Exploring and Controlling Energy Transport in Organic Semiconductors

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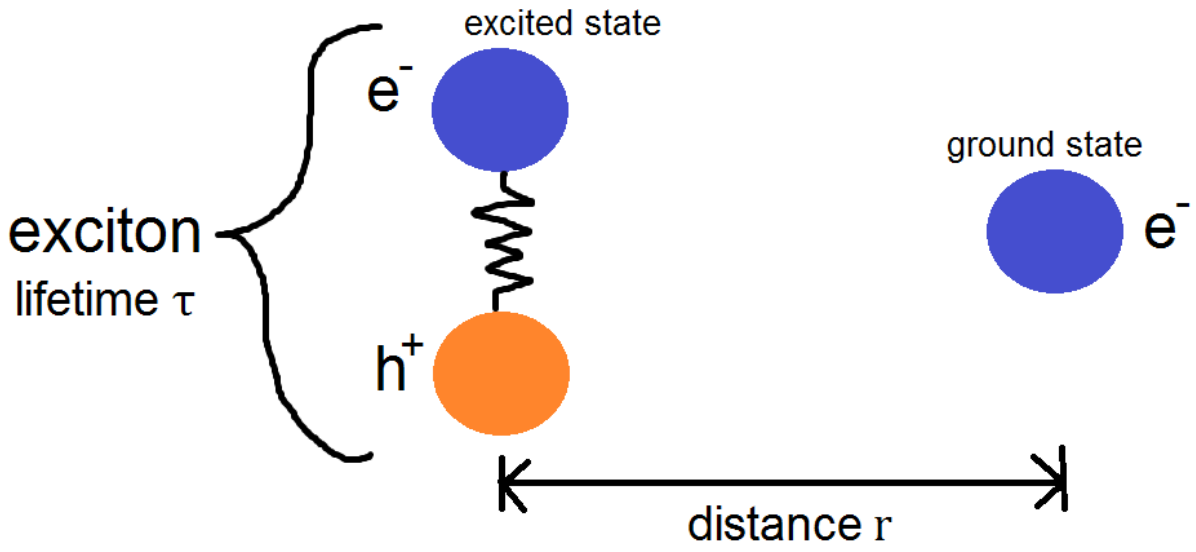
Excitons

- Organic materials have small permittivity ε_r
- Coulomb interaction strong, electron-hole binding energy large, $>k_BT$
- Charge carriers do not readily separate
- Electron-hole pair moves together as electrically-neutral quasiparticle that carries energy: the *exciton*
- Exciton must dissociate into e^- and h^+ at an interface between materials
- Exciton readily recombines on short timescale (~ns)

Förster Resonance Energy Transfer (FRET)

- Exciton acts as oscillating dipole
- Dipole-dipole coupling between exciton and electron in ground state allows energy transfer via near-field *radiationless* mechanism
- $k_{FRET} = \frac{1}{\tau}\left(\frac{R_0}{r}\right)^6$
- Exciton instantly *hops*



