Kinetic Monte Carlo simulation of organic photovoltaic and light emitting devices

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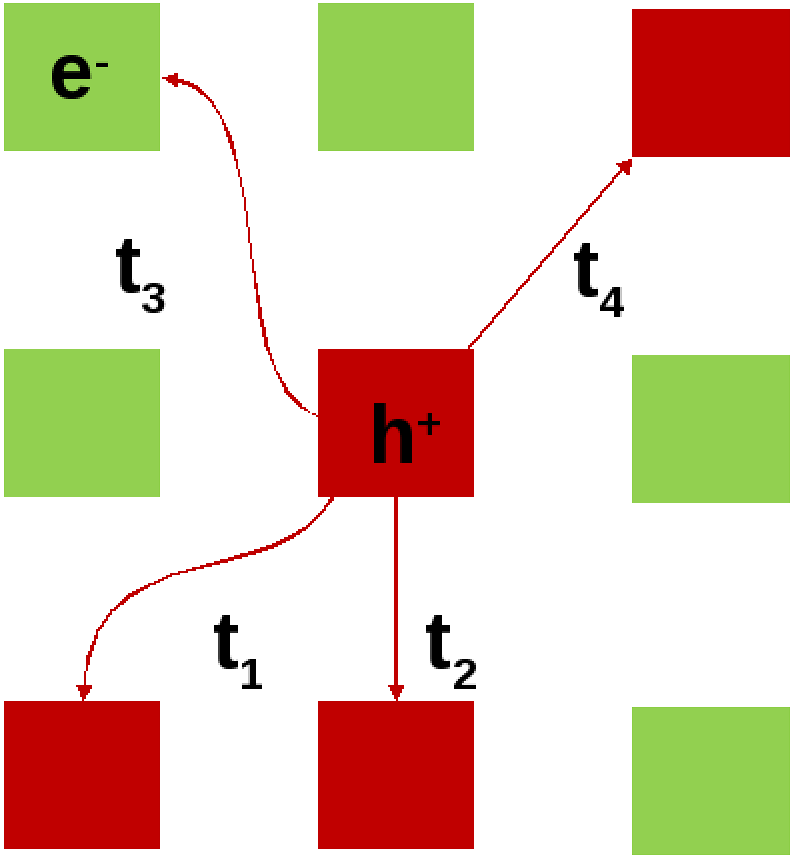
Topics

- Kinetic Monte Carlo method
- Multiscale model of exciton transport
- Organic photovoltaic device characteristics
- Stacked Organic Light Emitting Devices
- Doped organic semiconductors

Kinetic Monte Carlo method

Typical events

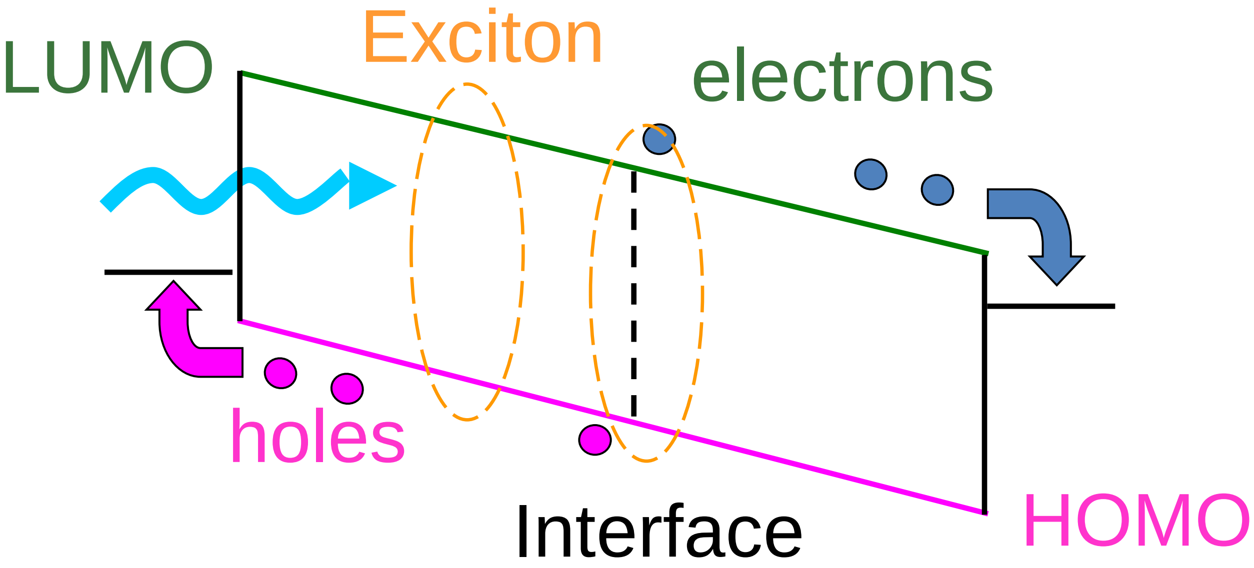


$$t_i = -\frac{\ln(R)}{k_i}$$

Advantages of Kinetic MC

- MC allows examination of morphology dependence
- Can handle any morphology.
- Can handle interacting particles
- Can see how neighbouring charges in Coulomb bound pairs behave
- Recombination models can be tested

