First-Principles Study of Exciton Diffusion and Dissociation in Organic Solar Cells

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Advantages of organic solar cells

- Inexpensive to fabricate
- Solution-processed in a roll-to-roll fashion with high throughput
- Low weight & flexible; Compatible with plastic substrates
- High optical adsorption coefficients that permit the use of very thin films
- Based on earth-abundant & non-toxic materials

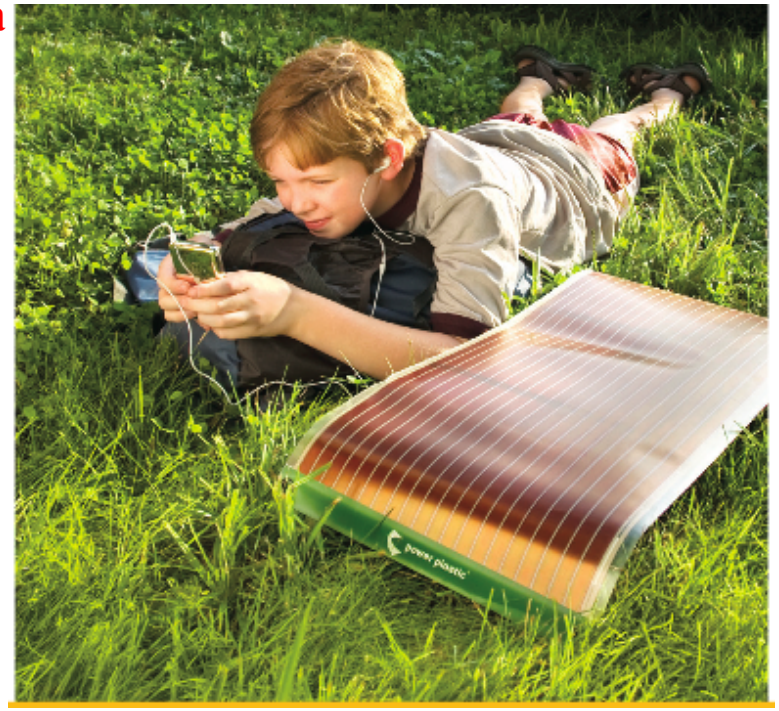
Problem: efficiency is too low (record: 5%); the goal is 10%

Major Bottlenecks of low efficiency

- Low exciton diffusion length
- Low carrier mobility

Plastic solar cell commercialized by Konarka

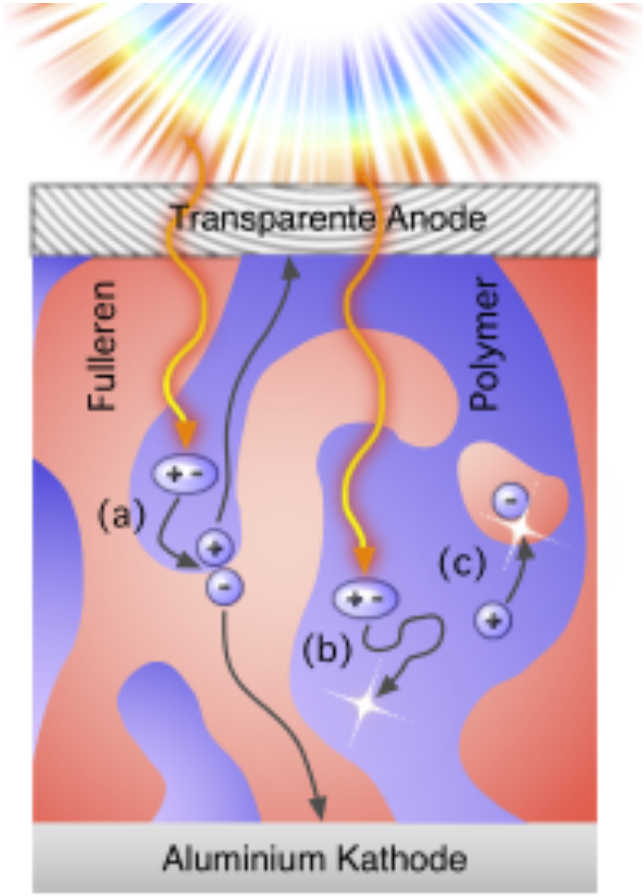
▼ Solar Powered Carport, West Palm Beach, FL



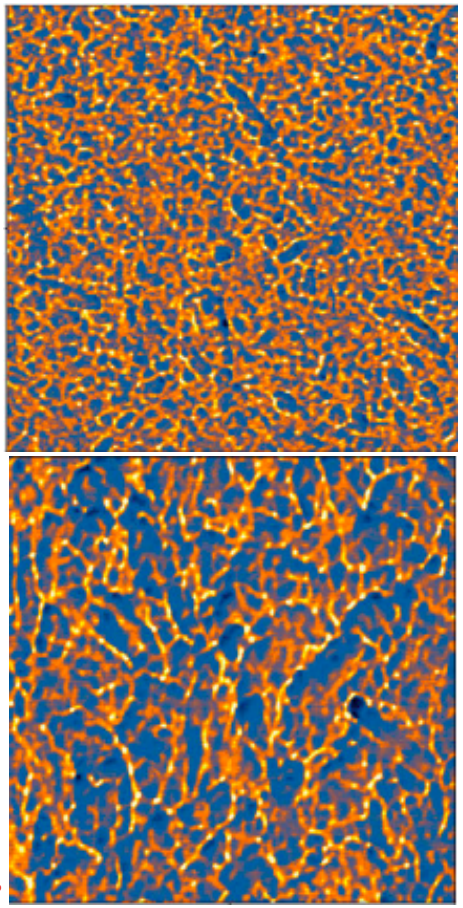
▼ Looking Through Semi-Transparent Power Plastic

Bulk Heterojunction (BHJ) Donor/Acceptor Architecture

Halls, et al., Nature (1995); Yu et al., Science (1995).



Bi-continuous donor & acceptor phases
Blue: donor (polymers)
Pink: acceptor (fullerenes)
Best material: P3HT/PCBM



2 μm x 2 μm

B. Walker (2009)

1. A photon excites donor phase creating an exciton **(Optimal band-gap to enhance adsorption)**

2. Exciton diffuses to D/A interface where it dissociates into a bound electron and hole pair. Excitons that do not reach the interface recombine and do not contribute to photocurrent **(Increase diffusion length)**

3. Bound electron-hole pair separates into free carriers **(enhance interfacial charge separation)**

4. Carrier transport to electrodes for collection **(high carrier mobility)**

First-principles prediction of carrier mobility in disordered semiconducting polymers as a function of T, carrier concentration and electric field.

Phys. Rev. B **82,** 205210 (2010)

Goal:

(1)Develop first-principles based method to predict exciton diffusion length and exciton interfacial dissociation

(2) Understand physical mechanisms underlying exciton dynamics

(3) Guide/accelerate experimental discovery of more efficient materials

First-principles description of exciton dynamics

Basic Ingredients:

1. Exciton states are **localized** due to disordered nature of amorphous polymer

2. Thermal fluctuation of molecular conformations gives rise to non-adiabatic transitions between excitonic states (phonons are important!)

Non-adiabatic *ab initio* molecular dynamics is essential to capture these transitions

3. Linear response theory of time-dependent DFT (LR-TDDFT) for describing exciton states

At each *ab initio* MD step *t*:

Exciton

$$\Psi(t) = \sum_I C_I(t)\Phi_I(t)$$

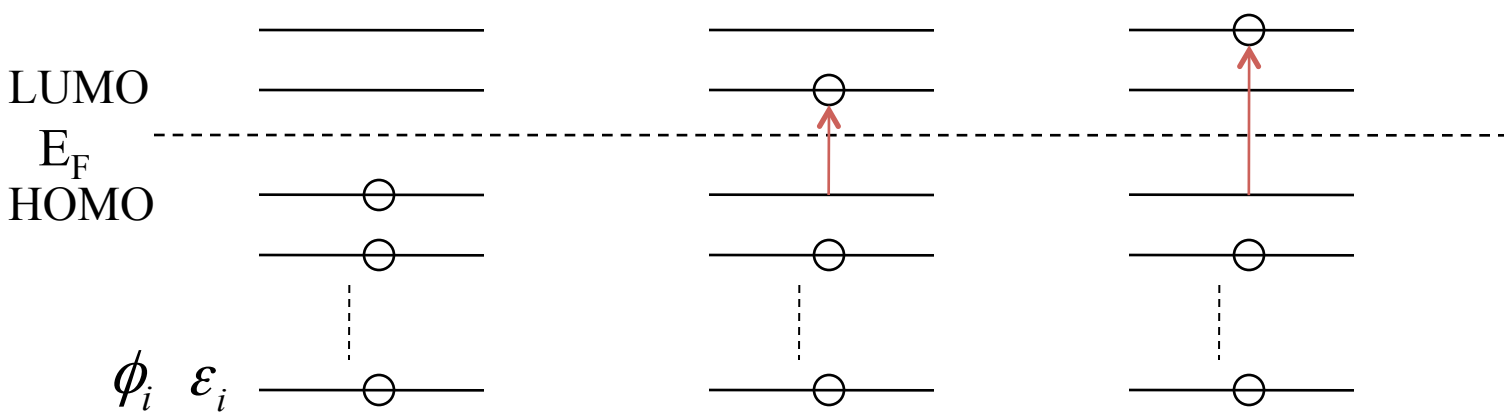
Expressed in terms of many-body **excited states** Φ_I & ω_I