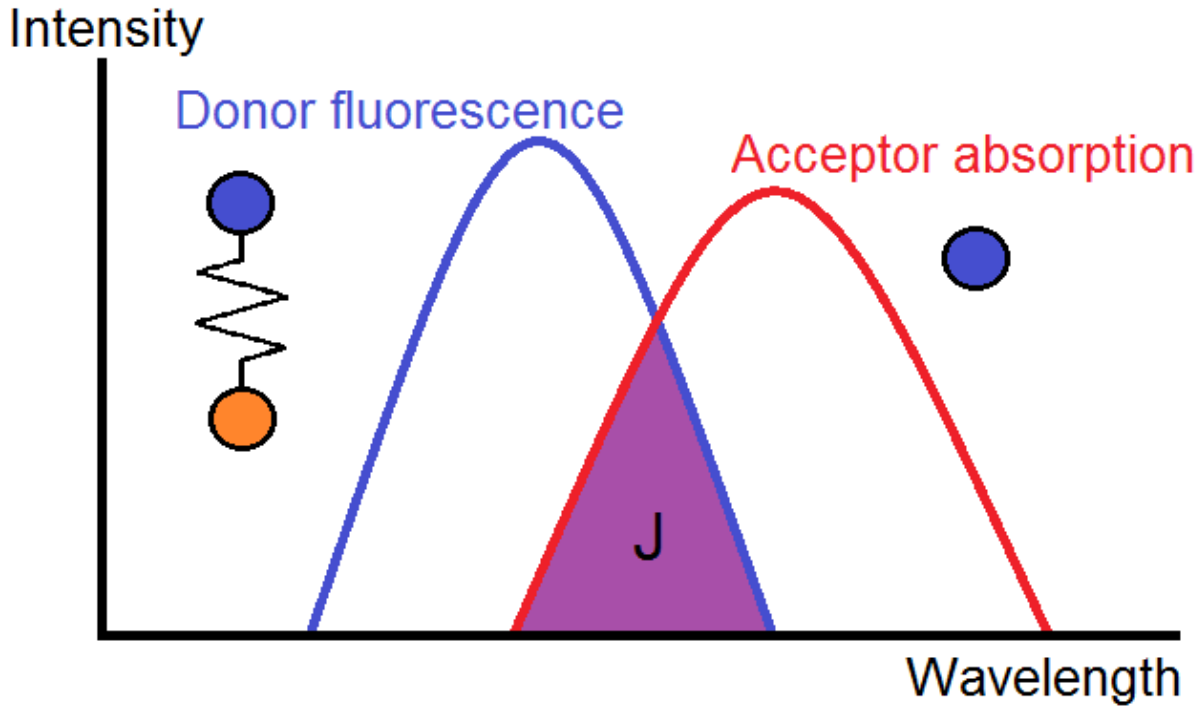
Förster Radius R_0

$$k_{FRET} = \frac{1}{\tau}\left(\frac{R_0}{r}\right)^6$$

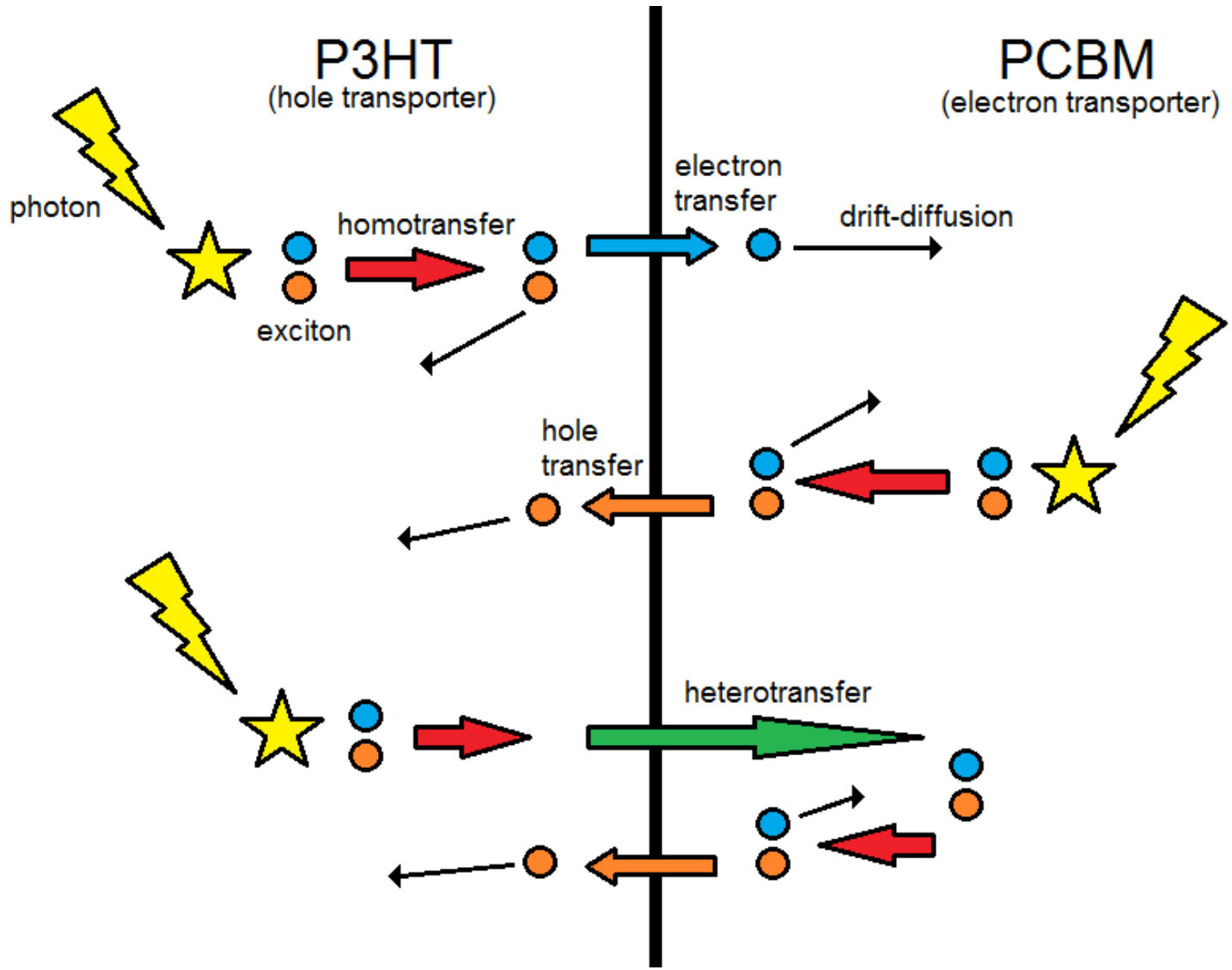
- R_0 is characteristic distance where FRET efficiency $E_{FRET} = \frac{k_{FRET}}{k_{FRET}+k_{recomb}} = \frac{1}{2}$ where $k_{recomb} = \frac{1}{\tau}$

From theory:

$$R_0{}^6 = \frac{9000\, Q_0 (\ln 10) \kappa^2}{128\, \pi^5 n^4 N_A} J$$

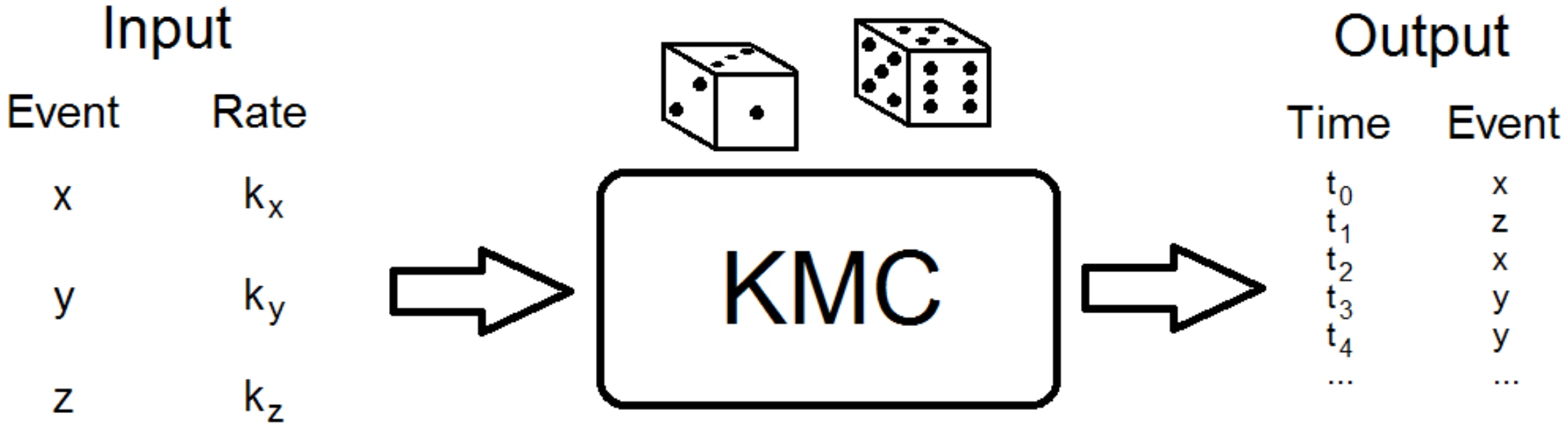


FRET and Dissociation



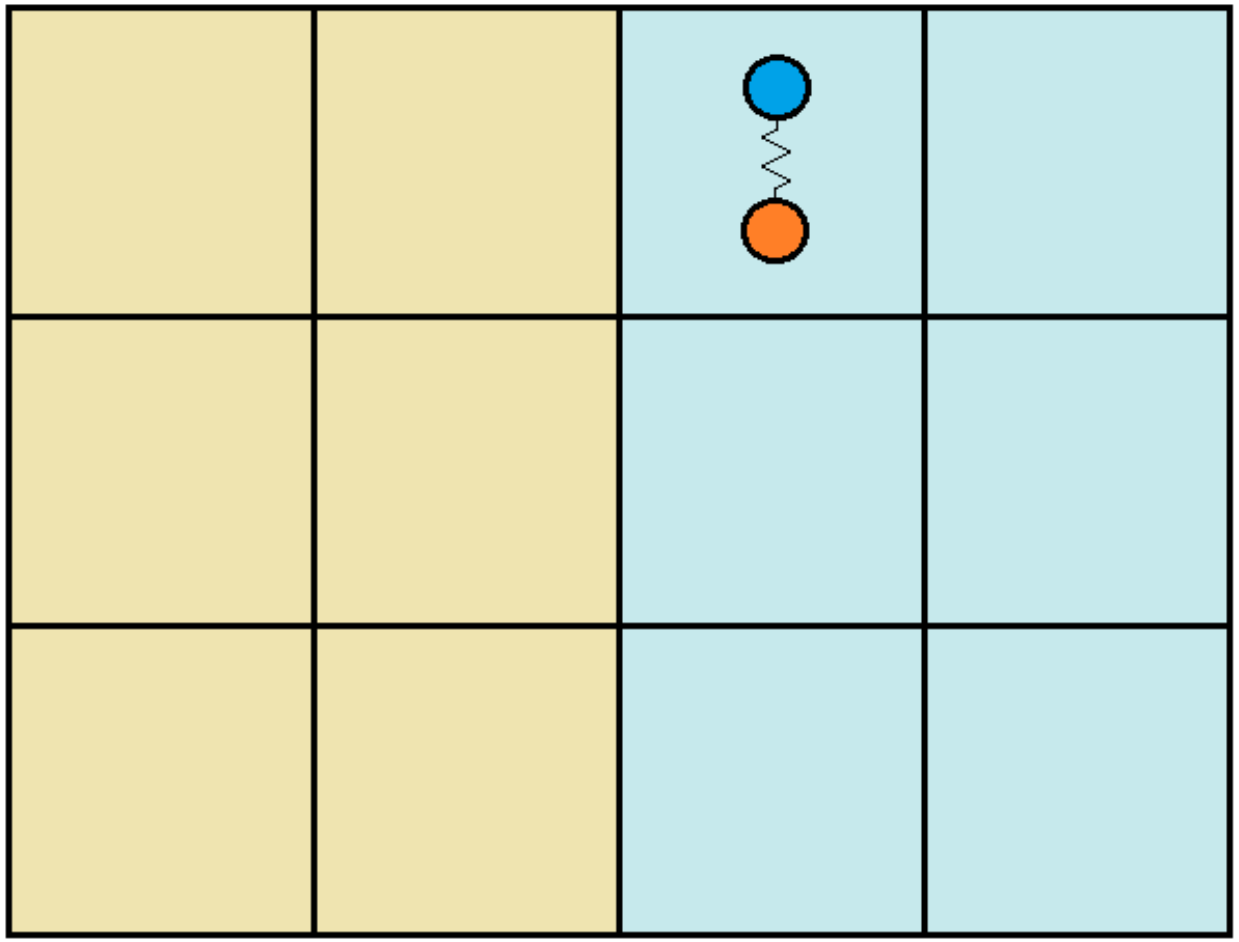
Kinetic Monte Carlo (KMC)

