Charge Separation Boosts Exciton Diffusion in Fused Ring Electron Acceptors Supporting Information

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Determining exciton states. To determine the energies and many-body wavefunctions of the excitons, we employ the linear-response time-dependent density functional theory (LR-TDDFT)^{1, 2} with an optimally tuned, screened and range-separated hybrid exchange-correlation functionals (OT-SRSH)³. The OT-SRSH involves the partition of the Coulombic interaction into a short-range and a long-range contribution based on the following expression⁴

$$\frac{1}{r} = \frac{1 - \left[\alpha + \beta erf(\gamma r)\right]}{r} + \frac{\alpha + \beta erf(\gamma r)}{r}.$$
 (1)

The hybrid exchange-correlation (XC) functional can be expressed as

$$E_{xc}^{RSH} = \alpha E_{xx} + \beta E_{xx}^{LR} + (1 - \alpha) E_{KSx} - \beta E_{KSx}^{LR} + E_{KSc}.$$
 (2)

Where E_{xx}/E_{xx}^{LR} is the Fock-like exact exchange energy, and E_{KSx}/E_{KSx}^{LR} and E_{KSc} are the semilocal Kohn-Sham (KS) exchange and correlation energy, respectively. LR labels the long-range XC terms. α determines the contribution from the exact exchange and β controls the contribution from the long-range exchange terms. γ is the range-separation parameter. Additionally, α and β satisfy the requirement of $\alpha + \beta = \varepsilon_0^{-1}$, where ε_0 is the scalar dielectric constant of the solid, thereby enforcing the correct asymptotic screening of the Coulomb tail⁵.

For the IDIC molecule, we set $\varepsilon = 1$ and $\alpha = 0$. The range-separation parameter γ is determined via Δ SCF method⁶ by minimizing the energy difference Δ E:

$$\Delta E(\gamma) = \left| E_h^{\gamma}(N) + I^{\gamma}(N) \right| + \left| E_h^{\gamma}(N+1) + I^{\gamma}(N+1) \right|$$
(3)

where $E_h^{\gamma}(N)$ is the HOMO of the N electron neutral system with a specific choice of γ and $I^{\gamma}(N)$ represents the energy difference between the ground state energy of N and N-1 electron systems with the same γ . All the total energies and eigenvalues for a single IDIC molecule are calculated with the range-separated functional. The minimum energy difference $\Delta E(\gamma)$ is achieved with $\gamma = 0.264$ Å⁻¹. For the amorphous IDIC solid, the average static dielectric constant ε is calculated as 4.25 with density functional perturbation theory (DFPT), which agrees with the estimated value of 4.86⁷ based on the polarizable continuum model. We set the same range-separation parameter γ of IDIC molecule for the solid, and $\alpha = 0.13$ is chosen to reproduce the experimental fundamental gap of 1.78 eV⁸. Note that an average fundamental gap obtained from 300 K MD simulations is used for the comparation with experimental value.

Phonon-assisted exciton transition rates. The thermal fluctuations of the ions could lead to an overlap between the exciton states in space and energy, and thus promote transitions between the excitonic states. Since these transitions can be nonadiabatic, the nonadiabatic *ab initio* molecular dynamics is used to describe the phonon-assisted exciton transitions⁹. During a molecular dynamics trajectory, the time-dependent many-body wave function of the excitonic state $\Psi(t)$ is expanded by a linear combination of a complete basis set consisting of the adiabatic ground state and the excited states $\Phi_I[R(t)]$ at the present ionic positions R(t):

$$\Psi(t) = \sum_{I=0}^{\infty} C_I(t) \Phi_I[R(t)]$$
(4)

where $C_I(t)$ is the expansion coefficient. Let the exciton start in a pure state *I* at t = 0 (i.e., $\Phi_I[R(t)]$) then the coefficient $C_I(t)$ in Eq. (4) can be labeled as $C_I^{(I)}(t)$ with the initial condition that $C_I^{(I)}(0) = \delta_{IJ}$. At t > 0, ions move and $\Psi(t)$ becomes a mixed state. Therefore $|C_I^{(I)}(t)|^2$ represents the probability that the exciton makes a transition from state *I* to state *J* during a small time interval of *t*. The phonon-assisted exciton transition rate from the state I to J, γ_{IJ}^{Phonon} is thus given by

$$\gamma^{Phonon}_{I,J} = \left\langle \frac{\left| \mathcal{C}_{J}^{(I)}(t) \right|^{2}}{t} \right\rangle_{\delta t}$$
(5)

The average is taken over a short MD trajectory of δt . Here we use $\delta t = 100$ fs to determine the phonon-assisted transition rates.