TDDFT Linear Response theory

Casida's formulation

Kohn-Sham orbital ϕ_i & ε_i

Slater determinants (SD) for single excitations



Casida's formulation

Pseudo-eigenvalue equation based on TDDFT linear response theory:

$$\Omega F_I = \omega_I^2 F_I$$

matrix in the basis of KS states $\{ij\sigma\}$

energy of I-th excited state

$$\Omega_{ij\sigma,kl\tau} = \delta_{i,k}\delta_{j,l}\delta_{\sigma,\tau}(\varepsilon_{l\tau} - \varepsilon_{k\tau})^2 + 2\sqrt{(f_{i\sigma} - f_{j\sigma})(\varepsilon_{j\sigma} - \varepsilon_{i\sigma})}$$

$$\times K_{ij\sigma,kl\tau}\sqrt{(f_{k\tau} - f_{l\tau})(\varepsilon_{l\tau} - \varepsilon_{k\tau})}$$

occupational number

energy of KS orbital

i and k run over **occupied** KS orbitals
j and l run over **unoccupied** KS orbitals

Coupling matrix describes linear response of KS effective potential to changes in charge density:

$$K_{ij\sigma,kl\tau} = \iint \phi_{i\sigma}^*(\vec{r})\phi_{j\sigma}(\vec{r})\frac{1}{|\vec{r} - \vec{r}'|}\phi_{k\tau}(\vec{r}')\phi_{l\tau}^*(\vec{r}')d\vec{r}d\vec{r}'$$

$$+ \iint \phi_{i\sigma}^*(\vec{r})\phi_{j\sigma}(\vec{r})\frac{\delta^2 E_{\mathrm{xc}}}{\delta\rho_\sigma(\vec{r})\delta\rho_\tau(\vec{r}')}\phi_{k\tau}(\vec{r}')\phi_{l\tau}^*(\vec{r}')d\vec{r}d\vec{r}'$$

charge density

KS orbital

Assignment ansatz of Casida gives many-body wave-function of I-th excited state:

$$\Phi_I \approx \sum_{ij\sigma} \underbrace{\sqrt{\frac{\varepsilon_{j\sigma} - \varepsilon_{i\sigma}}{\omega_I}} F_{I,ij\sigma}}_{z_{I,ij}} \hat{a}^+_{j\sigma} \hat{a}_{i\sigma} \Phi_0$$

Ground state many-body wave function: Single Slater Determinant **(SD)** of the occupied KS orbitals

annihilation operator acting on KS orbital

$\hat{a}^+_{j\sigma} \hat{a}_{i\sigma} \Phi_0$: one electron is excited from occupied KS state i to unoccupied KS state j (single excitations only)

Many-body wave function of an exciton:

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

linear combination of the adiabatic ground state (I=0) and excited states wave functions (I >0); $\{\vec{R}(t)\}$: position of ions

Expectation value of single-particle operators

N-electron system, the single-particle operator: $\hat{A} = \sum_{i=1}^{N} \hat{a}_i$

Expectation value **(analytic result)**:

***i*: occupied orbitals; *j*: unoccupied orbitals**

$$\langle \Phi_I | \hat{A} | \Phi_I \rangle = \langle \Phi_0 | \hat{A} | \Phi_0 \rangle + \underbrace{\sum_{i,jj'} z^*_{I,ij} z_{I,ij'} \langle \varphi_j | \hat{a} | \varphi_{j'} \rangle}_{\text{quasi-electron part}} - \underbrace{\sum_{ii',j'} z^*_{I,ij} z_{I,i'j} \langle \varphi_{i'} | \hat{a} | \varphi_i \rangle}_{\text{quasi-hole part}}$$

expectation value in ground state

E.g., for coordinate operator:

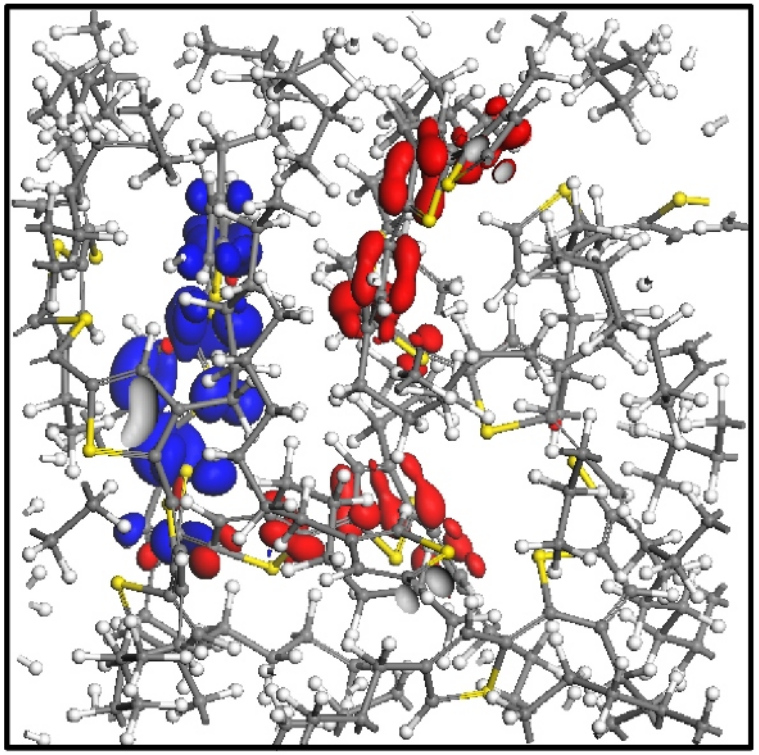
$$\langle \Phi_I | \hat{\vec{r}} | \Phi_I \rangle = \langle \Phi_0 | \hat{\vec{r}} | \Phi_0 \rangle + \underbrace{\sum_{i,jj'} z^*_{I,ij} z_{I,ij'} \langle \varphi_j | \vec{r} | \varphi_{j'} \rangle}_{\text{quasi-electron position } \vec{r}_e} - \underbrace{\sum_{ii',j'} z^*_{I,ij} z_{I,i'j} \langle \varphi_{i'} | \vec{r} | \varphi_i \rangle}_{\text{quasi-hole position } \vec{r}_h}$$

sum of positions of N electrons in ground state

Charge density operator: $\hat{\rho} = \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i)$

$$\langle \Phi_I | \hat{\rho} | \Phi_I \rangle = \rho_0(\vec{r}) + \underbrace{\sum_{i,jj'} z^*_{I,ij} z_{I,ij'} \varphi^*_j(\vec{r}) \varphi_{j'}(\vec{r})}_{\text{quasi-electron charge density}} - \underbrace{\sum_{ii',j'} z^*_{I,ij} z_{I,i'j} \varphi^*_{i'}(\vec{r}) \varphi_i(\vec{r})}_{\text{quasi-hole charge density}}$$

ground state charge density



18 Å

Charge density of the lowest energy exciton in disordered P3HT:

Blue: quasi-electron
Red: quasi-hole

Localized states!

