(E), defined for E > 0, conveniently combines information on the phonon density of states and the strength of the interaction of electronic excitations with phonons<sup>S5,S6</sup>

$$J(E) = \sum_{\xi} g_{\xi}^2 \delta(E - \hbar\omega_{\xi})$$
(S50)

Under these assumptions, all the quantities entering the expression for modified Redfield population transfer rates can be factorized into a product of one quantity that depends only on spatial properties of excitonic states involved and another quantity that depends only on the spectral density. In more detail,

$$\ddot{g}_{\bar{x}_2 x_2, \bar{x}_1 x_1}(t) = P_{\bar{x}_2 x_2, \bar{x}_1 x_1} \ddot{g}(t) \tag{S51}$$

with

$$P_{\bar{x}_2 x_2, \bar{x}_1 x_1} = \sum_i P^i_{\bar{x}_2 x_2} P^i_{\bar{x}_1 x_1} \tag{S52}$$

and

$$\ddot{g}(t) = \int_{0}^{+\infty} dE J(E) \left[ \coth\left(\frac{\beta E}{2}\right) \cos\left(\frac{Et}{\hbar}\right) - i\sin\left(\frac{Et}{\hbar}\right) \right]$$
(S53)

The quantity  $P_{\bar{x}_2x_2,\bar{x}_1x_1}$  represents a generalization of the so-called spatial proximity factor, which is obtained when  $\bar{x}_2 = \bar{x}_1$  and  $x_2 = x_1$ . Other quantities of our interest factorize as

$$\dot{g}_{\bar{x}_2 x_2, \bar{x}_1 x_1}(t) = P_{\bar{x}_2 x_2, \bar{x}_1 x_1} \dot{g}(t)$$
 (S54a)

$$\dot{g}(t) = \hbar \int_{0}^{+\infty} dE \, \frac{J(E)}{E} \left[ \coth\left(\frac{\beta E}{2}\right) \sin\left(\frac{Et}{\hbar}\right) - i\left(1 - \cos\left(\frac{Et}{\hbar}\right)\right) \right] \tag{S54b}$$

$$g_{\bar{x}_2 x_2, \bar{x}_1 x_1}(t) = P_{\bar{x}_2 x_2, \bar{x}_1 x_1} g(t)$$
 (S55a)

$$g(t) = \hbar^2 \int_0^{+\infty} dE \, \frac{J(E)}{E^2} \left[ \coth\left(\frac{\beta E}{2}\right) \left(1 - \cos\left(\frac{Et}{\hbar}\right)\right) + i\sin\left(\frac{Et}{\hbar}\right) - i\frac{Et}{\hbar} \right] \quad (S55b)$$

$$\lambda_{\bar{x}_2 x_2, \bar{x}_1 x_1} = P_{\bar{x}_2 x_2, \bar{x}_1 x_1} \lambda \tag{S56a}$$

$$\lambda = \int_0^{+\infty} \mathrm{d}E \, \frac{J(E)}{E} \tag{S56b}$$

Let us now discuss how quantities  $\ddot{g}, \dot{g}$ , and g are practically calculated once we specify the spectral density J(E). Enlarging the domain of J(E) by defining J(-E) = -J(E), eq S53 can be rewritten as

$$\ddot{g}(t) = \int_{-\infty}^{+\infty} \mathrm{d}E \, J(E) \frac{\mathrm{e}^{\mathrm{i}Et/\hbar}}{\mathrm{e}^{\beta E} - 1} \tag{S57}$$

If we now take that the spectral density is of the Drude–Lorentz form

$$J_{\rm DL}(E) = \frac{2}{\pi} \lambda \frac{E \cdot \hbar \gamma}{E^2 + (\hbar \gamma)^2},\tag{S58}$$

we see that the integral appearing in eq S57 can be evaluated by applying the Jordan lemma. Eventually, we express  $\ddot{g}(t)$  in terms of an (in principle infinite) series of exponentially decaying factors

$$\ddot{g}(t) = \sum_{m=0}^{+\infty} c_m \mathrm{e}^{-\mu_m t}$$
 (S59)

where complex constants  $c_m$  stem from residues, while real and positive constants  $\mu_m$  are connected to poles of the function under the integral sign in eq S57. The pole 0 stems from the pole of the Drude–Lorentz spectral function and is known as the Drude pole

$$\mu_0 = \gamma, \qquad c_0 = \lambda \cdot \hbar \gamma \left[ \cot\left(\frac{\beta \hbar \gamma}{2}\right) - \mathbf{i} \right]$$
 (S60)