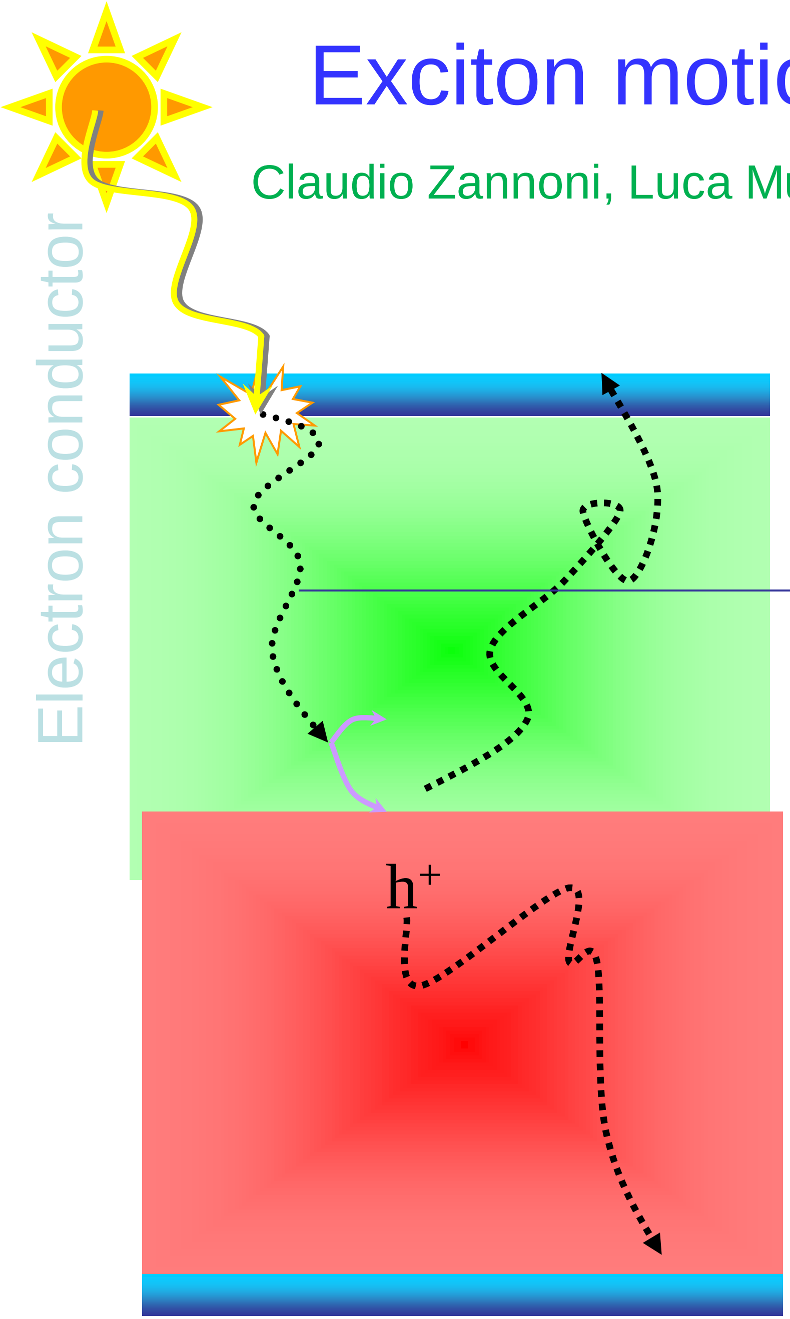
Organic Photovoltaic Devices



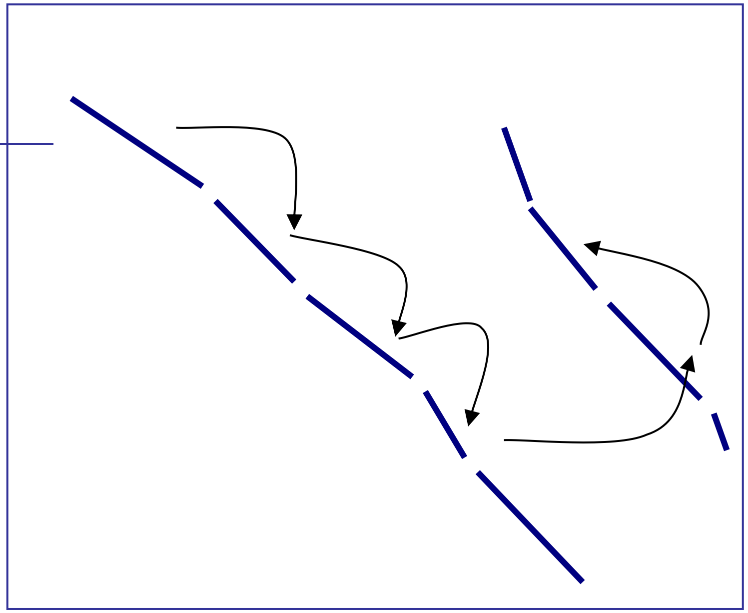
These are often made from blends of an electron and a hole conductor