Exciton diffusion

(1) Phonon-assisted transition (2) Spontaneous emission (decay)

(1) Phonon-assisted transition

Let exciton start in an excited many-body **pure** state I at t=0, i.e., $\Psi(0) = \Phi_I(\vec{R}(0))$

t > 0, ions move, the exciton state becomes a **mixed** many-body state

Introduce $C_J^{(I)}(t)$ so that $\Psi(t) = \sum_{J=0}^{\infty} C_J^{(I)}(t)\Phi_J(\vec{R}(t))$ $C_J^{(I)}(t)$: probability amplitude

with $C_J^{(I)}(0) = \delta_{I,J}$

Substitute Ψ(t) into time-dependent many-body Schrodinger equation:

$$i\hbar \frac{\partial}{\partial t}\Psi(t) = \underbrace{H(\vec{R}(t))}_{\text{many-body Hamiltonian}}\Psi(t)$$

Obtain dynamics of exciton transition:

$$\frac{\partial}{\partial t} C_J^{(I)}(t) = -\sum_K C_K^{(I)}(t)\left(\frac{i}{\hbar}\omega_K \delta_{JK} + D_{JK}\right)$$

$$D_{JK} = \left\langle \Phi_J \middle| \frac{\partial}{\partial t} \middle| \Phi_K \right\rangle = \sum_{i,j\neq j'} z^*_{I,ij} z_{J,ij'} d_{jj'} - \sum_{i\neq i',j} z^*_{I,ij} z_{J,i'j} d_{i'i}$$

$d_{i'i}$: non-adiabatic coupling between Kohn-Sham state *i* and *i*'

$$d_{i'i} = \left\langle \phi_{i'} \middle| \frac{\partial}{\partial t} \middle| \phi_i \right\rangle \approx \frac{1}{2\Delta t} \left(\left\langle \phi_{i'}(t) \middle| \phi_i(t+\Delta t) \right\rangle - \left\langle \phi_{i'}(t+\Delta t) \middle| \phi_i(t) \right\rangle \right)$$

Where $\phi_i(t)$ is the Kohn-Sham single particle wave function.

$|C_J^{(I)}(t)|^2$ **exciton transition probability from state *I* to state *J* at time *t***

$\gamma_{I,J}^{\text{Phonon}} = \left\langle \frac{|C_J^{(I)}(t)|^2}{t} \right\rangle_{\delta t}$ transition rate (average over time interval $\left[t, t+\delta t\right]$)

Transition rates

(2) Spontaneous emission (decay) without phonon assistance
Transition dipole moment approximation

$$\gamma_{I,J}^{\text{Dipole}} = \frac{4(\omega_I - \omega_J)^3 \left| \langle \Phi_I | \vec{r} | \Phi_J \rangle \right|^2}{3c^3}$$

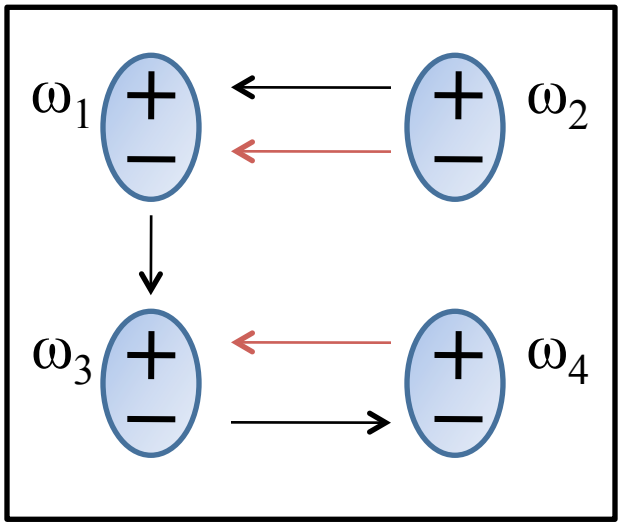
(3) Transition rate satisfying detailed balance:

$$\gamma_{I,J} = \begin{cases} \gamma_{I,J}^{\text{Phonon}} \exp\left(-\dfrac{\omega_J - \omega_I}{k_{\text{B}}T}\right), & \text{if } \omega_J \geq \omega_I \\ \gamma_{I,J}^{\text{Phonon}} + \gamma_{I,J}^{\text{Dipole}}, & \text{if } \omega_J < \omega_I \end{cases}$$

- Phonon assisted transition contributes to both the downhill and uphill transitions
- Spontaneous emission only contributes to the downhill transitions

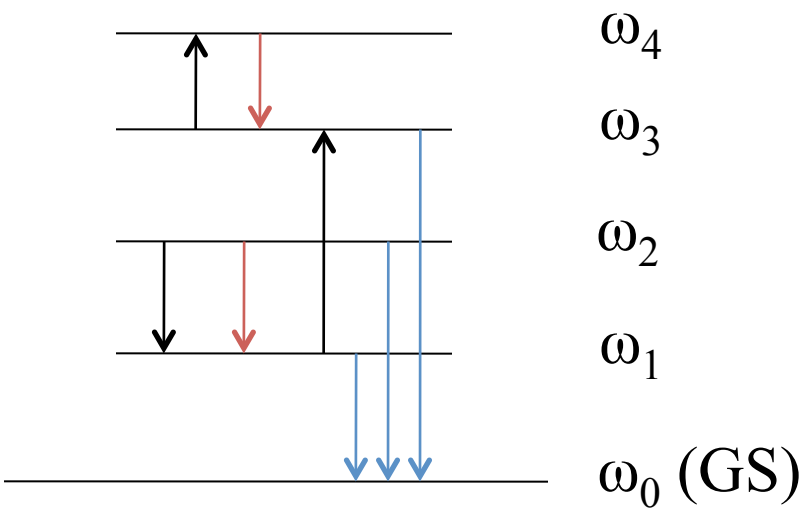
Exciton diffusion in real and energy space

Real space



$$\vec{r}_{ex} = \frac{\vec{r}_e + \vec{r}_h}{2}$$

Many-body energy space



Binding energy: 0.16 eV (disordered P3HT)
0.53 eV(single P3HT chain)

→ Phonon-assisted exciton transition (rate: $10^9 \sim 10^{12}$ s^{-1}, ps to ns)

→ Spontaneous emission (from high energy to low energy, $\leq 10^7$ s^{-1}, microsecond)

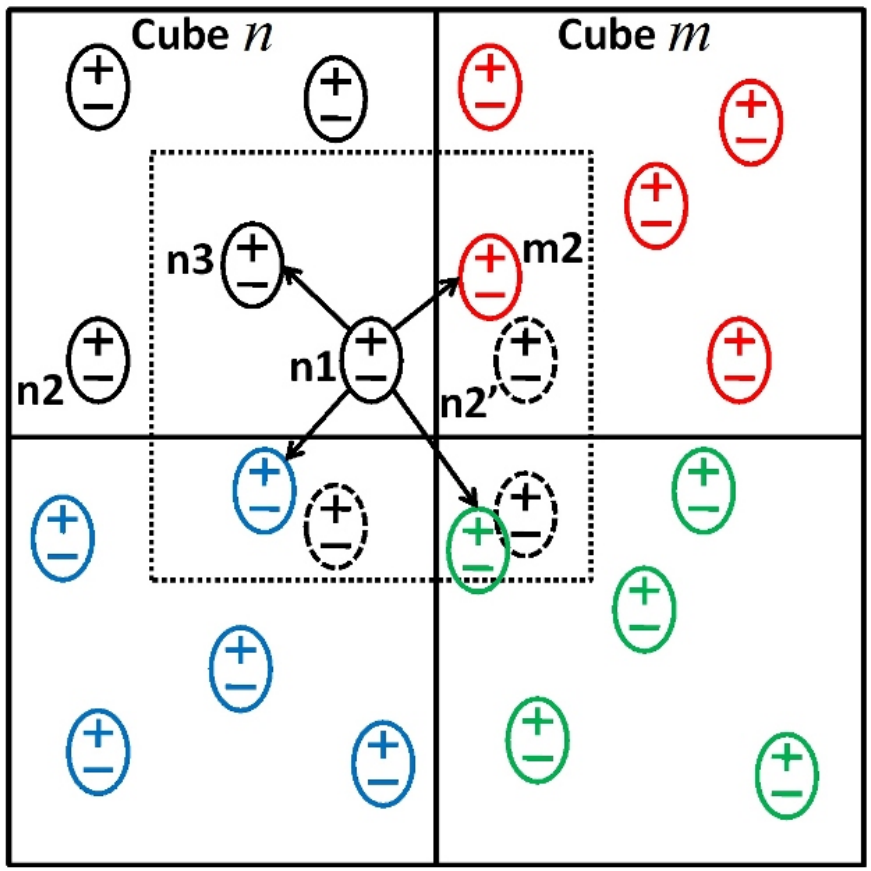
→ Exciton annihilation (from excited states to GS , 10^9 s^{-1}, ps)

Transition between exciton states ⇒ Exciton diffusion in real space

Construction of macroscopic system

Two daunting challenges: (1) to model macroscopic system with microns dimensions
(2) to model amorphous disordered system