The evolution of $C_J(t)$ can be determined from the nonadiabatic molecular dynamics (NAMD) at each time step. Substituting Eq. (4) into the time-dependent Schrödinger equation, one arrives at the following equation involving the expansion coefficient $C_J(t)$:

$$\frac{\partial}{\partial t}C_{J}(t) = -\sum_{K}C_{K}(t)(\frac{i}{\mathsf{h}}\omega_{K}\delta_{JK} + D_{JK}) (6)$$

A standard second-order finite-difference method with a timestep of 10^{-3} fs is employed to propagate the coefficient $C_J(t)$. And D_{JK} is the nonadiabatic coupling between two many-body electronic states *J* and *K*,

$$D_{JK} \equiv \left\langle \Phi_{J} \left| \nabla_{R} \right| \Phi_{K} \right\rangle \cdot \frac{dR}{dt} = \left\langle \Phi_{J} \left| \frac{\partial}{\partial t} \right| \Phi_{K} \right\rangle$$
(7)

The similar calculations are adopted for P3HT and DPP(TBFu)₂. For P3HT, the supercell of 18 Å is used to model the amorphous solid, including three P3HT chains (606 atoms) each with eight thiophene rings, leading to a mass density of 1.1 g/cm³. The six highest occupied KS orbitals and nine lowest unoccupied KS orbitals are included in the Casidas formulation to produce 54 exciton states. For the DPP(TBFu)₂, the supercell of 19 Å containing six DPP(TBFu)₂ is used, leading to a mass density of 1.1 g/cm³. The six highest occupied KS orbitals and six lowest unoccupied KS orbitals are included in the Casidas formulation to produce 54 exciton states. For the DPP(TBFu)₂, the supercell of 19 Å containing six DPP(TBFu)₂ is used, leading to a mass density of 1.1 g/cm³. The six highest occupied KS orbitals and six lowest unoccupied KS orbitals are included in the Casidas formulation to produce 36 exciton states. The calculated charge density of the lowest energy exciton in amorphous P3HT and DPP(TBFu)₂ are displayed in the Figure R2, both are intramolecular excitons.



Figure S1. The charge density of the lowest energy exciton for (a) P3HT and (b) DPP(TBFu)₂. The red (green) iso-surface represents the charge density of electron (hole) at $0.0005e/Å^3$.



Figure S2. The variation of total energy of IDIC solid with respect to the dimension of the box.



Figure S3. The charge densities of six lowest energy excitons of amorphous IDIC, the corrsponing exciton energies are listed on top. The red (green) isosurface illustrates the charge density distribution of quasi-electron (hole) at +(-) 0.0005 Å⁻³.



Figure S4. The charge densities of the lowest energy excitons of amorphous IDIC at different time during the BOMD simulation. The red (green) isosurface illustrates the charge density distribution of quasi-electron (hole) at $+(-) 0.0005 \text{ Å}^{-3}$.



Figure S5. The charge density of the lowest energy exciton for two IDIC molecules calculated with a dielectric constant of 2.0 in different configurations. The red (green) isosurface illustrates the charge density distribution of quasi-electron (hole) at $+(-) 0.0005 \text{ Å}^{-3}$. The total energy of each configuration is listed on the top. The schematic diagram for each configuration is also presented where the rectangle and line represent the top view and side view of the backbone of IDIC molecule, respectively.



Figure S6. The charge density of the lowest energy exciton for two IDIC molecules calculated with a dielectric constant of 4.25 in different configurations. The red (green) isosurface illustrates the charge density distribution of quasi-electron (hole) at +(-) 0.0005 Å⁻³. The total energy of each configuration is listed on the top. The schematic diagram for each configuration is also presented where the rectangle and line represent the top view and side view of the backbone of IDIC molecule, respectively.



Figure S7. Fourier transform (FT) of the time-dependent energy evolution of the lowest energy exciton for (a) IDIC, (b) DPP(TBFu)2, (c) P3HT, (d) diluted IDIC (75%) and (e) IDIC (50%). The average phonon frequencies contributed to the energy evolution of the exciton are listed on the top.



Figure S8. The charge density of the lowest energy exciton of amorphous IDIC with different mass densities. The IDIC (75%) and IDIC (50%) represent the diluted IDIC solid with 75% and 50% mass density of that of undiluted one, respectively. The red (green) isosurface illustrates the charge density distribution of quasi-electron (hole) at +(-) 0.0005 Å⁻³.

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