Exciton motion in PV

Claudio Zannoni, Luca Muccioli (Bologna), David Beljonne (Mons)



Exciton hopping between chromophores or molecules

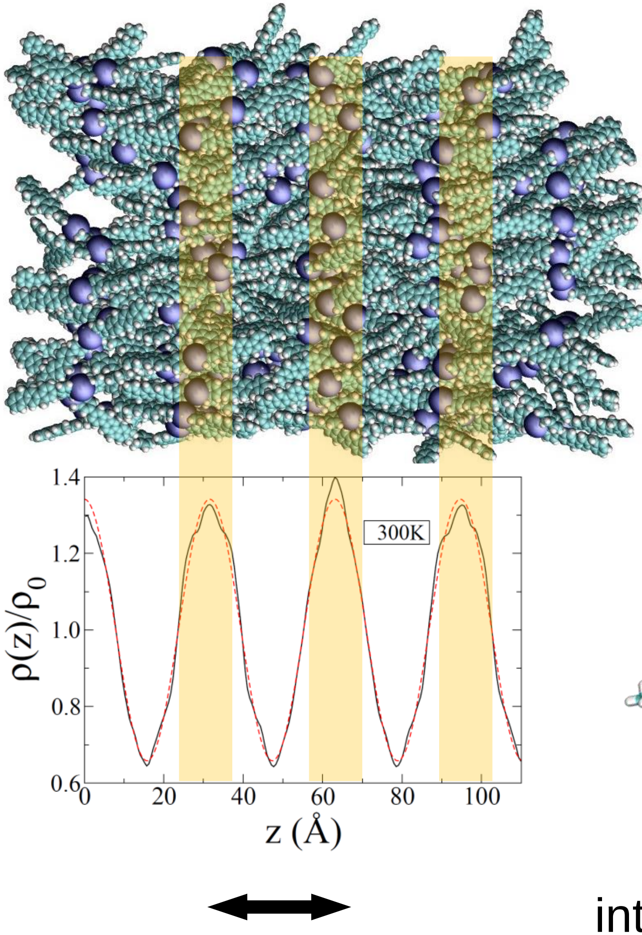


S Athanasopoulos et al
PRB **80** 195209 (2009)
E Emilianova et al PRB (2010)
T Papadopoulos et al
Chem Sci **2** 1025 (2011)