"Macroscopic" system: $l_x \times l_y \times l_z$ cubes



1. Cube n: home box in which transition rates have been calculated (5 excitons here)
2. KS states in each cube are **randomly selected and rotated** from MD snap-shots (to model amorphous structure)
3. Determine exciton position in each box

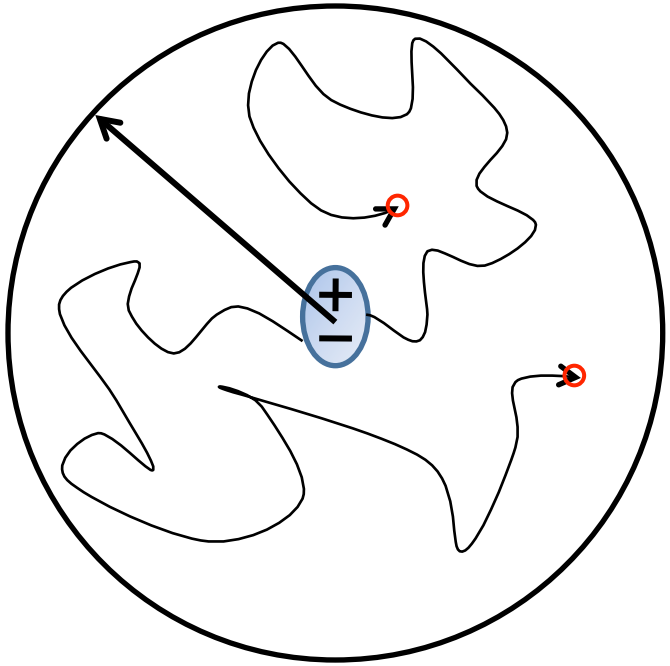
To determine inter-cube transition rate:
E.g. considering exciton $n1$:

Translate cube n so that $n1$ is at the center of the cube (dashed cube); etc. The transition rate $\gamma_{n1,m2}$ is replaced by $\gamma_{n1,n2'}$ or $\gamma_{n1,n2}$

$n1$ can only hop to 4 neighboring excitons

Monte Carlo Calculation

Maximum distance of exciton diffusion: diffusion length



○ Annihilation site

- Step 1: select an exciton I
- Step 2: list event table with transition probability

• Annihilation: $P_1 = \gamma_{I,0} \times \Delta t$

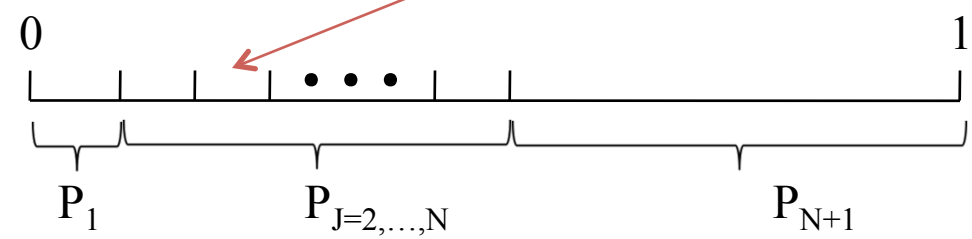
• Inter-state transition: $P_{J=2,3,\ldots,N} = \gamma_{I,J} \times \Delta t$

• Stay in the same state: $P_{N+1} = 1 - (P_1 + P_2 + \cdots + P_N)$

N: number of excitons in a cube (54)

Δt: time step in MC (10 fs)

- Step 3: for a given random number, execute an MC move



Diffusion length $L_D = \langle d_{\max} \rangle$

Diffusion time $\tau = \langle t \rangle$

Diffusivity $D = \dfrac{\langle d_{\max}^2 \rangle}{3\langle t \rangle}$

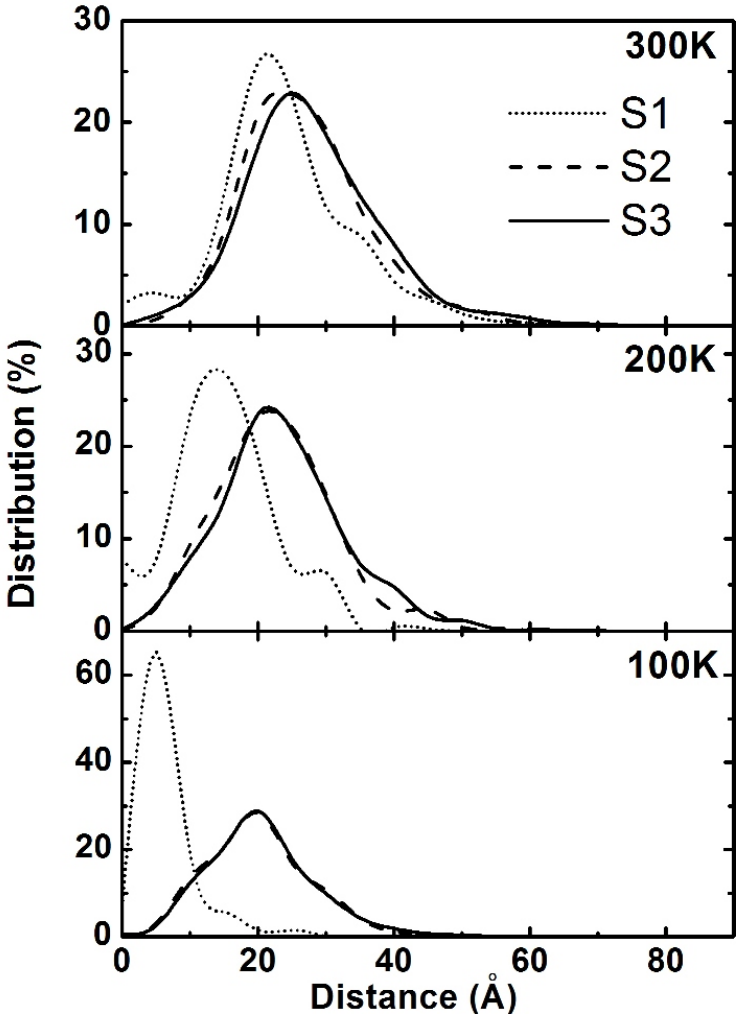
- Step 4: continue Step 3 until exciton annihilates for one MC trajectory.
- Step 5: continue for many trajectories.
- Step 6: take average of all trajectories
- Step 7: continue for different excitons

Simulation Flowchart

1. Static relaxation of initial structure (636 atoms); heat up to desired temperatures; stay at the desired temperature with 500 MD steps to reach thermal equilibrium. MD step size 1 fs. Simulation performed by VASP.
2. Run a micro-canonical MD for 1000 fs. Determining $\omega_I \,\&\, \Phi_I$ and spontaneous emission rate at each MD step. 6 occupied KS orbitals and 9 unoccupied KS orbitals are considered to produce 54 excited states.
3. To calculate phonon-assisted transition rate $\gamma_{I,J}^{\text{phonon}}(t)$ at time t, TDDFT is run from t to $t+\delta t$ (δt=100 fs) with the KS states determined from MD.
4. Construct macroscopic system using $l_x \times l_y \times l_z$ cubes.
5. Perform Monte Carlo calculation.

Results for disordered P3HT

Statistics (percentage) of exciton diffusion distance for 10^4 trajectories



Three exciton states are examined:

- S1: lowest energy exciton state
- S2: exciton state ~ 0.6 eV higher than S1
- S3: exciton state ~ 1.2 eV higher than S1

- Higher energy excitions diffuse farther
- S2&S3 have (almost) the identical diffusion behavior
- Diffusion length increases with temperature; particularly so for lower energy excitons

Calculated diffusion length L_D (nm), lifetime τ (ns), and diffusivity D ($10^{-9}m^2/s$)

	300K			200K			100K		
	s1	s2	s3	s1	s2	s3	s1	s2	s3
L_D	2.6	3.0	3.1	1.7	2.5	2.6	0.9	2.2	2.3
τ	2.0	1.8	1.7	3.6	3.9	3.8	4.2	4.4	4.3
D	4.1	5.3	6.0	1.0	1.9	2.0	0.2	1.3	1.4