The remaining poles arise from the following representation of the Bose–Einstein factor

$$\frac{1}{e^z - 1} = \frac{1}{z} - \frac{1}{2} + \sum_{m=1}^{+\infty} \eta_m \left[ \frac{1}{z - i\xi_m} + \frac{1}{z + i\xi_m} \right]$$
(S61)

so that

$$\mu_m = \frac{\xi_m}{\beta\hbar}, \qquad c_m = 4 \cdot \eta_m \cdot \lambda \cdot k_B T \frac{\gamma\mu_m}{\mu_m^2 - \gamma^2}, \quad m \ge 1$$
(S62)

In the Matsubara representation,  $\xi_m = 2\pi \cdot m$ ,  $\eta_m = 1$ , while, in numerical computations, better convergence properties of the series entering eq S59 are achieved by employing Padé representation, as introduced in refs S7,S8.

The expressions for other quantities are

$$\dot{g}(t) = \sum_{m=0}^{+\infty} c_m \frac{1 - e^{-\mu_m t}}{\mu_m}$$
(S63)

$$g(t) = \sum_{m=0}^{+\infty} c_m \frac{\mathrm{e}^{-\mu_m t} + \mu_m t - 1}{\mu_m^2}$$
(S64)

### S2.4 Derivation of Förster and Marcus Transition Rates

In this subsection, we will show that modified Redfield transition rates reduce in appropriate limits to Förster and Marcus transition rates. We first derive the Förster transition rate by making certain approximations in the expression for transition rates given in eq 16 in the main part of the manuscript. Throughout the derivation we assume that exciton states x and x' are well spatially separated from each other. The derivation largely follows ref S9.

First, we neglect the terms  $\ddot{g}_{x'x,xx}(t)$  that represent the correlations between fluctuations of the energy of state x and fluctuations of the coupling between x and x'. Therefore, we have  $\ddot{g}_{x'x,xx}(t) = 0$ . Consequently,  $\dot{g}_{x'x,xx}$  does not depend on time. Since it is equal to zero at t = 0 (as can be seen from eq S54b), we have  $\dot{g}_{x'x,xx}(t) = 0$  for each t. In a similar manner, we conclude that  $\dot{g}_{x'x,x'x'}(t) = 0$ ,  $\dot{g}_{xx',xx}(t) = 0$ , and  $\dot{g}_{xx',x'x'}(t) = 0$ . The fact that  $\dot{g}_{x'x,x'x'}(t) = 0$  also implies that  $\lambda_{x'x,x'x'} = 0$  since it can be shown that  $-\lim_{t\to\infty} \operatorname{Im} \dot{g}_{x'x,x'x'}(t) = \hbar \lambda_{x'x,x'x'}$ . Next, we assume that autocorrelation of the coupling between x and x' is static, i.e.  $\ddot{g}_{x'x,xx'}(t) = |V_{xx'}|^2$ , where  $|V_{xx'}|^2$  does not depend on time. Our next assumption concerns the correlation between fluctuations of the energy of the state x and x', which is neglected, i.e.  $\ddot{g}_{x'x',xx}(t) = 0$ . Since  $\dot{g}_{x'x',xx}(t) = 0$  (as can be seen from eq S54b), we then conclude that  $\dot{g}_{x'x',xx}(t) = 0$  for each t. Since  $g_{x'x',xx}(t=0) = 0$  (as can be seen from eq S55b), we also conclude that  $g_{x'x',xx}(t) = 0$  for each t. For spatially well separated states x and x' the proximity factor  $P_{x'x',xx}$  is much smaller than  $P_{xx,xx}$  and  $P_{x'x',x'x'}$ . For this reason  $\lambda_{x'x',xx}$  can be neglected in comparison to  $\lambda_{xx,xx}$  and  $\lambda_{x'x',x'x'}$ . Making use of all these approximations, eq 16 from the main part of the manuscript takes the form

$$w_{xx'} = \frac{|V_{xx'}|^2}{\hbar^2} \int_{-\infty}^{\infty} \mathrm{d}t \; F_{x'}^*(t) \; A_x(t) \tag{S65}$$

where

$$A_x(t) = \exp\left(-i\tilde{\omega}_x t - \frac{1}{\hbar^2}g_{xx,xx}(t) - \frac{i}{\hbar}\lambda_{xx,xx}t\right)$$
(S66)

$$F_x^*(t) = \exp\left(i\tilde{\omega}_x t - \frac{1}{\hbar^2}g_{xx,xx}(t) - \frac{i}{\hbar}\lambda_{xx,xx}t\right)$$
(S67)

Equation S65 is in the form of Förster transition rate where  $F_{x'}$  has the meaning of the fluorescence of the donor,  $A_x$  is the absorption of the acceptor, while  $|V_{xx'}|^2$  represents the

coupling between the donor and the acceptor.