- Stochastic method for simulation evolution of system over time (built-in clock)
- Allows tracking of trajectories of individual entities
- We use First Reaction Method (FRM)



System

- Cubic lattice, spacing 1 nm
- Each site is a certain material (e.g. P3HT)
- Excitons exist on sites
- Site occupancy limited to 1
- Where site is adjacent to another site of a different material, it is an *interface site*

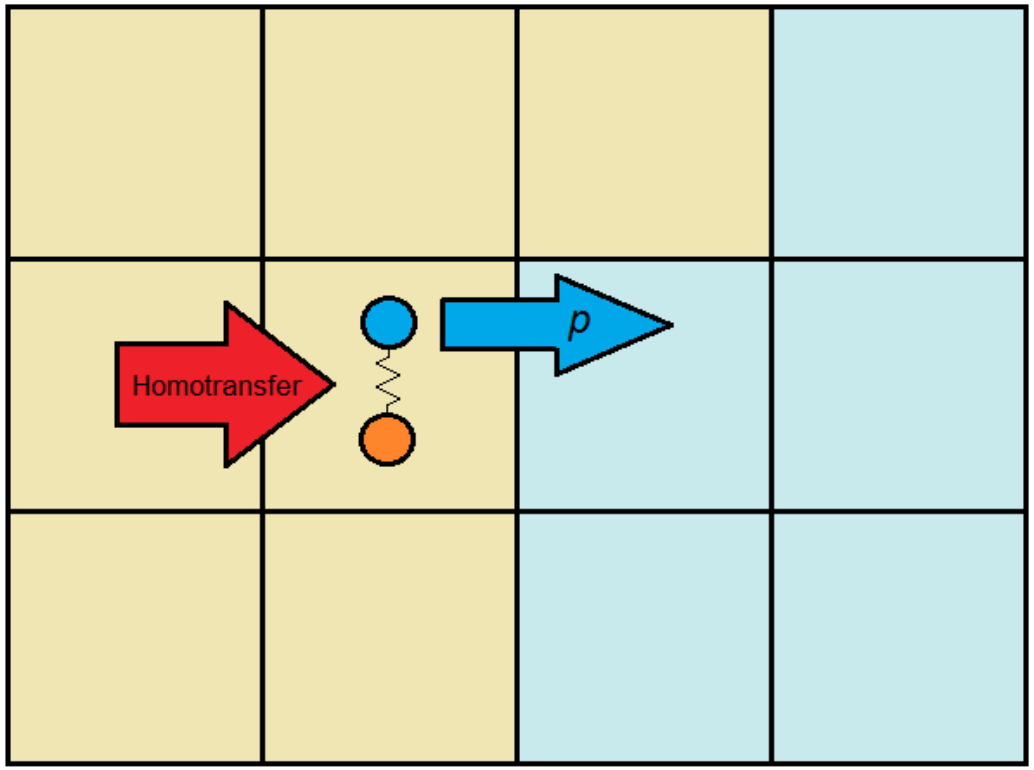


Events

- Hop via FRET: $k_{FRET} = \frac{1}{\tau}\left(\frac{R_0}{r}\right)^6 \times \begin{cases} 1 & \Delta E \leq 0 \\ \exp\left(-\frac{\Delta E}{k_B T}\right) & \Delta E > 0 \end{cases}$
- Recombination: $k_{recomb} = \frac{1}{\tau}$
- Generation: $k_{gen} = 10$ s^{-1} per lattice site (equivalent to AM1.5)

Dissociation

- Treated differently to other events
- When executed event places an exciton at a boundary site, probability *p* that the exciton instantly dissociates, otherwise no effect



KMC Queue

- Queue is chronologically ordered list of events
- Events are executed in order
- When event occurs, newly enabled events added to queue
- Time until event *i* occurs $t_i = -\frac{1}{k_i}\ln(u)$ where *u* in range (0, 1]
- This draws times from exponential distribution
- For mutually exclusive events, e.g. hopping, only shortest time need be inserted into queue

KMC Method

- Remove invalid events from start of queue
- Execute first (valid) event, *i*
- Reduce times for all other events by t_i
- Add newly enabled events
- Repeat

Material Values

Materials	**Q_0 (%)**	**L (nm)**	**Exciton lifetime (ns)**	**σ (eV)**
P3HT	25	15 [2]	0.9 [5]	0.06
PCBM	8.3×10^{-2} [1]	9 [3]	1.4 [1]	0.09
DIBSq	-	3 [4]	4.9 [5]	0.05

Unreferenced values have been determined from our experimental work

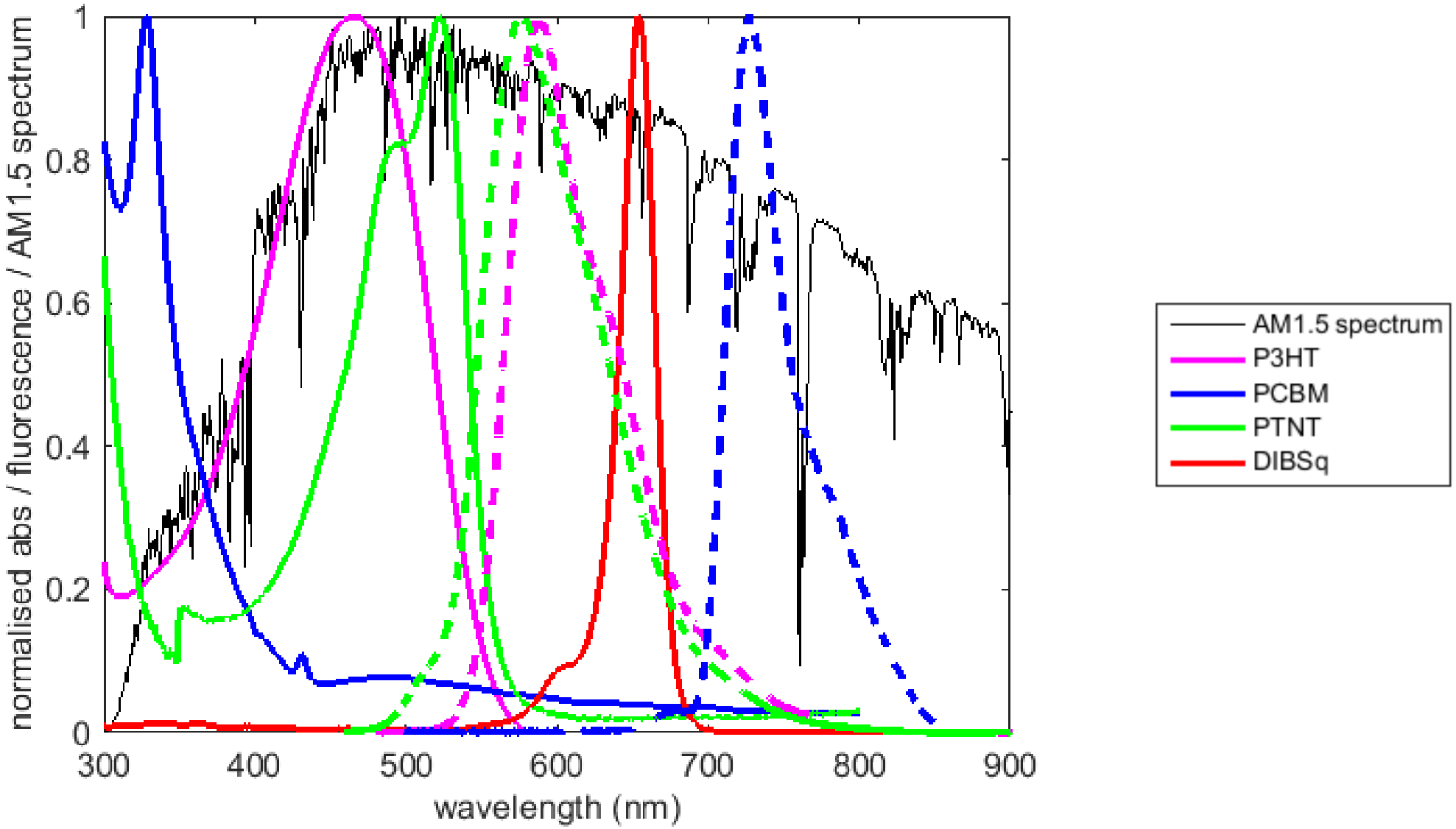
[1] Wang, H., He, Y., Li, Y. & Su, H. Photophysical and electronic properties of five PCBM-like C 60 derivatives: Spectral and quantum chemical view. *J. Phys. Chem. A* **116,** 255–262 (2012).
[2] Shaw, P. E., Ruseckas, A. & Samuel, I. D. W. Exciton Diffusion Measurements in Poly(3-hexylthiophene). *Adv. Mater.* **20,** 3516–3520 (2008).
[3] Cook, S., Furube, A., Katoh, R. & Han, L. Estimate of singlet diffusion lengths in PCBM films by time-resolved emission studies. *Chem. Phys. Lett.* **478,** 33–36 (2009).
[4] Wei, G. *et al.* Functionalized squaraine donors for nanocrystalline organic photovoltaics. *ACS Nano* **6,** 972–978 (2012).
[5] An, Q. *et al.* Improved Efficiency of Bulk Heterojunction Polymer Solar Cells by Doping Low Bandgap Small Molecule. *ACS Appl. Mater. Interfaces* (2014).