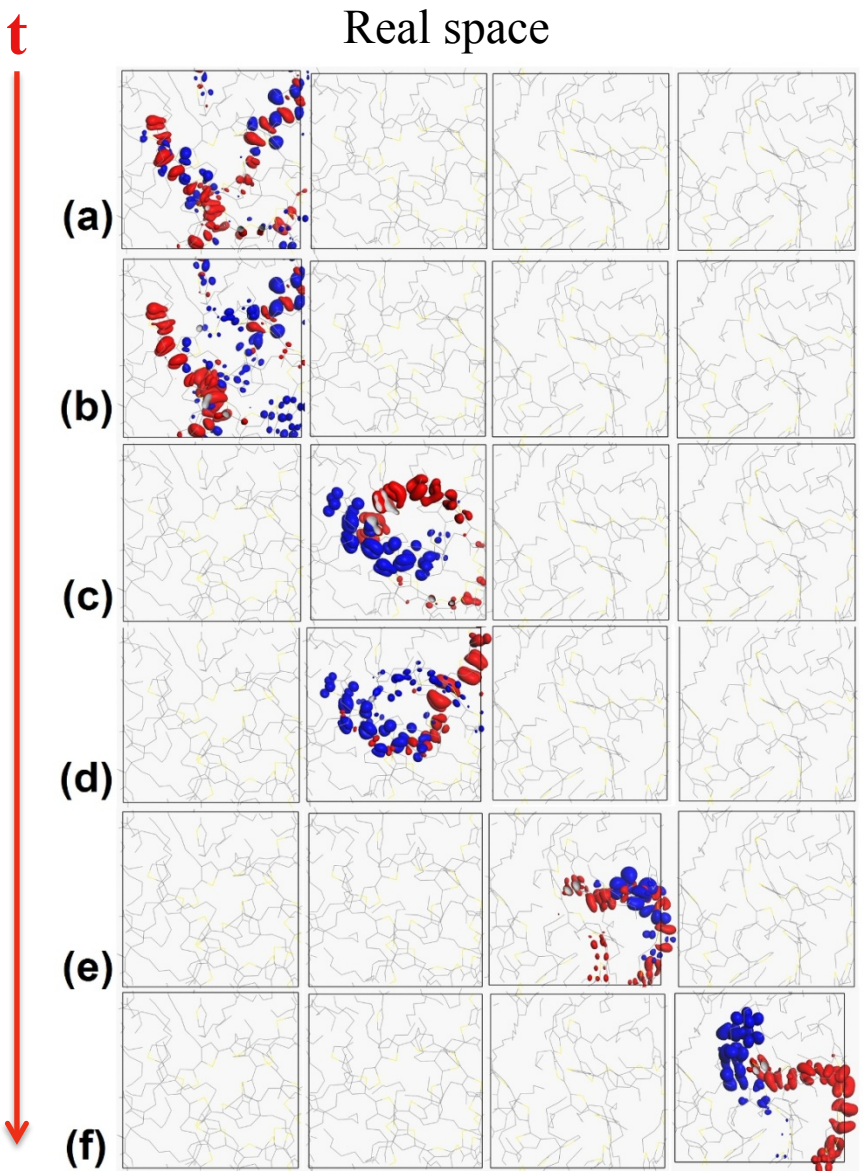
Experimental results at 300K:

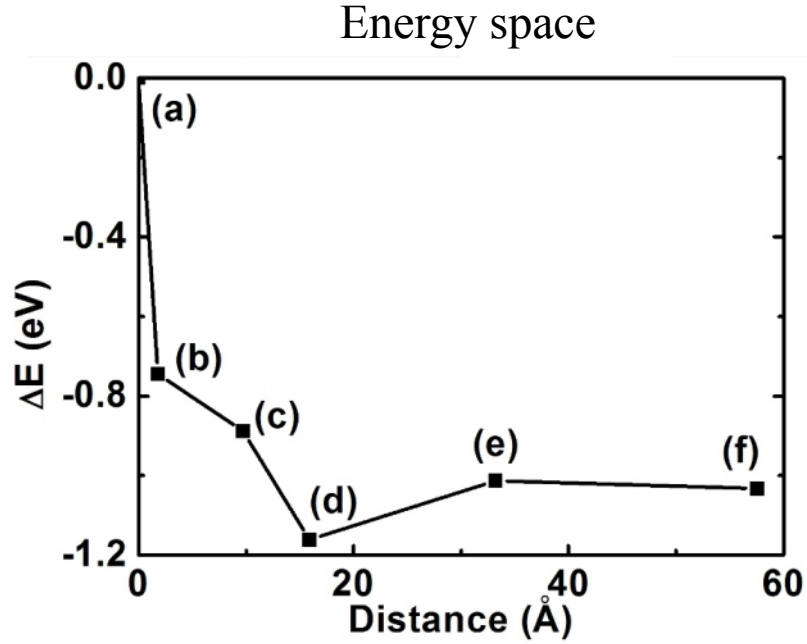
L_D= 4 nm [1]

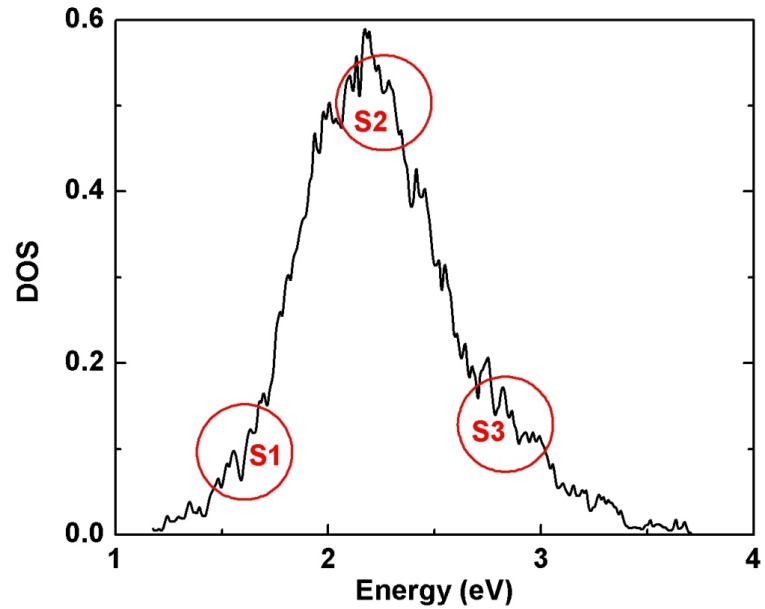
L_D= 2.6 ~ 5.3 nm [2]

[1] L. Luer, H. J. Egelhaaf, D. Oelkrug, G. Cerullo, G. Lanzani, B. H. Huisman, D. de Leeuw, Org. Electron. 5, 83 (2004).
[2] J. E. Kroeze, T. J. Savenije, M. J. W. Vermeulen, and J. M. Warman, J. Phys. Chem. B 107, 7696 (2003).