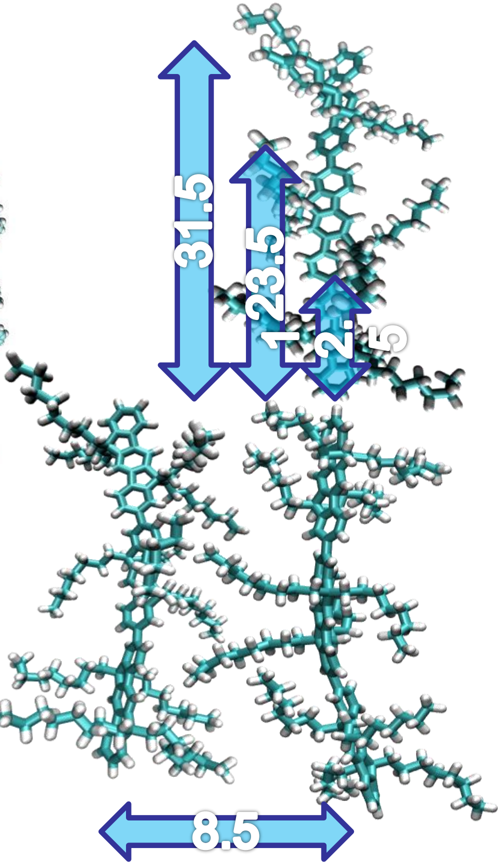
IF3 packing in smectic phase

● IF3 centre of mass

Ground state not planar:
Intramolecular dihedral
angle is 38°

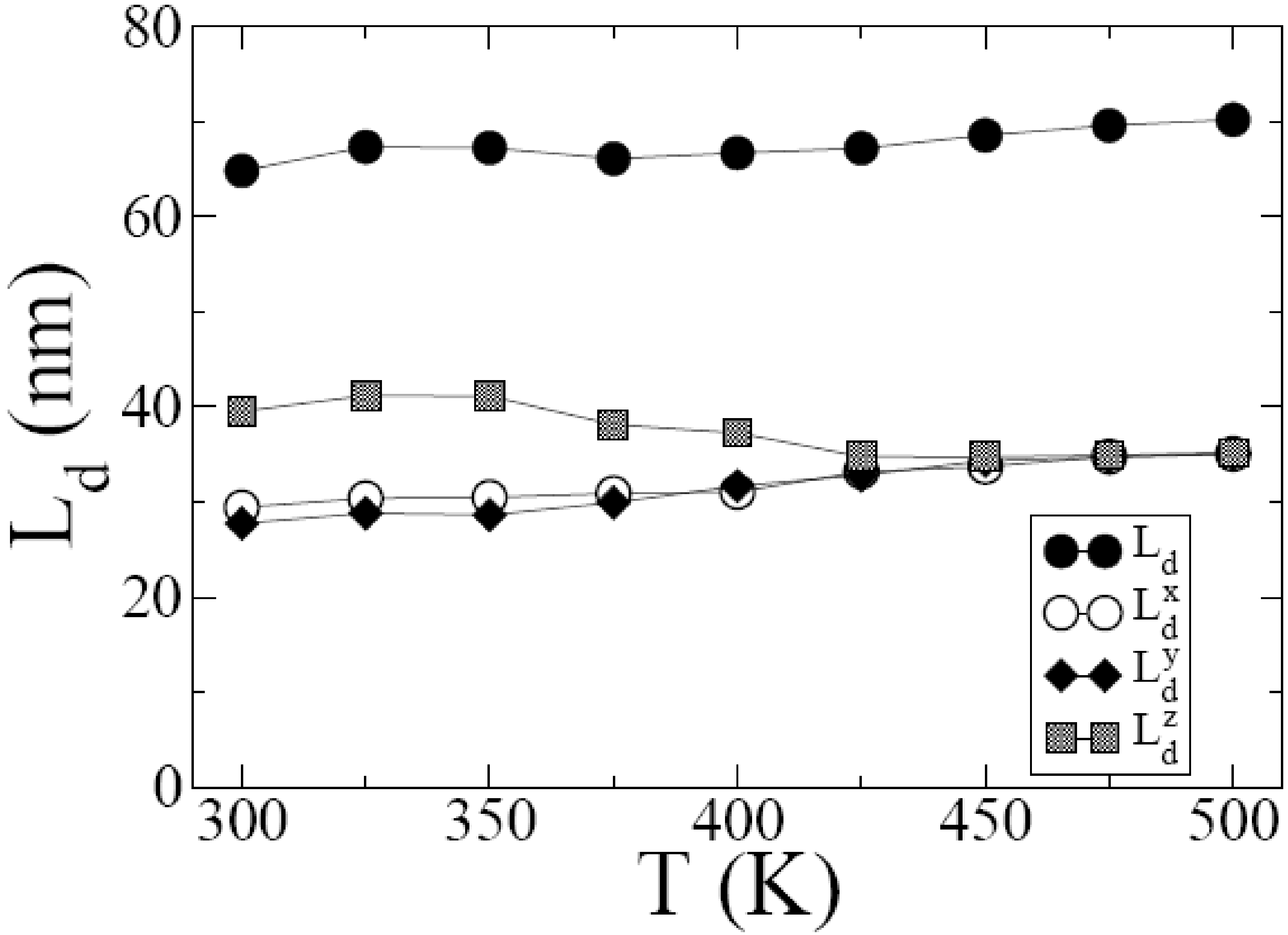


31.5 Å



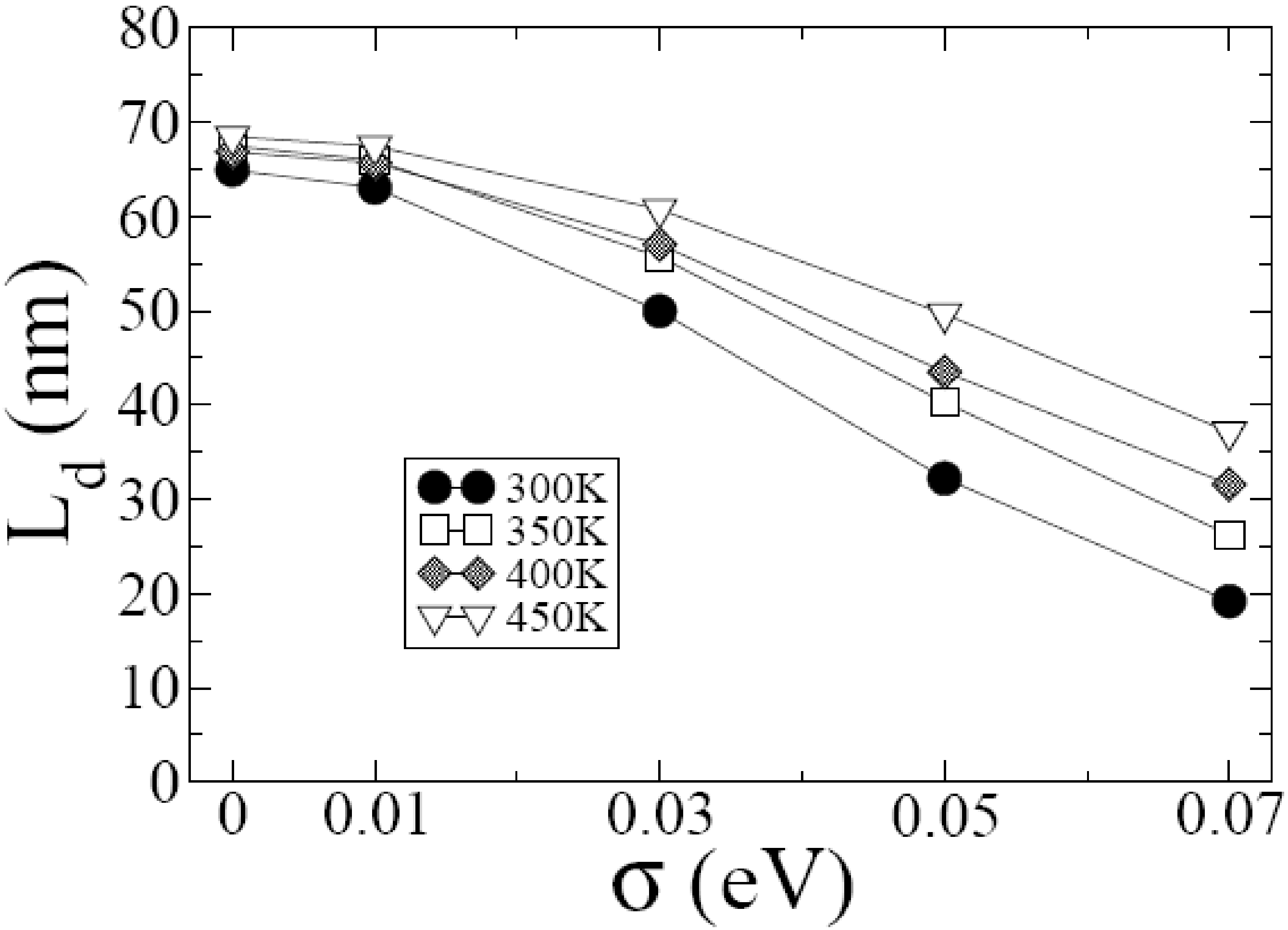
intermonomer distances in
the smectic phase (Å)