It is known from the literature (see, e.g., Ch. 7.4.2 of ref S5 or ref S10) that a formula analogous to eq S65 holds also in the case of electron transfer. In this case,  $F_{x'}$  should be interpreted in terms of the charge disassociation from the donor state, while  $A_x$  should be interpreted in terms of the charge association to the acceptor state. Also, the static autocorrelation of the coupling between x' and x,  $|V_{xx'}|^2$ , is then meant to originate from the electronic coupling. Let us pass to the limit of high temperature and strong coupling to phonons, when the function under the integral sign in eq S65 quickly decays to zero as |t| is increased from zero. To evaluate the function g(t) from eq S55b we make use of the approximations  $\cos \frac{Et}{\hbar} = 1 - \frac{1}{2} \left(\frac{Et}{\hbar}\right)^2$  and  $\sin \frac{Et}{\hbar} = \frac{Et}{\hbar}$  that are valid for small values of the argument  $\frac{Et}{\hbar}$  and the approximation  $\operatorname{cth} \frac{\beta E}{2} = \frac{2}{\beta E}$  which is valid since the argument  $\frac{\beta E}{2}$  is small when the temperature is high. Making use of eq S56b, we obtain that  $g(t) = \frac{\lambda}{\beta}t^2$  in this limit. Substituting this result for g(t) in eq S65 and performing the integration we obtain

$$w_{xx'} = \frac{2\pi}{\hbar} |V_{xx'}|^2 \frac{1}{\sqrt{4\pi k_B T (\lambda_{xx,xx} + \lambda_{x'x',x'x'})}} \exp\left[-\frac{(\hbar \tilde{\omega}_x - \hbar \tilde{\omega}_{x'} + (\lambda_{xx,xx} + \lambda_{x'x',x'x'}))^2}{4k_B T (\lambda_{xx,xx} + \lambda_{x'x',x'x'})}\right]$$
(S68)

Equation S68 assumes the form of the well-known Marcus formula (in the case when the donor and acceptor have two independent sets of vibrational coordinates).

### S2.5 Computation of Modified Redfield Population Transition Rates

In our computations, excitonic wavefunctions  $\psi^x_{(i\alpha_i)(j\beta_j)}$  are purely real. This can help us (by virtue of eq S44) reduce the expression for the population transition rate  $w_{xx'}$  from state  $|x'\rangle$ 

to state  $|x\rangle$  (given in the main text) to the following form

$$w_{xx'} = \gamma \int_{-\infty}^{+\infty} dz \, \exp\left(\mathrm{i}\frac{\widetilde{\omega}_{x'} - \widetilde{\omega}_x}{\gamma} z\right) \exp\left(-\mathcal{P}_{xx'} \operatorname{Re}\left\{G(z)\right\}\right) \times \\ \times \exp\left(-\mathrm{i}\mathcal{P}_{xx'}\left(\operatorname{Im}\left\{G(z)\right\} + \frac{\lambda}{\hbar\gamma} z\right)\right) \times \\ \times \left[P_{x'x,x'x}\ddot{G}(z) - \left(\left(P_{x'x,xx} - P_{x'x,x'x'}\right)\dot{G}(z) - 2\mathrm{i}P_{x'x,x'x'}\frac{\lambda}{\hbar\gamma}\right)^2\right]$$
(S69)

In the last equation, z is a real dimensionless variable  $(z = \gamma t, \text{ where } t \text{ is time})$ ,

$$\mathcal{P}_{xx'} = P_{xx,xx} - 2P_{xx,x'x'} + P_{x'x',x'x'} \tag{S70}$$

while dimensionless functions  $\ddot{G}, \dot{G}, G$  of dimensionless variable z are introduced as

$$\ddot{G}(z) = (\hbar\gamma)^{-2} \ddot{g}(\gamma^{-1}z), \quad \dot{G}(z) = (\hbar\gamma)^{-1} \hbar^{-1} \dot{g}(\gamma^{-1}z), \quad G(z) = \hbar^{-2} g(\gamma^{-1}z)$$
(S71)