Förster Radii

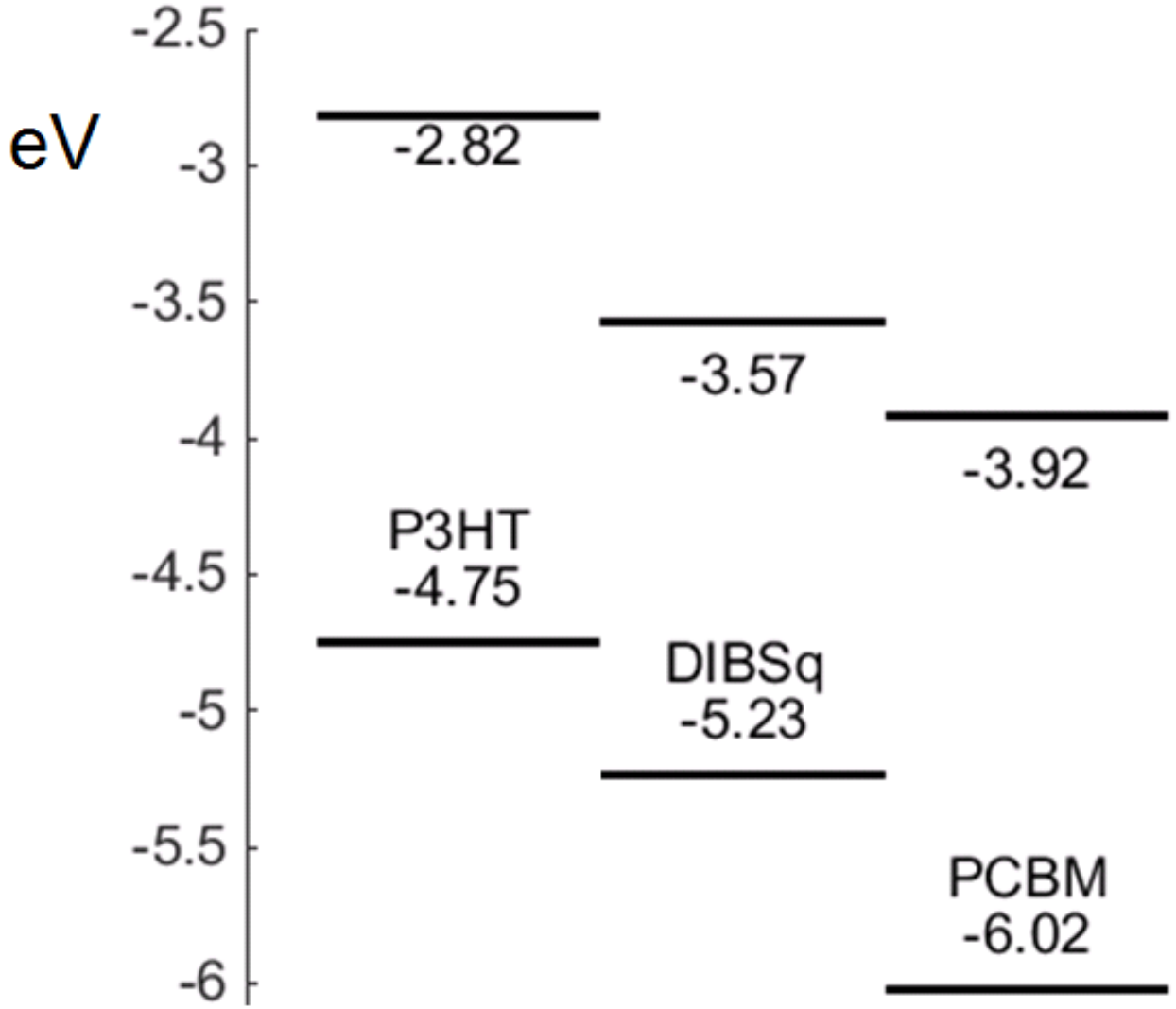
R_0 (nm)		Energy acceptor		
		P3HT	PCBM	DIBSq
Energy donor	P3HT	2.3	2.7	5.0
	PCBM	-	2.3	1.2
	DIBSq	-	-	1.1

- Heterotransfer R_0 was calculated based on absorption and fluorescence measurements
- Homotransfer R_0 was calculated based on exciton diffusion length and energy disorder