Exciton Diffusion Length

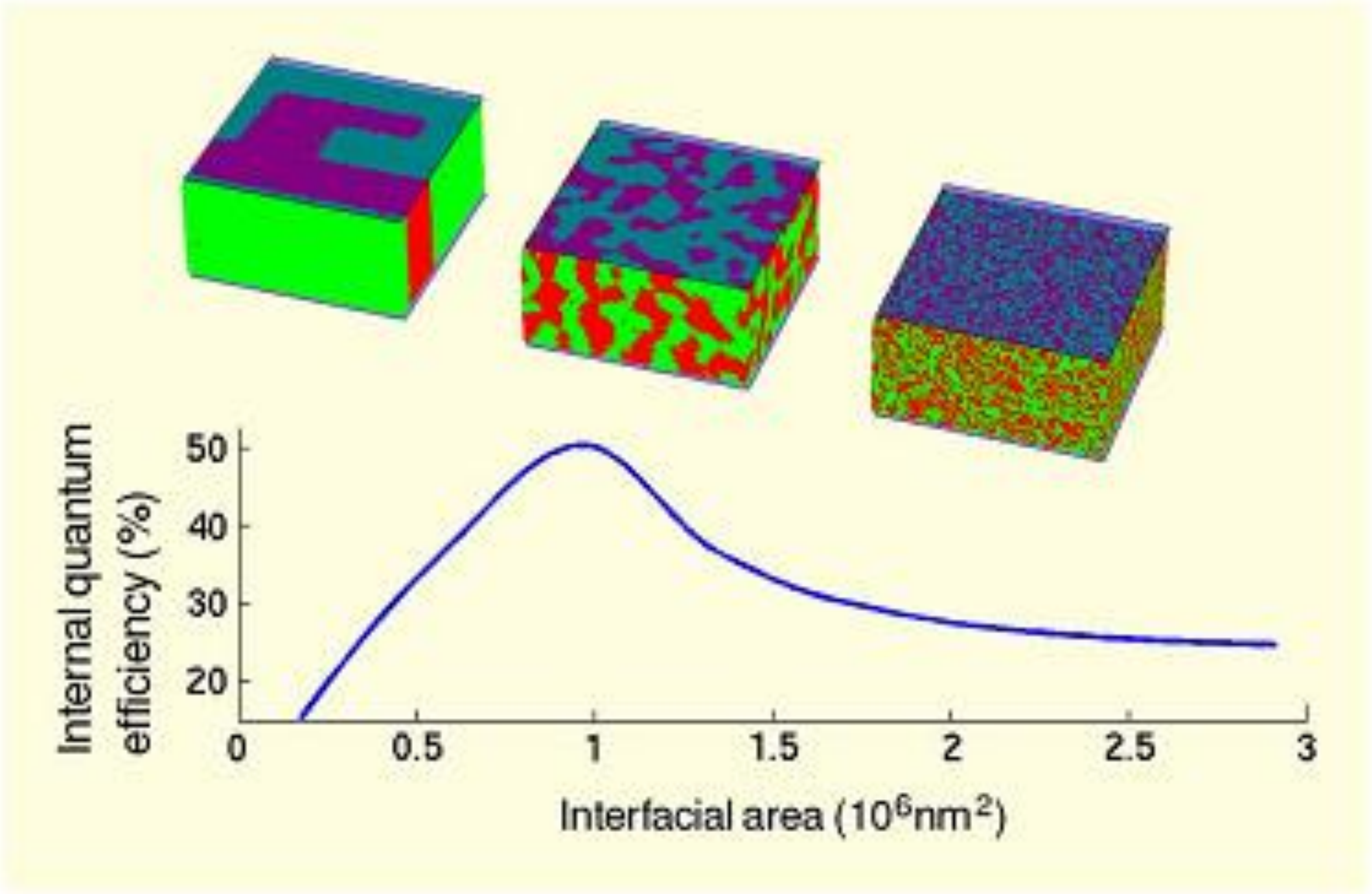


In the smectic phase, excitons travel further normal to the layers of IF3 molecules so we predict anisotropy in the fluorescence initially with a decay time of 0.2 ps ie within a few hops