Bearing in mind that, for large z, G(z) is proportional to z (see eq S64), the interval on which the integration in eq S69 has to be performed is essentially determined by the decay constant of the exponent exp  $(-\mathcal{P}_{xx'} \operatorname{Re} \{G(z)\})$ . The decay constant of the exponent is easily determined to be

decay constant<sub>xx'</sub> = 
$$\left\{ \mathcal{P}_{xx'} \frac{\lambda}{\hbar\gamma} \left[ \cot\left(\frac{\beta\hbar\gamma}{2}\right) + 4\sum_{m} \frac{\eta_m/(\beta\hbar\gamma)}{(\xi_m/(\beta\hbar\gamma))^2 - 1} \right] \right\}^{-1}$$

In order to perform integrations for all transitions on the same grid of z values, we first compute the maximum decay constant, which is attained for the minimum value of  $\mathcal{P}_{xx'}$ . Then, the infinities in eq S69 in numerical integrations become a multiple of the maximum decay constant. That way, we compute functions  $\ddot{G}, \dot{G}, G$  once for all possible transitions, and subsequently perform all integrations using these precomputed values. By virtue of the detailed balance condition (eq S30), we compute only rates of transitions that are downward in renormalized energy, i.e.,  $\tilde{\omega}_{x'} > \tilde{\omega}_x$ . Now that we know the length of the integration interval, it is important to specify the integration step, i.e., to know how dense the grid on which we compute  $\ddot{G}, \dot{G}, G$  is. The integration in eq S69 can be numerically challenging due to the presence of the oscillatory exponential exp (i( $(\tilde{\omega}_{x'} - \tilde{\omega}_x)/\gamma$ )z), whose oscillation frequency can be large. Numerical integration of eq S69 is implemented using the so-called Filon-trapezoidal rule.<sup>S11</sup> The integral

$$F(\omega) = \int_{-Z}^{Z} \mathrm{d}z \,\mathrm{e}^{\mathrm{i}\omega z} f(z) \tag{S72}$$

can be approximated as

$$F(\omega) \approx \Delta z \sum_{n=-N}^{N} w_n e^{i\omega n \Delta z} f(n\Delta z)$$
 (S73)

where  $Z = N\Delta z$ , while the weights  $w_n$  read as

$$w_n = \begin{cases} (1 + i\omega\Delta z - e^{i\omega\Delta z})/(\omega\Delta z)^2, & n = -N\\ \sin^2(\omega\Delta z/2)/(\omega\Delta z/2)^2, & n \neq \pm N\\ (1 - i\omega\Delta z - e^{-i\omega\Delta z})/(\omega\Delta z)^2. & n = N \end{cases}$$
(S74)

These weights are obtained by assuming that, on an interval of length  $\Delta z$ , f(z) can be approximated by a linear function. On the other hand, the ordinary trapezoidal rule assumes that the whole function under the integral sign,  $e^{i\omega z}f(z)$ , can be approximated by a straight line on the same interval. This assumption is not satisfied when the frequency  $\omega$  is large.

When the integration range is infinite, as is in our case, the Filon-trapezoidal rule is simply the result of the ordinary trapezoidal rule multiplied by  $\sin^2(\omega\Delta z/2)/(\omega\Delta z/2)^2$ . In numerical integration of eq S69, we use  $\Delta z = 10^{-2}$ . For the exemplary value of  $\gamma$ ,  $\gamma^{-1} = 100$  fs, the integration step in the time domain in  $\Delta t = 1$  fs.