Absorption and Fluorescence Spectra

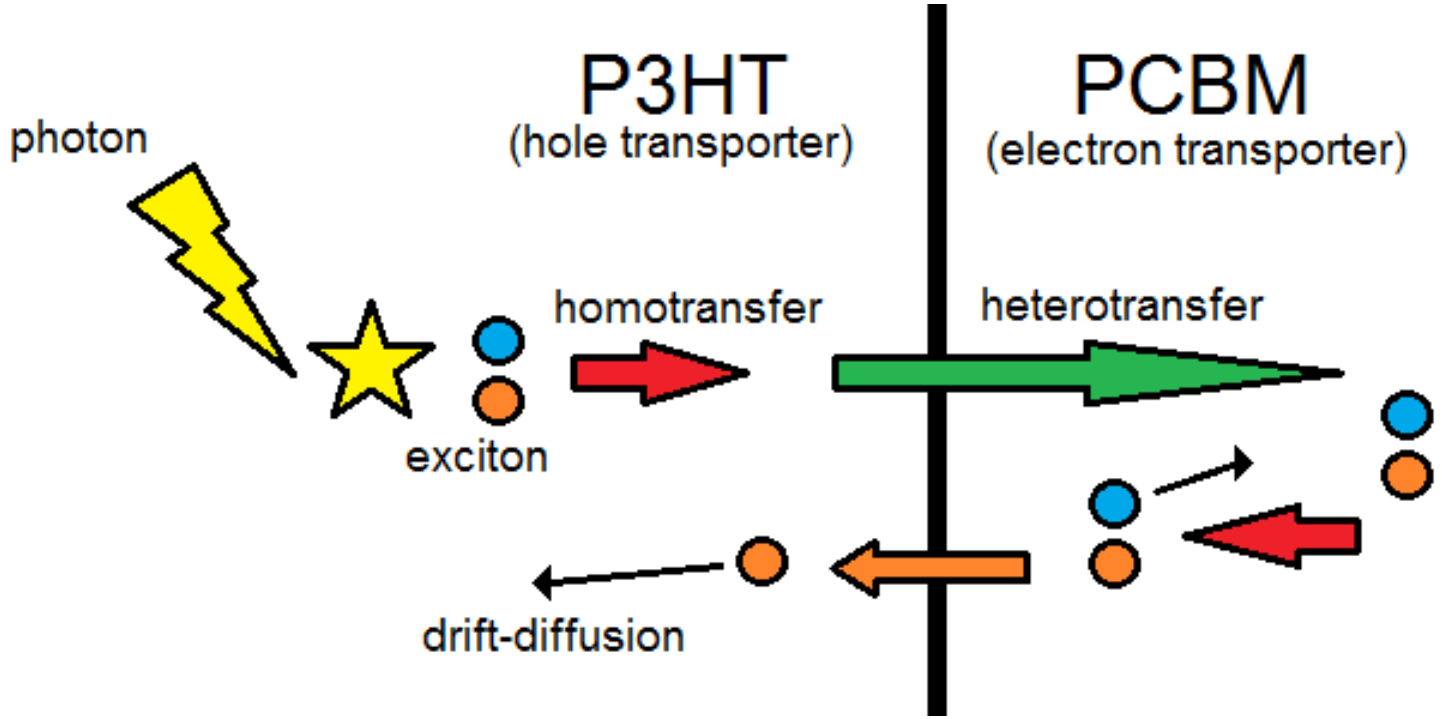


Energy Levels



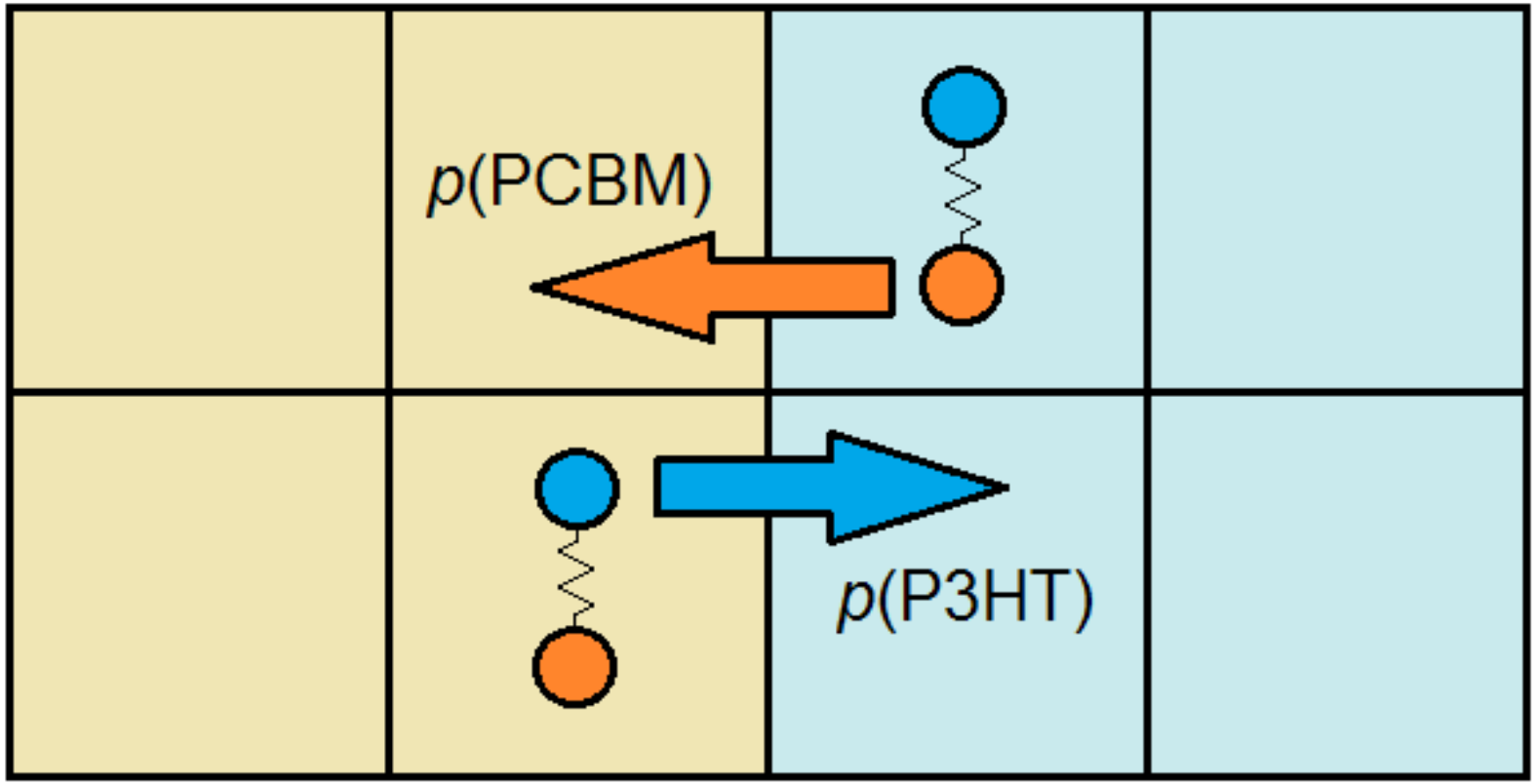
FRET and Dissociation in Binary BHJs

- Most KMC models ignore heterotransfer
- We study fraction of dissociated excitons that underwent heterotransfer