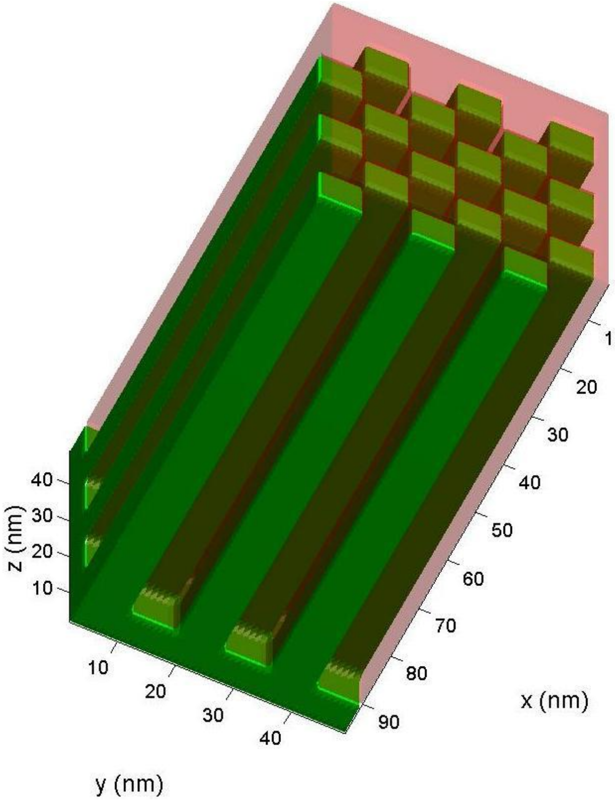
Energetic disorder

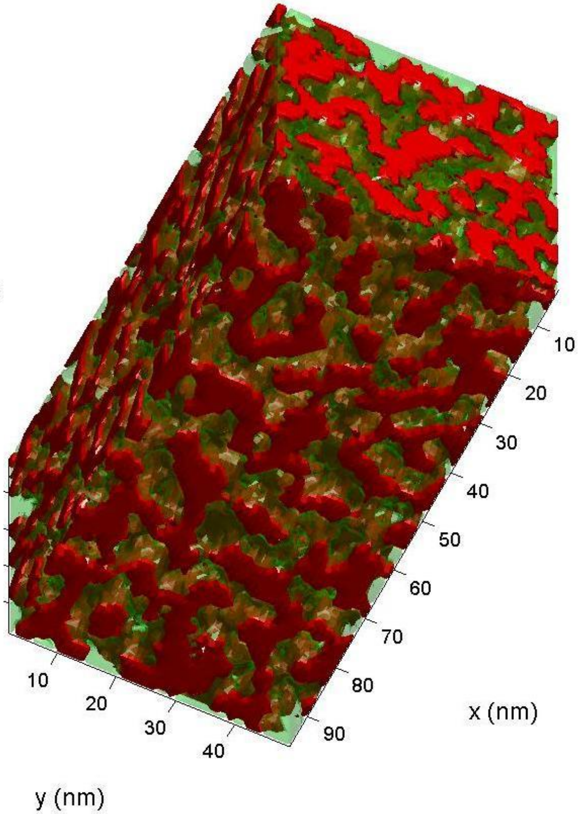


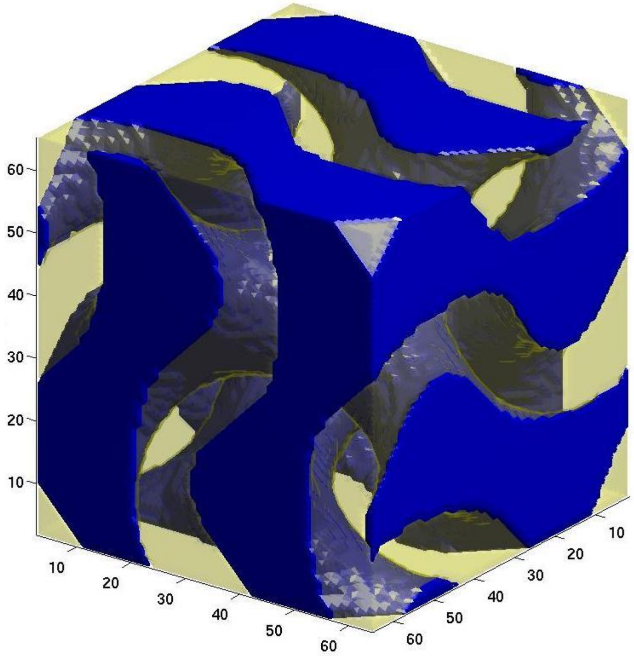
Organic blend PV



P K Watkins, A B Walker, G L B Verschoor *Nano Letts* **5**, 1814 (2005)