Exciton diffusion (S3) in real and energy space at 300K

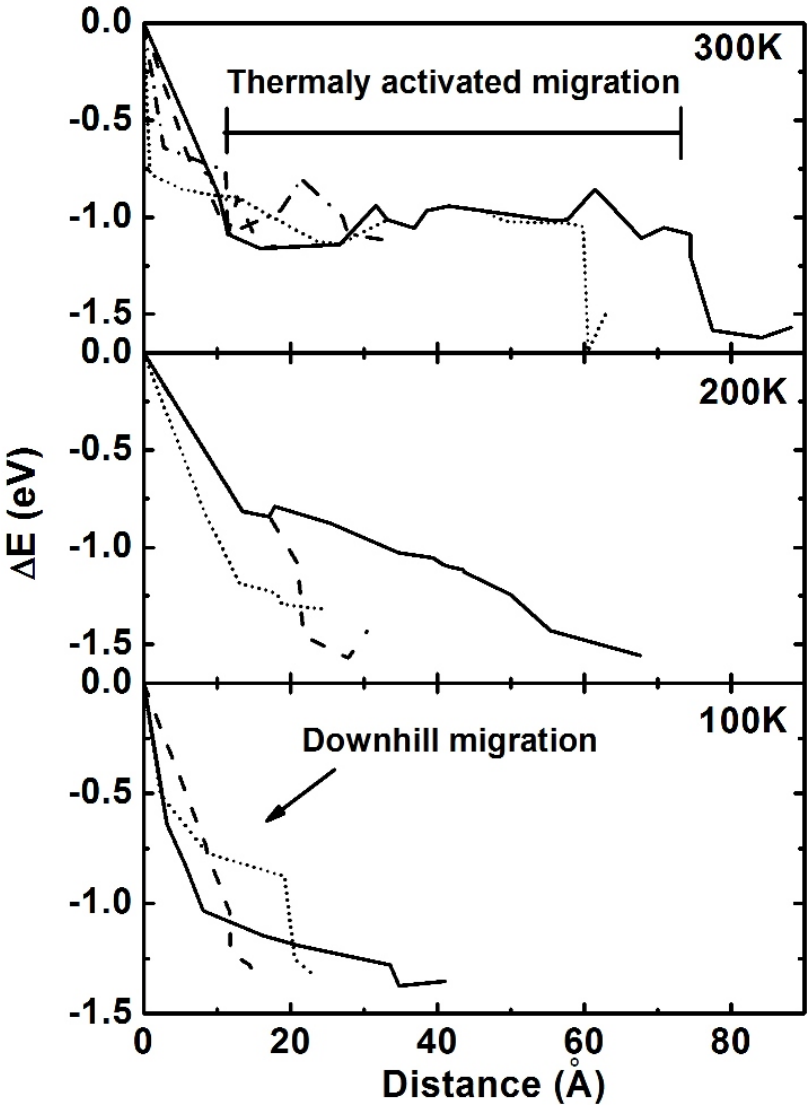






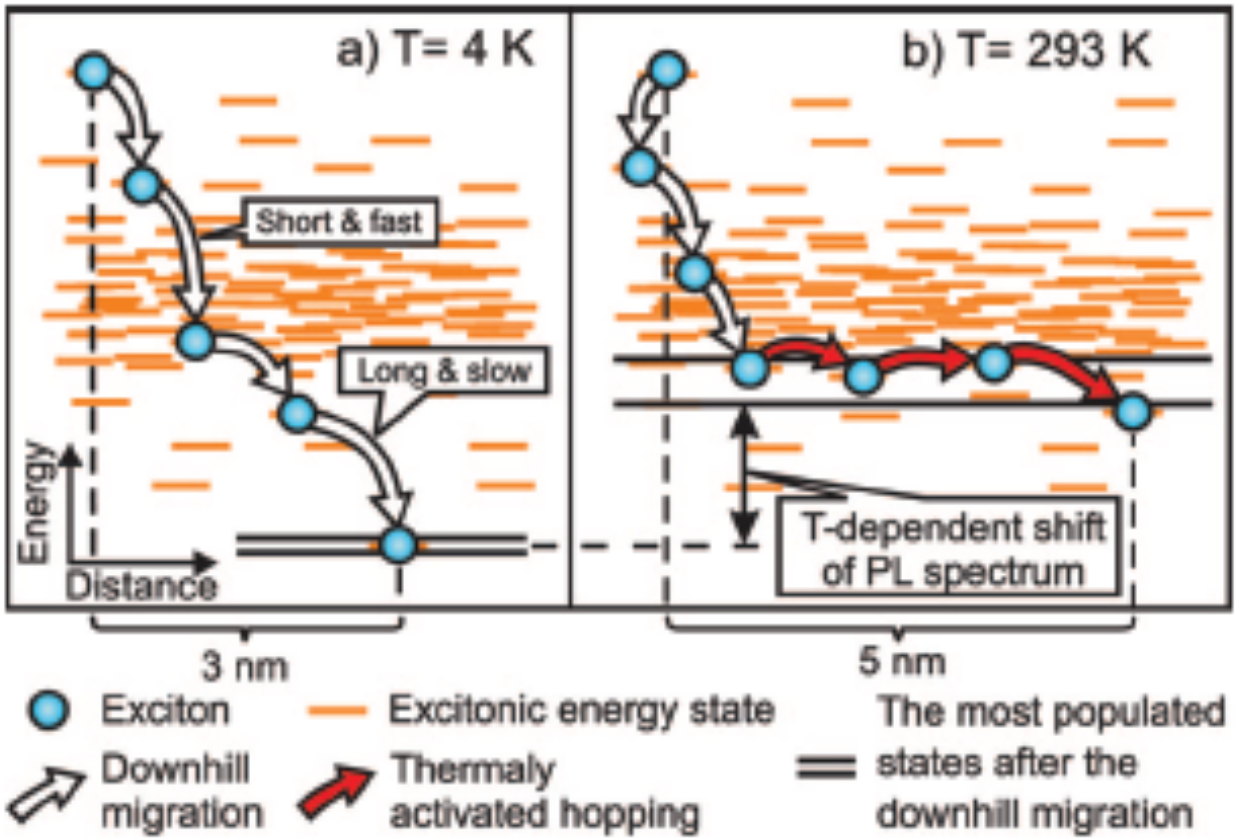
Exciton diffusion mechanisms

exciton energy vs. diffusion distance



- **Downhill migration**: quickly dumps energy, but has minor contribution to diffusion length - doesn't need phonons
- **Thermally activated migration**: dominate exciton diffusion without significant change of exciton energy - need phonon assistance
- At low temperature, downhill migration dominates
- At higher temperature, downhill migration followed by thermally activated migration

Two regimes for exciton diffusion*



(1)Downhill migration, temperature regime 4 - 150 K
(2)Thermally activated migration, temperature regime > 150 K

O. V. Mikhnenko, F. Cordella, A. B. Sieval, J. C. Hummelen, P. W. M. Blom, and M. A. Loi,** *J. Phys. Chem. B* ***2008, 112, 11601–11604

Interfacial Exciton Dissociation

Simplified Fewest switch surface hopping (FSSH)

In original FSSH [1], an electron (exciton) always stays at **one** excited state at any given time, but it can hop from one state to another. Here, we use a simplified FSSH method [2], in which a hop-rejection in the original FSSH is replaced by multiplying the hop probability with Boltzmann factor for an energetic upward transition. The probability from state J to K during the time-step δt is

$$g_{JK} = \begin{cases} [\max(0, \frac{b_{KJ}\delta t}{a_{JJ}})] \bullet \exp(\frac{-(\varepsilon_K - \varepsilon_J)}{kT}), & \varepsilon_K > \varepsilon_J \\ [\max(0, \frac{b_{KJ}\delta t}{a_{JJ}})], & \varepsilon_K \le \varepsilon_J \end{cases}$$

where

$$a_{KJ} = C_K^*(t) C_J(t) \qquad b_{KJ} = -2\,\mathrm{Re}(a_{KJ} D_{KJ})$$

With FSSH, we know precisely which state the exciton is at in any time. We can determine the position and charge density of the exciton (and quasi-electron and quasi-hole). Examine electron-hole (e-h) distance and charge distribution as a function of time

[1] J.C. Tully, J. Chem. Phys. 93 1061 (1990).
[2] W. R. Duncan, C. F. Craig, and O. V. Prezhdo, J. Am. Chem. Soc. **129**, 8528 (2007).

Simulation Flowchart

1. Static relaxation of initial structure; heating system to desired temperature; stay at the desired temperature with 500 MD steps to reach thermal equilibrium. MD step size 1 fs. The simulation performed by VASP.

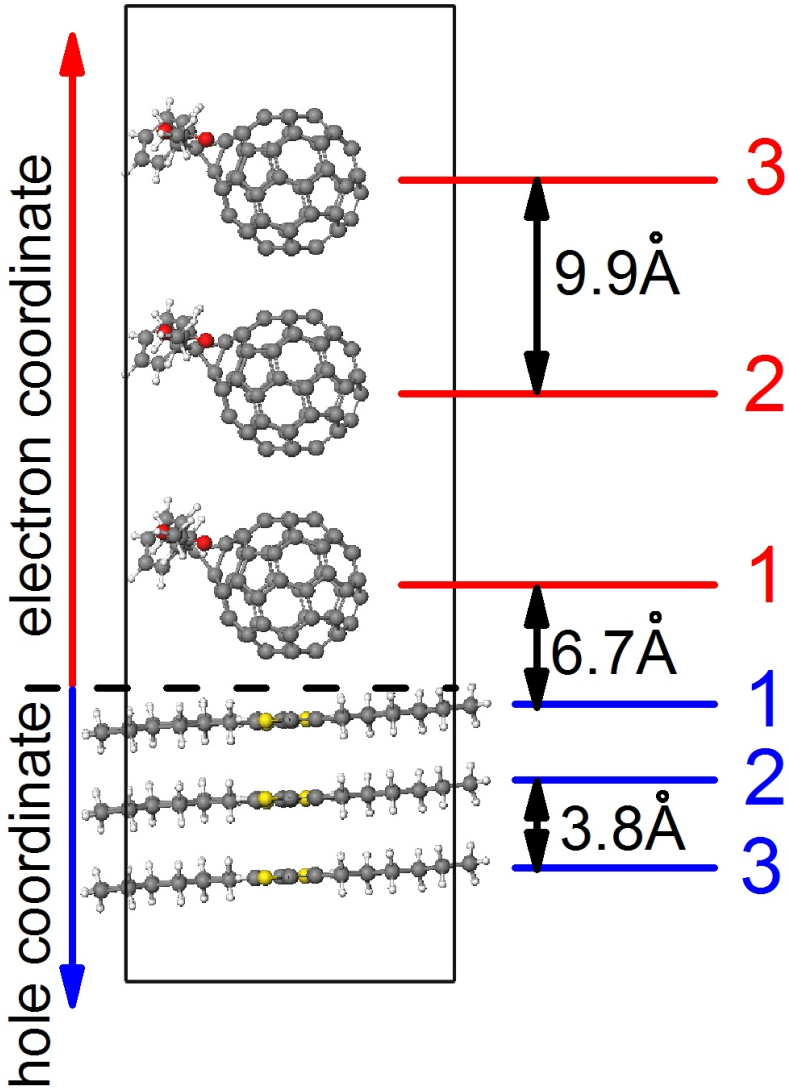
2. Run a micro-canonical MD for 1000 fs. Determining $\omega_I \,\&\, \Phi_I$ at each MD step. 3 occupied KS orbitals and 9 unoccupied KS orbitals are used to obtain 27 excited states. The non-adiabatic coupling and position of Kohn-sham states are also determined.