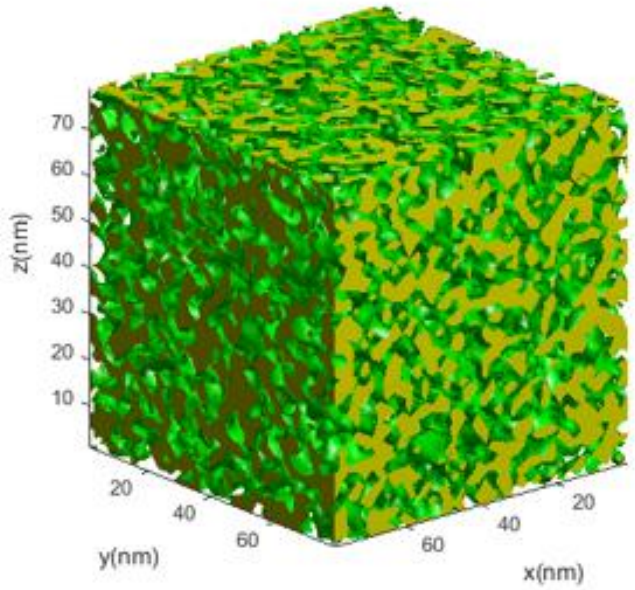


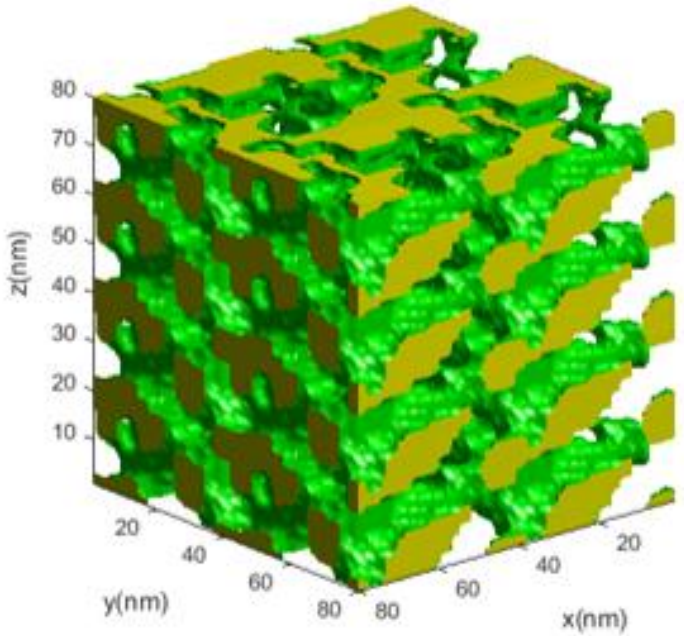
FRET and Dissociation in Binary BHJs

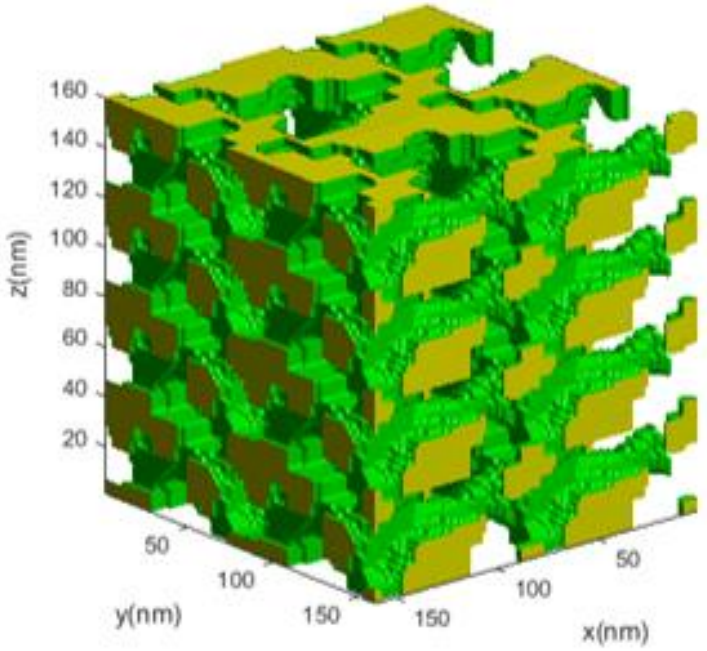
- We also vary *p* for each side of the interface and observe the effect on the exciton dissociation efficiency *η*