In the end, let us comment on the number of terms in eq S59 that is sufficient to reliably approximate function  $\ddot{g}$ . The same number of terms then appears in eqs S63 and S64 that are used to calculate functions  $\dot{g}$  and g. Namely, the Redfield transition rate is entirely expressed in terms of the Fourier component of  $\ddot{g}$ 

$$w_{xx'}^{\text{Red}} = P_{x'x,xx'} \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} \mathrm{d}t \, \mathrm{e}^{\mathrm{i}(\omega_{x'} - \omega_x)t} \ddot{g}(t) \tag{S75}$$

Therefore, one may compute the last integral numerically and compare the value thus obtained to the analytical solution, which is expressed in terms of the spectral density and Bose–Einstein factor

$$\frac{1}{\hbar^2} \int_{-\infty}^{+\infty} \mathrm{d}t \, \mathrm{e}^{\mathrm{i}(\omega_{x'} - \omega_x)t} \ddot{g}(t) = \frac{2\pi}{\hbar} J(|\hbar\omega_x - \hbar\omega_{x'}|) \times \begin{cases} n_{\mathrm{BE}}(\hbar\omega_x - \hbar\omega_{x'}), & \omega_x > \omega_{x'} \\ 1 + n_{\mathrm{BE}}(\hbar\omega_{x'} - \hbar\omega_x), & \omega_x < \omega_{x'} \end{cases}$$
(S76)

Since the energy gap between the highest and the lowest excitonic state in a single disorder realization can be  $\gtrsim 1 \text{ eV}$ , it is important to take enough poles in order to numerically reproduce Redfield rates between states distant in energy. As we have already mentioned, we use the Padé decomposition of the Bose–Einstein function  $(e^z - 1)^{-1}$  and implement the algorithm outlined in Refs. S7,S8 to obtain coefficients  $c_m$  and  $\mu_m$  for  $m \geq 1$ . Focusing on energetically downward transitions, we find that, taking into account 5 Padé poles (in addition to the Drude pole labeled by 0), numerically computed transition rate does not deviate more that 1% from its exact value in the whole range of energy gaps from 0 to 1 eV. Therefore, in all the computations, we take that index m in eq S59 can assume values from 0 to 5.

### S2.6 Solving the System of Rate Equations

Since our aim is to understand not only the time scales and pathways of charge separation, but also that of exciton recombination, in addition to excitonic populations  $f_x(t)$ , we also consider the ground-state population  $f_{GS}(t)$  as an independent variable. Similarly to our recent study,<sup>S2</sup> we assume that free-charge states and the ground state act as absorbing states, that is, once an exciton performs a transition to a free-charge state or to the ground state, it cannot perform any further transitions. Therefore, if  $|x\rangle$  is not a free-charge state, the population  $f_x(t)$  evolves according to

$$\partial_t f_x(t) = \sum_{\substack{x'(\neq x)\\x'\notin \text{free}}} w_{xx'} f_{x'}(t) - \sum_{x'(\neq x)} w_{x'x} f_x(t) - \tau_x^{-1} f_x(t), \quad x \notin \text{free}$$
(S77)

If  $|x\rangle$  is a free-charge state or the ground state, it can only gain population from states that are not free-charge states

$$\partial_t f_x(t) = \sum_{x' \notin \text{free}} w_{xx'} f_{x'}(t), \quad x \in \text{free}$$
 (S78)

$$\partial_t f_{\rm GS}(t) = \sum_{x \notin \text{free}} \tau_x^{-1} f_x(t) \tag{S79}$$

Our treatment of external contacts is therefore idealized in the sense that we assumed that each electron-hole pair that reaches the free charge state leads to a flowing charge in the external circuit. Realistic contacts are never perfect and the charge yield could further deteriorate due to the effects in contacts. The system of rate equations for excitonic populations can be written in the matrix form as

$$\partial_t f_x(t) = \sum_{x'} A_{xx'} f_{x'}(t) \tag{S80}$$

where time-independent matrix  $\hat{A}$  has the following nonzero entries

$$A_{xx'} = (1 - \delta_{xx'})w_{xx'} - \delta_{xx'} \left(\sum_{\tilde{x} \neq x} w_{\tilde{x}x} + \tau_x^{-1}\right) \text{ if } x \notin \text{ free and } x' \notin \text{ free}$$
(S81)

$$A_{xx'} = \sum_{x' \notin \text{free}} w_{xx'} \text{ if } x \in \text{free}$$
(S82)

$$A_{\mathrm{GS},x'} = \tau_{x'}^{-1} \text{ if } x' \notin \text{free}$$
(S83)

Once initial conditions  $f_x(0)$  are known, eq S80 is formally solved as

$$f_x(t) = \langle x | f(t) \rangle = \langle x | e^{\hat{A}t} | f(0) \rangle$$
(S84)

However, the calculation of the matrix exponent  $\exp(\hat{A}t)$  is somewhat involved, since matrix  $\hat{A}$  is nonsymmetric. Although it is, in principle, possible to obtain eigenvalues, right and left eigenvectors of matrix  $\hat{A}$ , that is, to obtain the spectral decomposition of  $\hat{A}$ , our computations revealed that this method is not numerically stable. Therefore, in the following text, we describe our approach to solving eq S80.