Gyroids

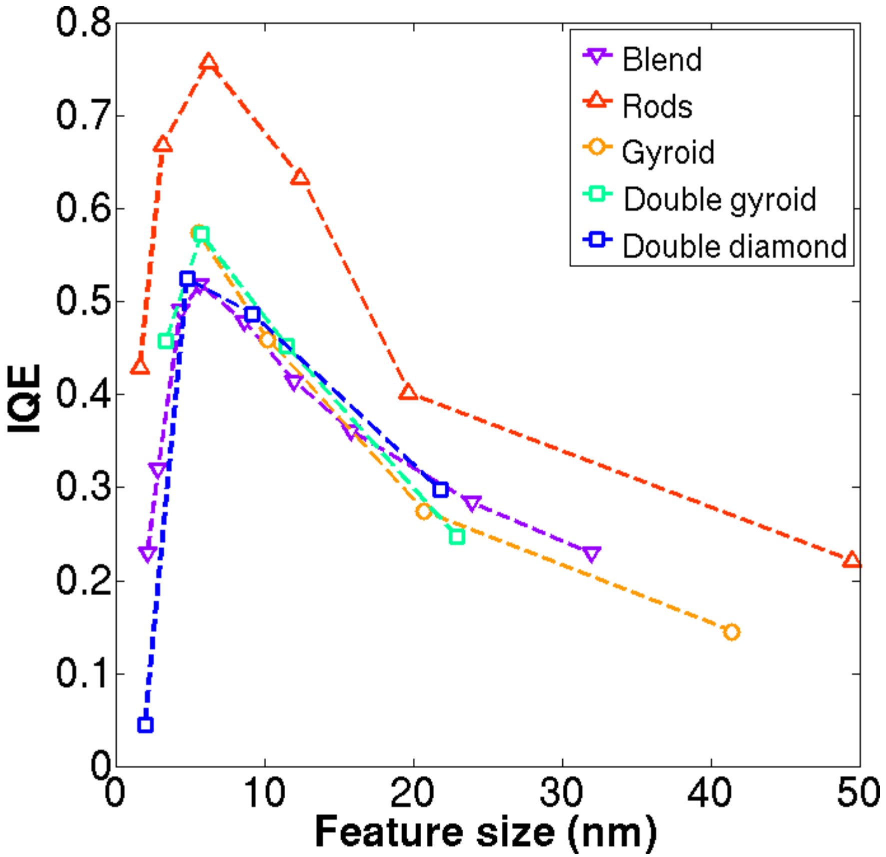
R G E Kimber et al Phys Chem Chem Phys (2010) **12** 84

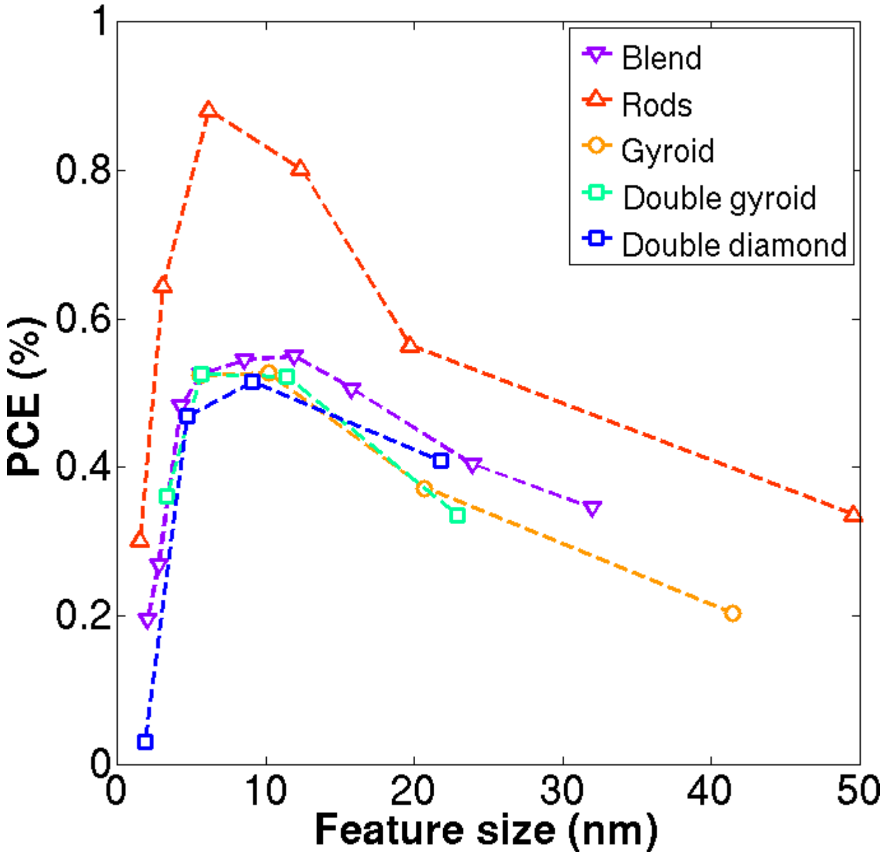
Continuous charge transport pathways, no disconnected or ‘cul-de-sac’ features