Binary BHJ Morphologies







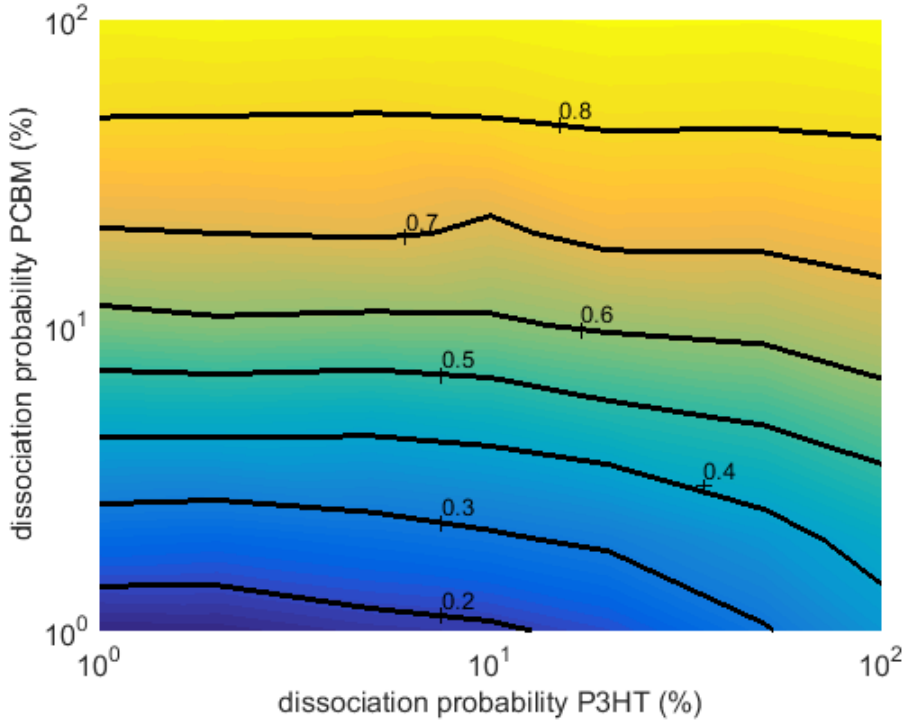
Random

F = 15 nm

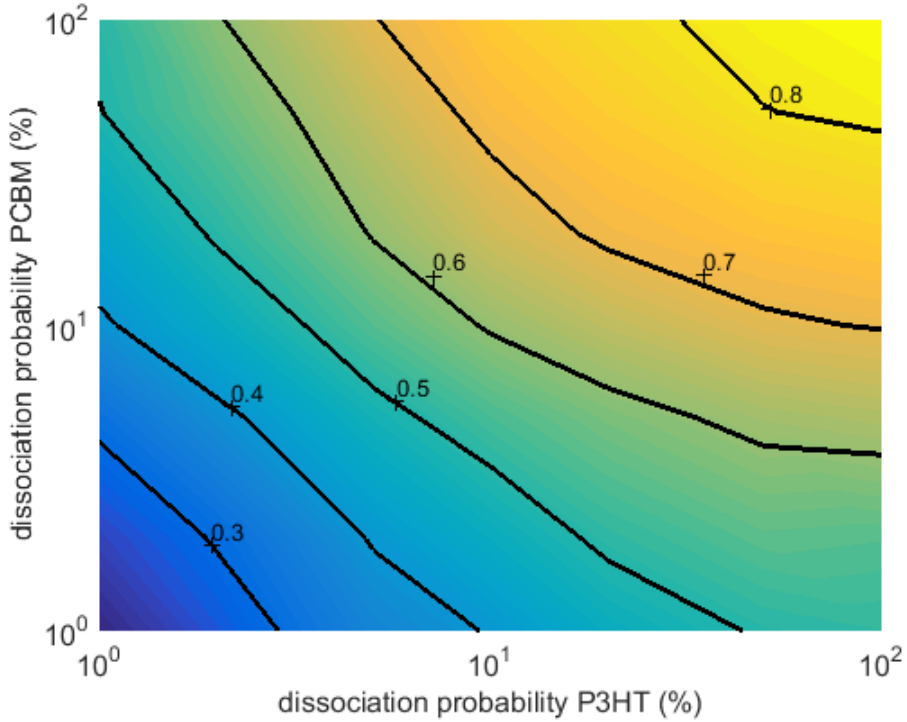
F = 31 nm

Feature size F = 3 V / A

η in P3HT:PCBM BHJ

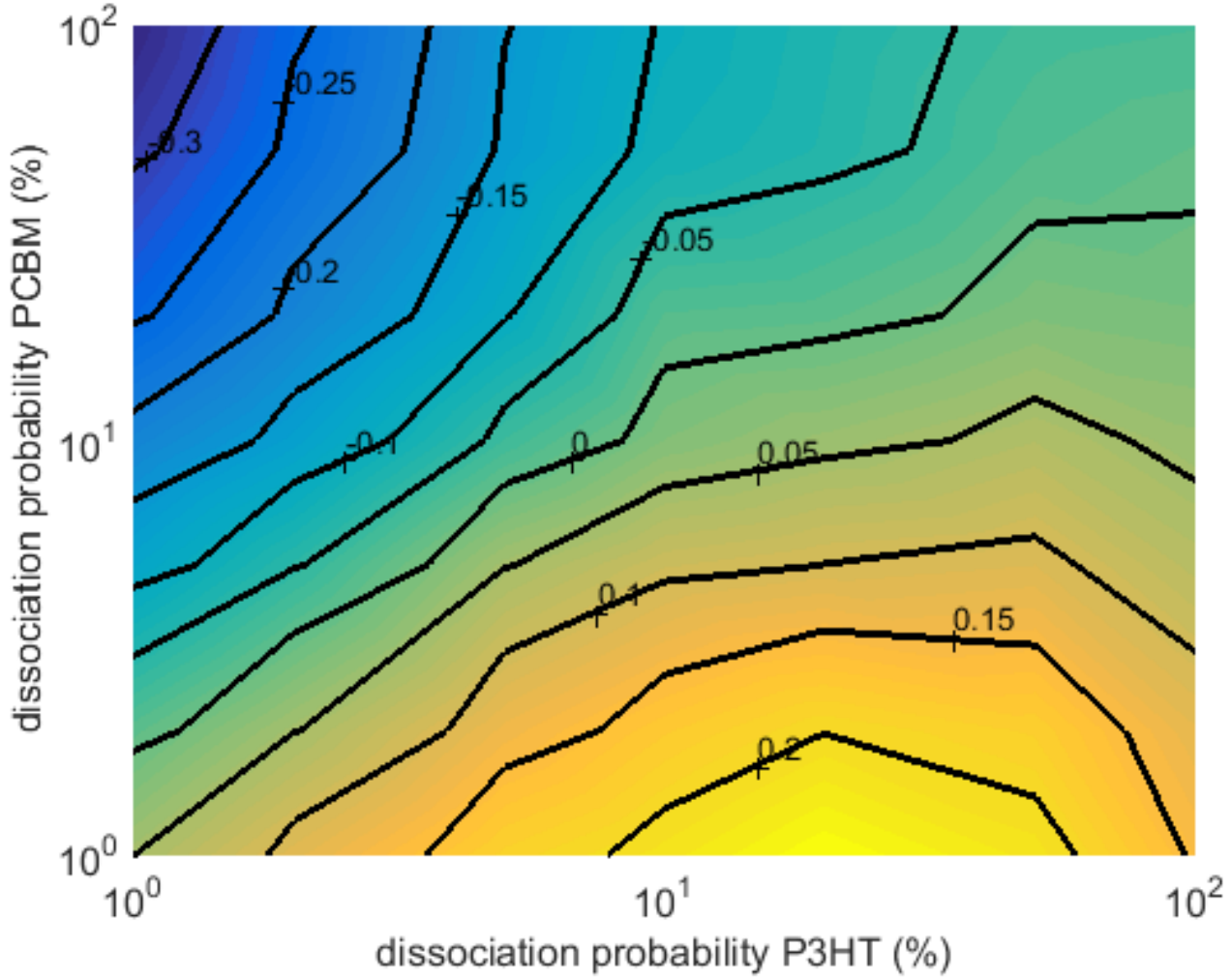


With Heterotransfer

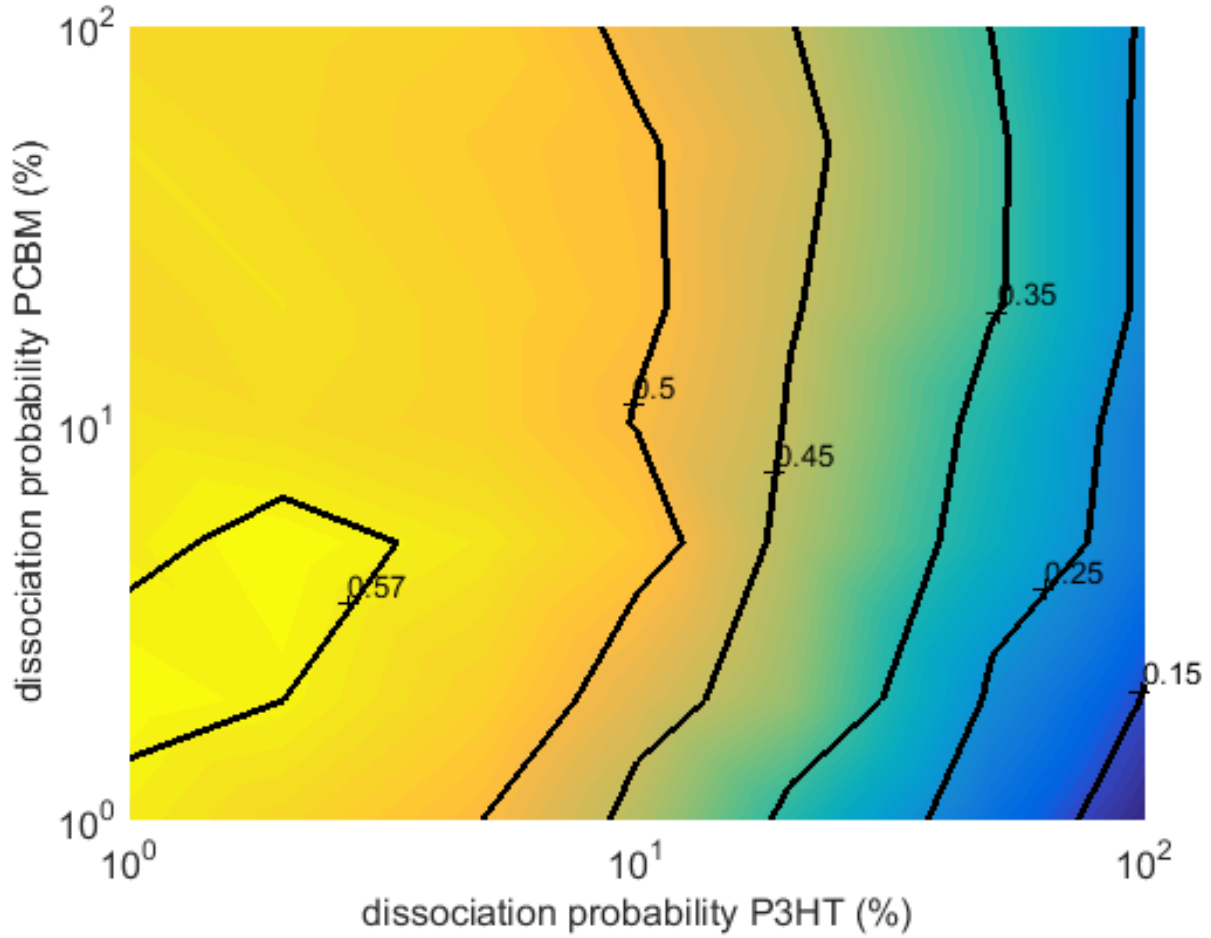


Without Heterotransfer

Difference (Without minus With)



Dissociated Excitons That Undergo 2 Step Dissociation in P3HT:PCBM BHJ



Experimental evidence:
Lloyd *et al.* (2008)