We seek the solution to eq S80 in the form

$$f_x^{\text{part}}(t) = e^{\lambda_k t} c_{xk} \tag{S85}$$

Inserting eq S85 into eq S80, we obtain that constants  $\lambda_k$  and  $c_{xk}$  satisfy

$$\sum_{x'} A_{xx'} c_{x'k} = \lambda_k c_{xk} \tag{S86}$$

In other words,  $\lambda_k$  are eigenvalues of matrix  $\hat{A}$ , while  $c_{xk}$  is the x-th component of its kth right eigenvector. The general solution can be found as the superposition of particular solutions given in eq S85

$$f_x(t) = \sum_k \alpha_k \mathrm{e}^{\lambda_k t} c_{xk} \tag{S87}$$

Using the initial conditions  $f_x(0)$ , we find that the amplitudes  $\alpha_k$  satisfy the following system of linear algebraic equations

$$f_x(0) = \sum_k \alpha_k c_{xk} \tag{S88}$$

Therefore, the algorithm to solve for the time evolution of eq S80 for arbitrary t may proceed as follows:

1. solve the eigenvalue problem (eq S86) and find eigenvalues  $\lambda_k$  and right eigenvectors

 $c_{xk}$  of matrix  $\hat{A}$ ;

- 2. using initial conditions for excitonic populations, determine the amplitudes  $\alpha_k$  by solving the system of linear algebraic equations given in eq S88;
- 3. using eq S87, we can compute populations at an arbitrary instant t.

Let us note that our algorithm leans on the nondegeneracy of eigenvalues of matrix A. There is no manner in which this nondegeneracy can be proven in the general case. However, since the entries of matrix  $\hat{A}$  are basically determined by random numbers stemming from the disordered electron and hole on-site energies, we may hope that the eigenvalues of  $\hat{A}$  are nondegenerate.

In the end, let us mention how we achieve resolution of separation and recombination events in terms of character of states from which they start. Integrating eq S78, in which we replace populations  $f_{x'}(t)$  of non-free states by the expression given in eq S87, we obtain

$$f_x(t) = \sum_{x' \notin \text{free}} \sum_k w_{xx'} \alpha_k c_{x'k} \frac{e^{\lambda_k t} - 1}{\lambda_k}$$
(S89)

The total population of free-charge states at instant t can be decomposed as a sum of populations that have been transferred up to t from various groups of non-free states

$$\sum_{x \in \text{free}} f_x(t) = \left(\sum_{x' \in \text{CT}} + \sum_{x' \in \text{XA}} + \sum_{x' \in \text{XD}} + \sum_{x' \in \text{CS}}\right) \sum_{x \in \text{free}} \sum_k w_{xx'} \alpha_k c_{x'k} \frac{e^{\lambda_k t} - 1}{\lambda_k}$$
(S90)

so that the four summands on the right-hand side of the last equation represent the total population transferred to all free states from CT, XA, XD, and CS states, respectively, up to time t. In a similar manner, analyzing the population of the ground state  $f_{\rm GS}(t)$ , we can resolve the recombination events by using

$$f_{\rm GS}(t) = \left(\sum_{x'\in{\rm CT}} +\sum_{x'\in{\rm XA}} +\sum_{x'\in{\rm XD}} +\sum_{x'\in{\rm CS}}\right) \sum_k \tau_{x'}^{-1} \alpha_k c_{x'k} \frac{e^{\lambda_k t} - 1}{\lambda_k}$$
(S91)

where the four summands on the right-hand side represent the total population transferred up to time t from CT, XA, XD, and CS states to the ground state.