3. Choose different (~100) initial structures from the MD trajectory, each with 200 fs long.

4. For each selected short trajectory, FSSH evolution of the exciton state is performed.
   (1) choose the initial exciton with the shortest e-h distance
   (2) evolve $C_J(t)$ and calculate the hopping probability
   (3) generate different (~100) random number sequences to determine the exciton trajectories and the corresponding position and charge density
   (4) average over different random number sequences.

5. Take ensemble average of the different trajectories

Exciton dissociation at P3HT/PCBM interface



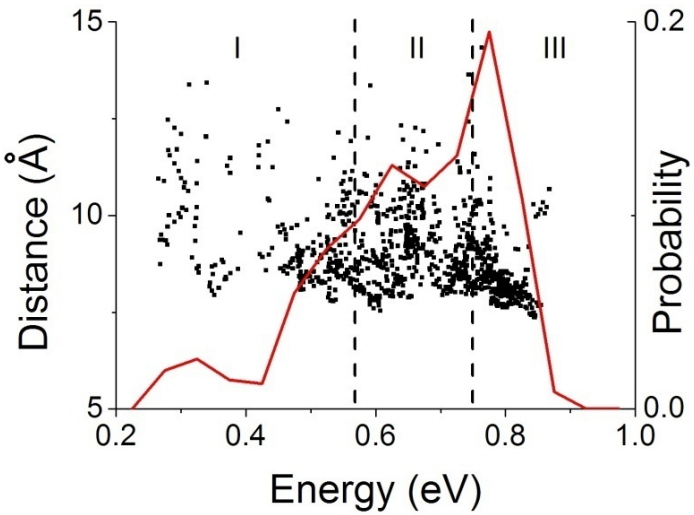
Simulation box: 48.0Å x 16.2Å x 15.7Å

Lowest interfacial exciton state energy: 0.20 eV
Band gap by ΔSCF: 0.55 eV

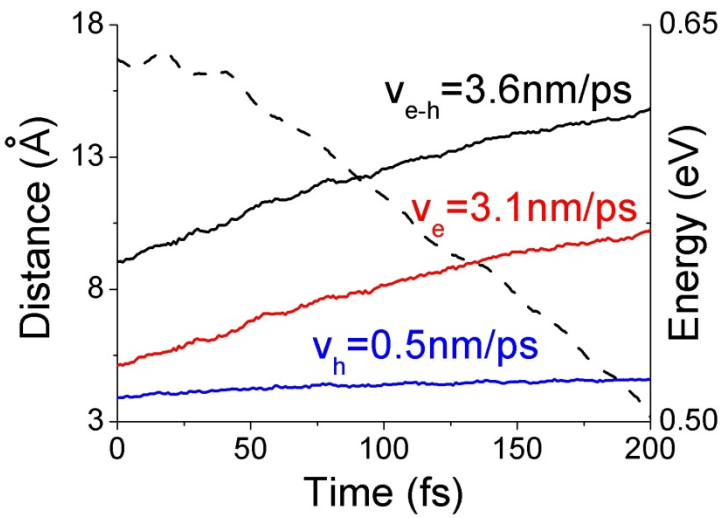
Interfacial exciton binding energy: 0.35 eV

Experimental estimate of binding energy:
0.1-1 eV

Exciton dissociation process



Distribution of initial exciton states:
e-h distance: 7-11 Å
Exciton energy: 0.5-0.8 eV



e-h distance (black solid line) and exciton energy (black dash line) vs. time

Interfacial electron moves faster than hole, similar to the case in **bulk**, in which electron mobility is larger than hole.

Energy decreases from 0.64 to 0.5 eV, providing a driving force for dissociation.

Estimate of dissociation timescale

According to Onsager theory [1], Coulomb capture radius r_c is defined as the distance at which the Coulomb attraction energy equals the thermal energy $k_B T$.

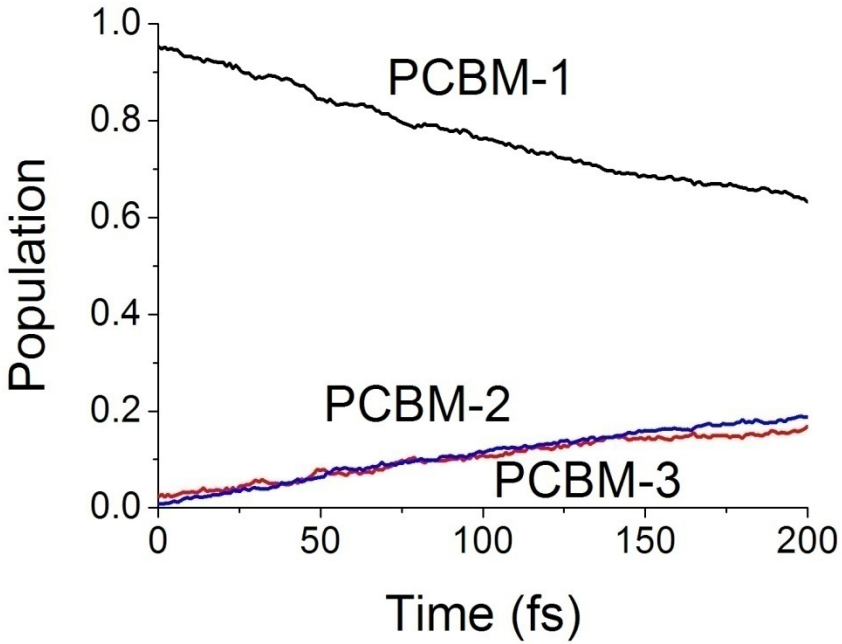
$$r_c = \frac{e^2}{4\pi\varepsilon_r \varepsilon_0 k_B T}$$

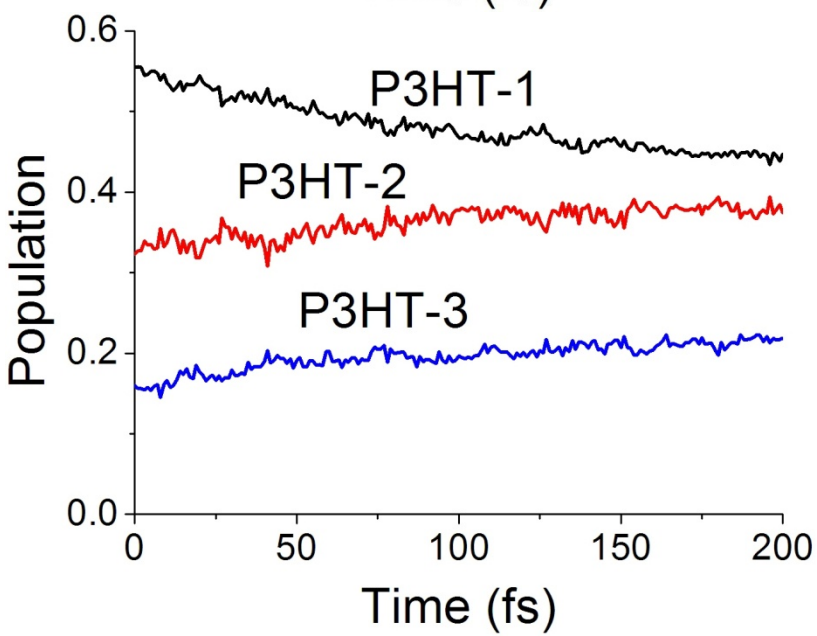
With $\varepsilon_r = 4$ and $T = 300$ K, we have $r_c = 13.9$ nm

We assume that (i) once the e-h distance is larger than r_c, the dissociation process completes; (ii) the electron and hole dissociate with a constant velocity (3.1 nm/ps for e^- and 0.5 nm/ps for h^+), we can estimate dissociation time of 3.9 ps, consistent with experimental result 4.0 ps [2].