Hole transfer very fast, electron transfer is slower

η in Ternary BHJs

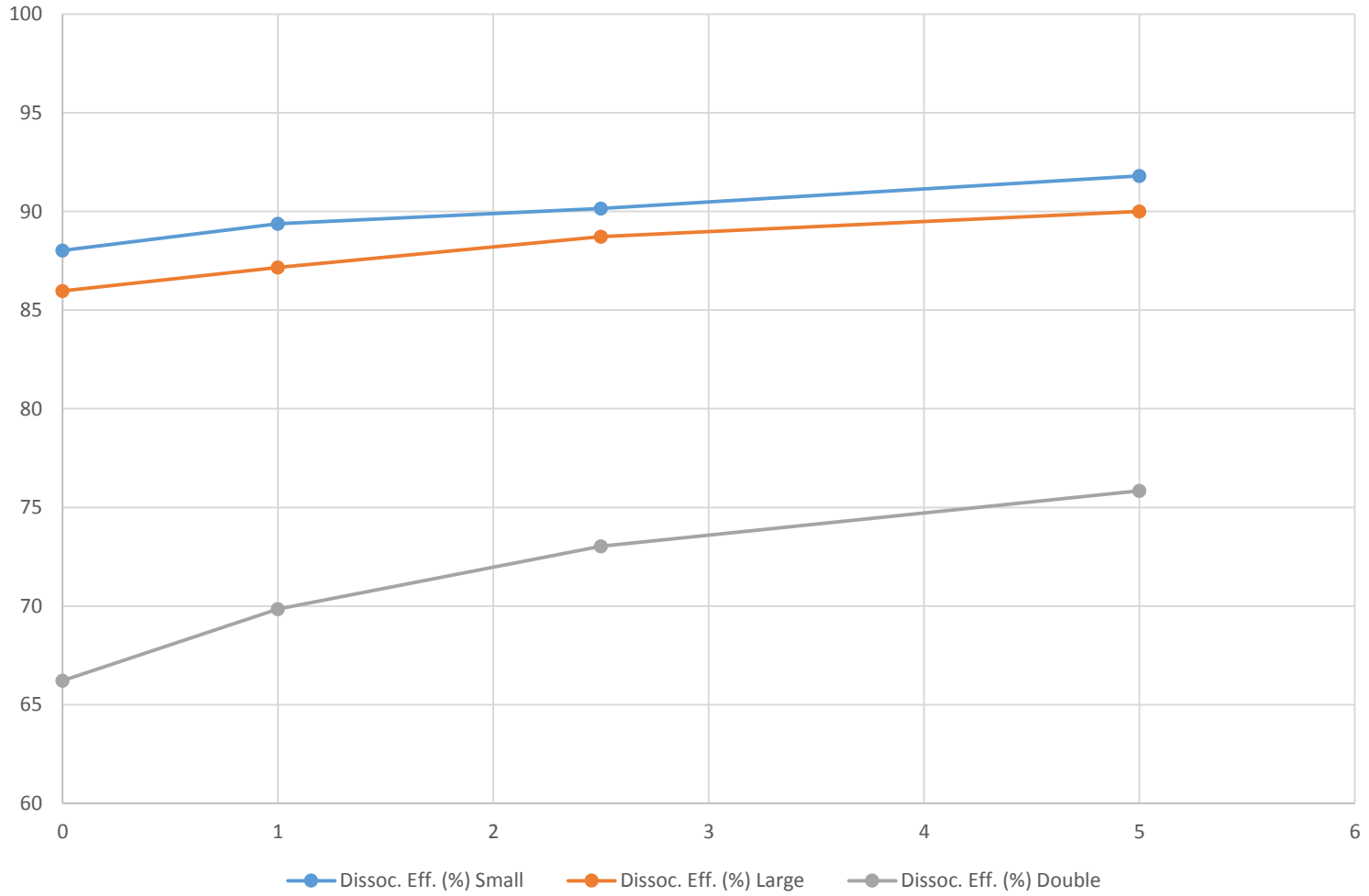
- Can also make ternary BHJ structures
- We use DIBSq as our third material
- Random interface sites replaced with DIBSq

Exciton dissociation efficiency vs DIBSq concentration for various feature sizes (P3HT)

- FRET helps with exciton dissociation, allowing for larger feature size, which is better for charge extraction

- Dissociation efficiency η as function of DIBSq concentration

F = 14, 15, 31 nm

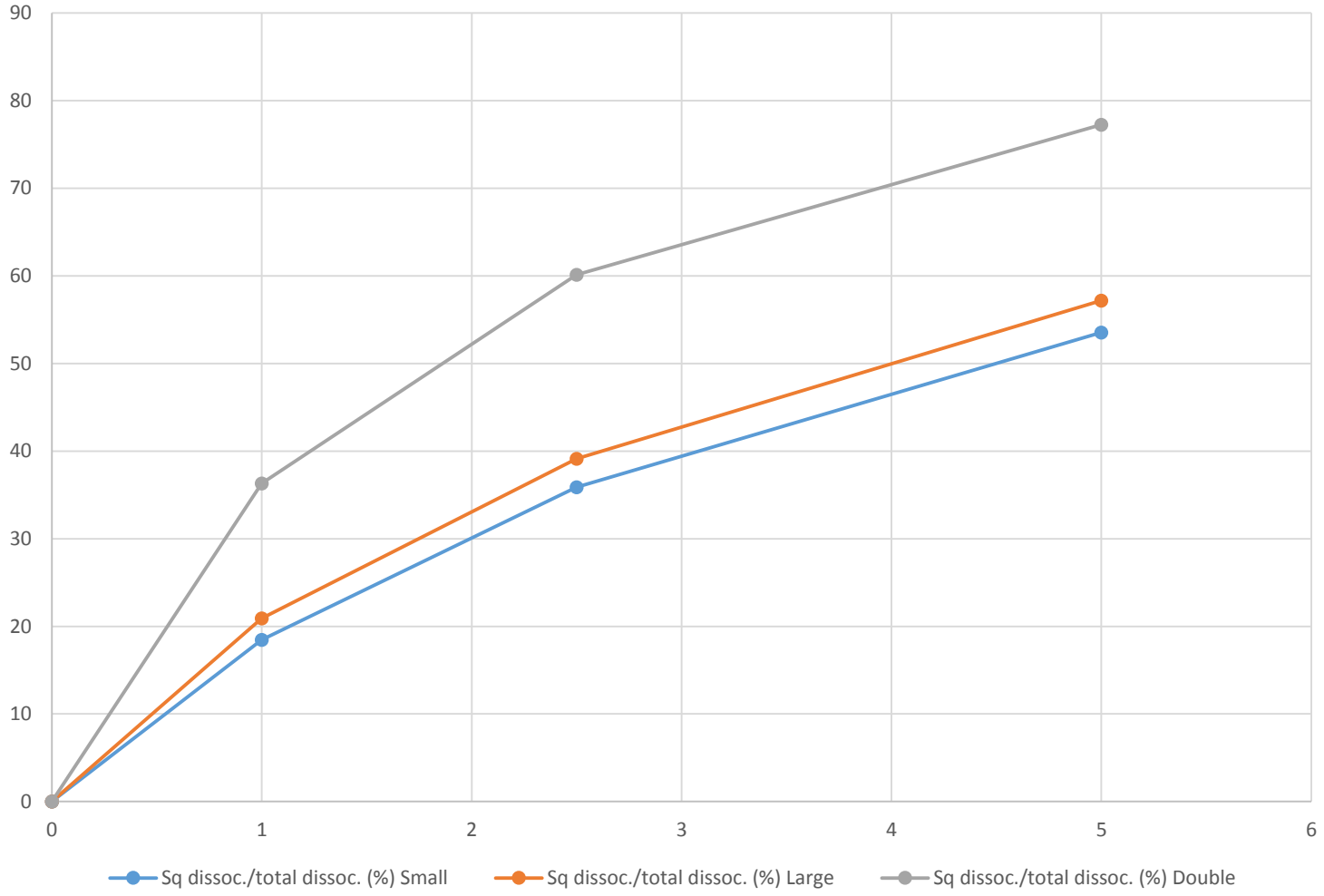


Exciton dissociation efficiency vs DIBSq concentration for various feature sizes (P3HT)

- FRET helps with exciton dissociation, allowing for larger feature size, which is better for charge extraction

- Fraction of excitons that dissociate at a DIBSq interface

F = 14, 15, 31 nm



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