# S3 Useful Identities

Here, we give a list of identities that we used to calculate the bath correlation function in Sec. S2.2. These are the identities for equilibrium expectation values in the case of a single bosonic mode. In the following,  $z_1$  and  $z_2$  are complex numbers,  $b^{\dagger}$  and b are Bose creation and annihilation operator, the Hamiltonian is  $\hbar \omega b^{\dagger} b$ , the averaging is with respect to the canonical distribution at temperature T, and  $n^{\text{ph}} = (e^{\beta\hbar\omega} - 1)^{-1}$ .

$$\left\langle e^{z_1 b^{\dagger} + z_2 b} \right\rangle_{eq} = e^{z_1 z_2 \left( n^{ph} + \frac{1}{2} \right)}$$
(S92)

$$\left\langle b^{\dagger} \mathrm{e}^{z_1 b^{\dagger} + z_2 b} \right\rangle_{\mathrm{eq}} = z_2 n^{\mathrm{ph}} \mathrm{e}^{z_1 z_2 \left( n^{\mathrm{ph}} + \frac{1}{2} \right)} \tag{S93}$$

$$\left\langle b e^{z_1 b^{\dagger} + z_2 b} \right\rangle_{\text{eq}} = z_1 (n^{\text{ph}} + 1) e^{z_1 z_2 \left( n^{\text{ph}} + \frac{1}{2} \right)}$$
 (S94)

$$\left\langle \mathrm{e}^{z_1 b^{\dagger} + z_2 b} b \right\rangle_{\mathrm{eq}} = z_1 n^{\mathrm{ph}} \mathrm{e}^{z_1 z_2 \left( n^{\mathrm{ph}} + \frac{1}{2} \right)} \tag{S95}$$

$$\left\langle e^{z_1 b^{\dagger} + z_2 b} b^{\dagger} \right\rangle_{eq} = z_2 (n^{ph} + 1) e^{z_1 z_2 \left( n^{ph} + \frac{1}{2} \right)}$$
 (S96)

$$\left\langle b e^{z_1 b^{\dagger} + z_2 b} b \right\rangle_{eq} = z_1^2 n^{ph} (n^{ph} + 1) e^{z_1 z_2 \left( n^{ph} + \frac{1}{2} \right)}$$
(S97)

$$\left\langle b^{\dagger} \mathrm{e}^{z_1 b^{\dagger} + z_2 b} b \right\rangle_{\mathrm{eq}} = n^{\mathrm{ph}} (1 + z_1 z_2 n^{\mathrm{ph}}) \mathrm{e}^{z_1 z_2 \left( n^{\mathrm{ph}} + \frac{1}{2} \right)}$$
(S98)

$$\left\langle b \mathrm{e}^{z_1 b^{\dagger} + z_2 b} b^{\dagger} \right\rangle_{\mathrm{eq}} = (1 + n^{\mathrm{ph}}) [1 + z_1 z_2 (1 + n^{\mathrm{ph}})] \mathrm{e}^{z_1 z_2 \left(n^{\mathrm{ph}} + \frac{1}{2}\right)}$$
(S99)

$$\left\langle b^{\dagger} \mathrm{e}^{z_1 b^{\dagger} + z_2 b} b^{\dagger} \right\rangle_{\mathrm{eq}} = z_2^2 n^{\mathrm{ph}} (1 + n^{\mathrm{ph}}) \mathrm{e}^{z_1 z_2 \left( n^{\mathrm{ph}} + \frac{1}{2} \right)}$$
(S100)

# S4 Supplemental Figures



Figure S2: Spatial properties of the initial donor states of different energies and in different disorder realizations. (a) and (b) Participation ratio for the electron and hole (see eq S14). (c) Mean electron-hole distance (in units of lattice spacing a). Data for the initial donor states located around 2000, 2200, and 2400 meV are represented by black circles, red squares, and blue triangles, respectively. Disorder-averaged data are summarized in the following table.

initial XD state	$2000~{\rm meV}$	$2200~{\rm meV}$	2400  meV
PR for the Electron	3.39	6.11	9.72
PR for the Hole	3.59	6.69	10.6
Electron–Hole Separation $(a)$	0.410	0.702	3.26



Figure S3: Spatial properties of the initial CT state in different disorder realizations. (a) and (b) Participation ratio for the electron and hole (see eq S14). (c) Mean electron-hole distance (in units of lattice spacing a). Disorder-averaged data are summarized in the following table.

initial CT state	
PR for the Electron	1.87
PR for the Hole	3.61
Electron–Hole Separation $(a)$	3.20



Figure S4: Delocalization properties of (a) and (b) XD, (c) and (d) CT, and (e) and (f) CS states quantified by the PR (see eq S14) of the constitutive carriers [electron in (a), (c), and (e), and hole in (b), (d), and (f)]. The graphs show PR as a function of the rescaled energy of excitonic states. The energy rescaling is performed assuming that the initial state  $|x_0\rangle$  is XD state with energy around 2200 meV. The graphs contain data for all states in all disorder realizations considered, and one dot represents one excitonic state. We note that higher-lying XD states feature more delocalized carriers. Also, in CT and CS states, the PR for the hole is larger than the PR for the electron because the magnitude of the transfer integral for holes in the donor is larger than the magnitude transfer integrals for electrons in the acceptor (see Table S1). We also note that in the states that are mainly involved in the separation process (see blue traces in Figure 6 of the main body of the manuscript), both carriers are well localized.