[1] L. Onsager, Physical Review **54**, 554 (1938).
[2] I. W. Hwang, D. Moses, and A. J. Heeger, J. Phys. Chem. C **112**, 4350 (2008).

Charge separation





Quasi-electron:

At beginning, charge mainly localized on PCBM-1.

In time, the population on PCBM-1 decreases, but the population on PCBM-2 and PCBM-3 increases

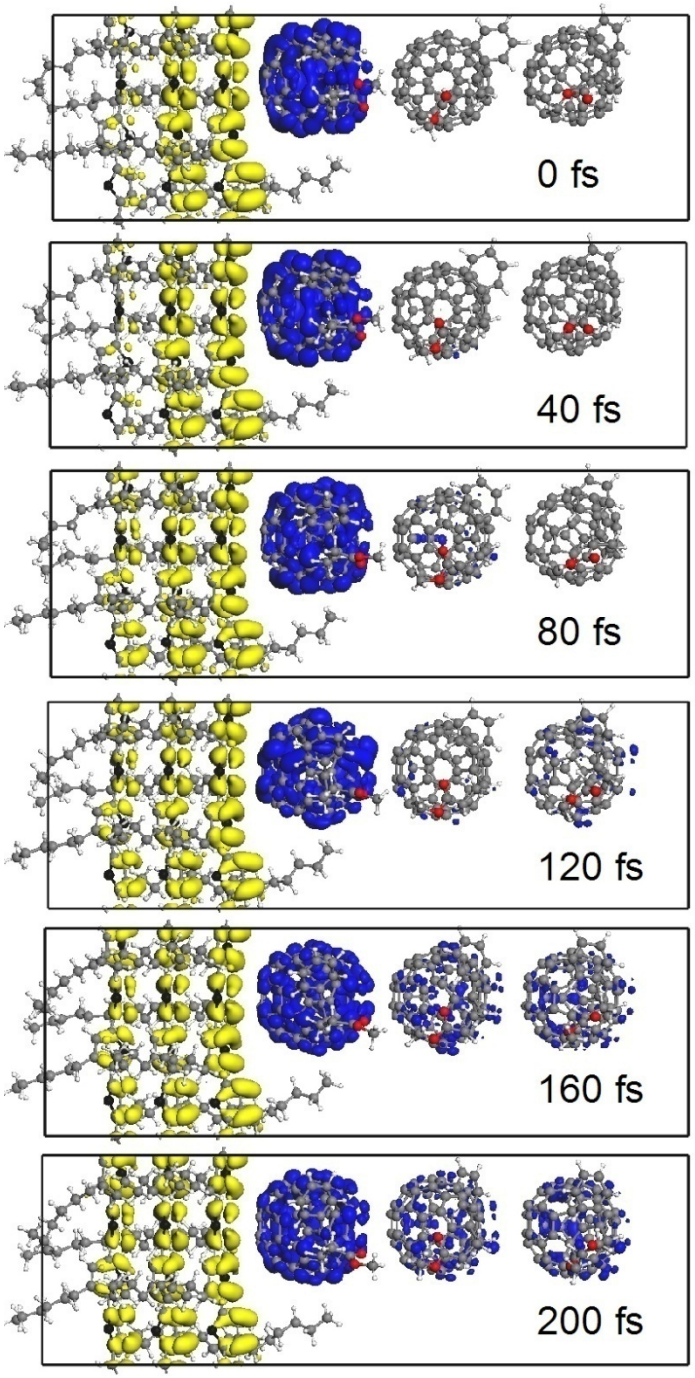
Quasi-hole:

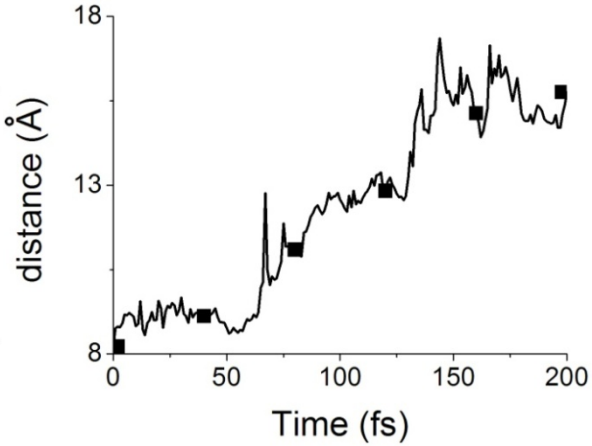
At beginning, delocalized on all three P3HT. The farther the molecule, the smaller the population

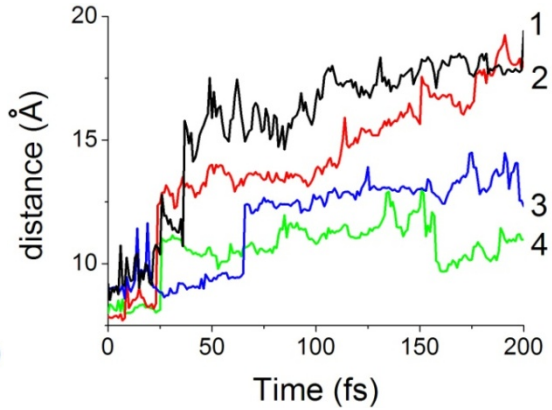
In time, the population on P3HT-1 decreases, population on P3HT-2 and P3HT-3 increases

Clear evidence of charge separation across interface

Exciton dissociation from one MD trajectory







In this example, e-h distance increases with time

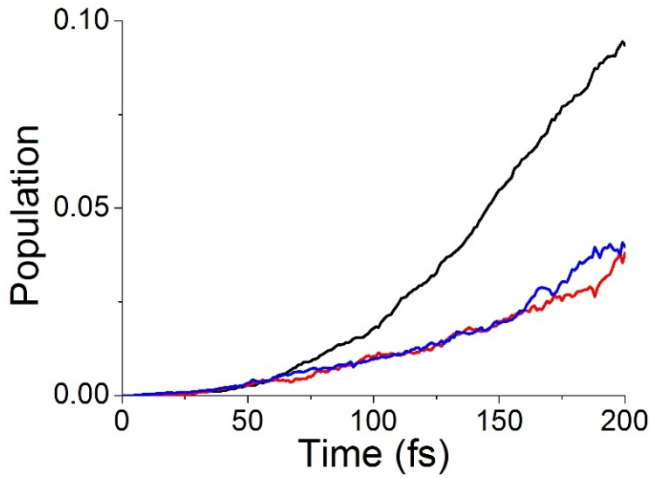
t=0, e^- on the PCBM-1 and h^+ delocalized on the first and second P3HT.

t=200 fs, significant charge separation

Exciton could have different dissociation behaviors as shown in trajectory 1-4 (**charge trapped in 4**)

Other processes at P3HT/PCBM interface

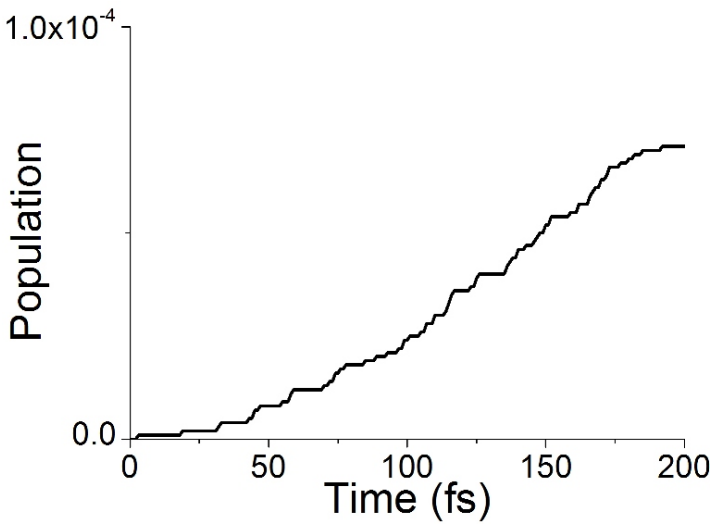
population of the lowest three states



Exciton relaxation from higher to lower excited states:

- Estimated time scale: 2.2 ps
- Time scale similar to exciton dissociation, competition of the two processes

population of the ground state



Exciton from the lowest excited state to ground state (recombination process):

- Estimated time scale: 2.8 ns
- Time scale much longer than dissociation, negligible influence on dissociation process