Figure S5: Comparison of excitonic population [(a), (c), and (e)] and recombination [(b), (d), and (f)] dynamics predicted by modified Redfield (MR) and Redfield (R) approaches for polaron binding energy  $\lambda = 5 \text{ meV}$  [(a) and (b)],  $\lambda = 80 \text{ meV}$  [(c) and (d)], and  $\lambda = 180 \text{ meV}$  [(e) and (f)]. Charge separation dynamics predicted by the MR approach is somewhat slower than that predicted by the R approach, mainly because the rates for the most important transitions for the full charge separation (XD $\rightarrow$ CT and CT $\rightarrow$ CS) are somewhat smaller in the MR than in the R approach. This is seen as increased recombination probability in (b), (d), and (f).



Figure S6: Comparison of transition rates  $w_R$  computed using the Redfield theory and transition rates  $w_{MR}$  computed using the modified Redfield theory. The plots presented originate from four different disorder realizations. Each point represents one pair  $(w_R, w_{MR})$ of transition rates between two excitonic states. We show data only for transitions for which  $w_R \ge 10^9 \text{ s}^{-1}$ . We find that around 90% of pairs shown in each plot lie within the area bounded by the two dashed red lines, i.e., the respective transition rates satisfy  $0.1 \le w_{MR}/w_R \le 10$ .



Figure S7: Time dependence of the number of CT excitons, 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 for disorder strength of  $\sigma = 50$  meV and three different values of parameter  $\gamma$ .



Figure S8: Time dependence of the number of CT excitons, 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 for disorder strength of  $\sigma = 100$  meV and three different values of parameter  $\gamma$ .



Figure S9: Time dependence of the number of CT excitons, XA excitons, XD excitons, CS excitons, free charges (free) and recombined pairs (GS) when initial state is a low-energy CT state. The results are shown at four different values of disorder strength  $\sigma$ .



Figure S10: Left panels: Time dependence of the number of recombined pairs from CT states (CT 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  $\sigma$ . Initial state is a low-energy CT state.



Figure S11: Energy and time resolved population of XD states  $[a_{XD}(e,t)]$ , CT states  $[a_{CT}(e,t)]$ , CS states  $[a_{CS}(e,t)]$  and free charges  $[a_{free}(e,t)]$ . Gaussian broadening of  $\sigma_E = 5 \text{ meV}$  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 2000 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.



Figure S12: Energy and time resolved population of XD states  $[a_{XD}(e,t)]$ , CT states  $[a_{CT}(e,t)]$ , CS states  $[a_{CS}(e,t)]$  and free charges  $[a_{free}(e,t)]$ . Gaussian broadening of  $\sigma_E = 5 \text{ meV}$  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 2400 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.



Figure S13: Energy and time resolved population of XD states  $[a_{\rm XD}(e,t)]$ , CT states  $[a_{\rm CT}(e,t)]$ , CS states  $[a_{\rm CS}(e,t)]$  and free charges  $[a_{\rm free}(e,t)]$ . Gaussian broadening of  $\sigma_E = 5 \text{ meV}$  was used to calculate these quantities. Initial state is XD state with energy around 2200 meV and disorder strength is  $\sigma = 50 \text{ meV}$ . 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 zero corresponds to lowest energy in a certain configuration, while 1 corresponds to highest energy of that configuration.



Figure S14: Dependence of separation yield on polaron binding energy  $\lambda$  when transition rates are modeled within modified Redfield theory for disorder strength of  $\sigma = 50 \text{ meV}$  (label MR-50) and  $\sigma = 100 \text{ meV}$  (label MR-100), and when transition rates are modeled within Redfield theory for disorder strength of  $\sigma = 50 \text{ meV}$  (label R-50) and  $\sigma = 100 \text{ meV}$  (label R-100). Initial state is a low-energy CT state.

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