First Reaction Method

C Groves et al J. Chem. Phys.(2010) **133** 144110

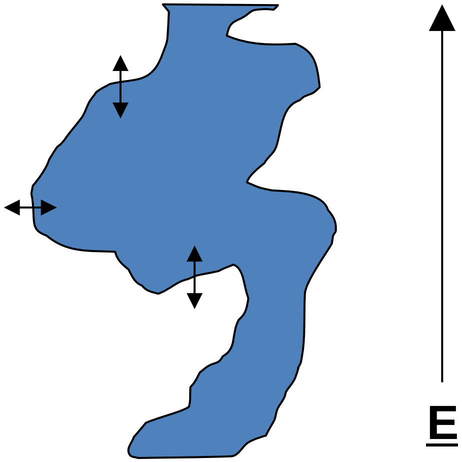
Device characteristics





Why?

Angle	η_{gr}
0°	~22%
90°	~26%
180°	~83%



- Most time is spent ‘tracking’ at the interface.
- A polymer with a range of interface angles is far less efficient than a vertical structure.

Islands

- Reduce the composition purity by adding islands of material

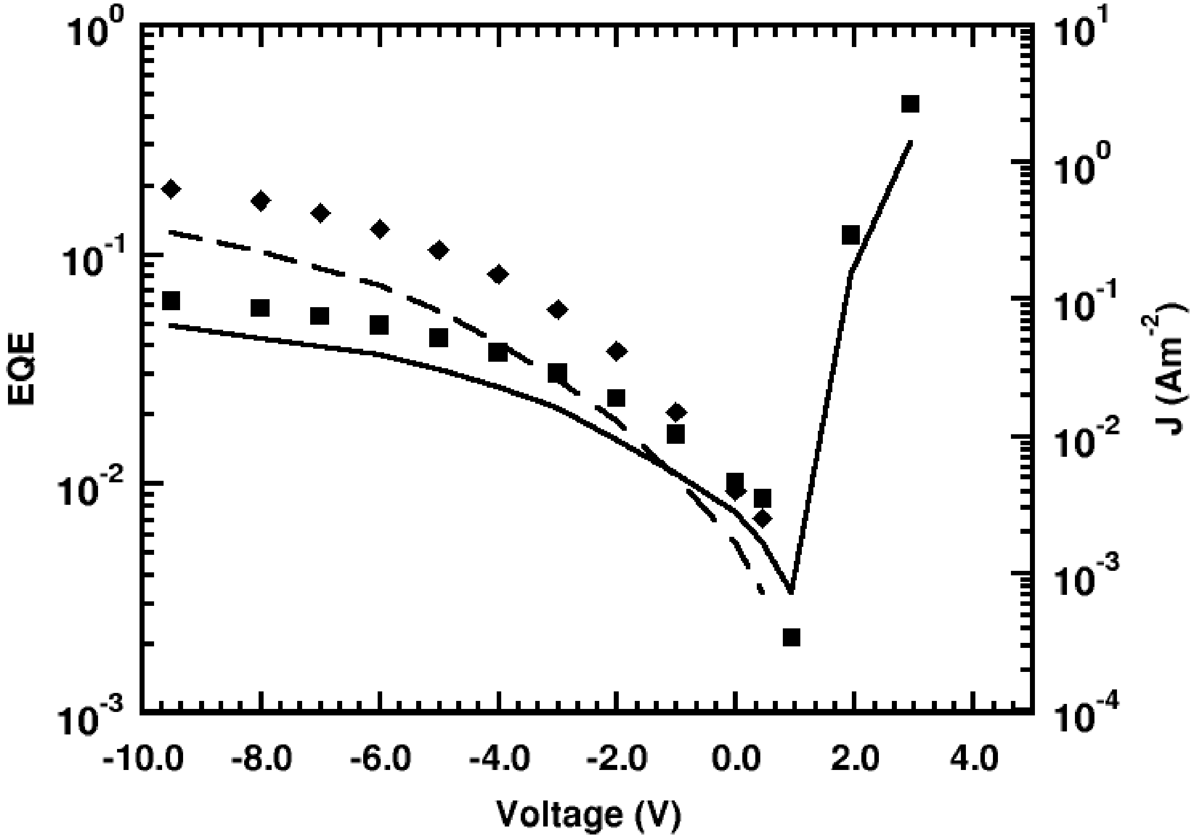
- Repeat simulations and plot against previous feature sizes

Islands	IQE	Optimum feature size
0%	0.55	5.6 nm
1%	0.50	6.4 nm
5%	0.48	7.5 nm

Allowing for islands which would not be visible in experiment shifts the apparent optimum feature size.

R G E Kimber et al Phys. Chem Chem Phys **12** 844 (2009)

KMC vs experiment OPV blend device



Building blocks approach to fitting data.

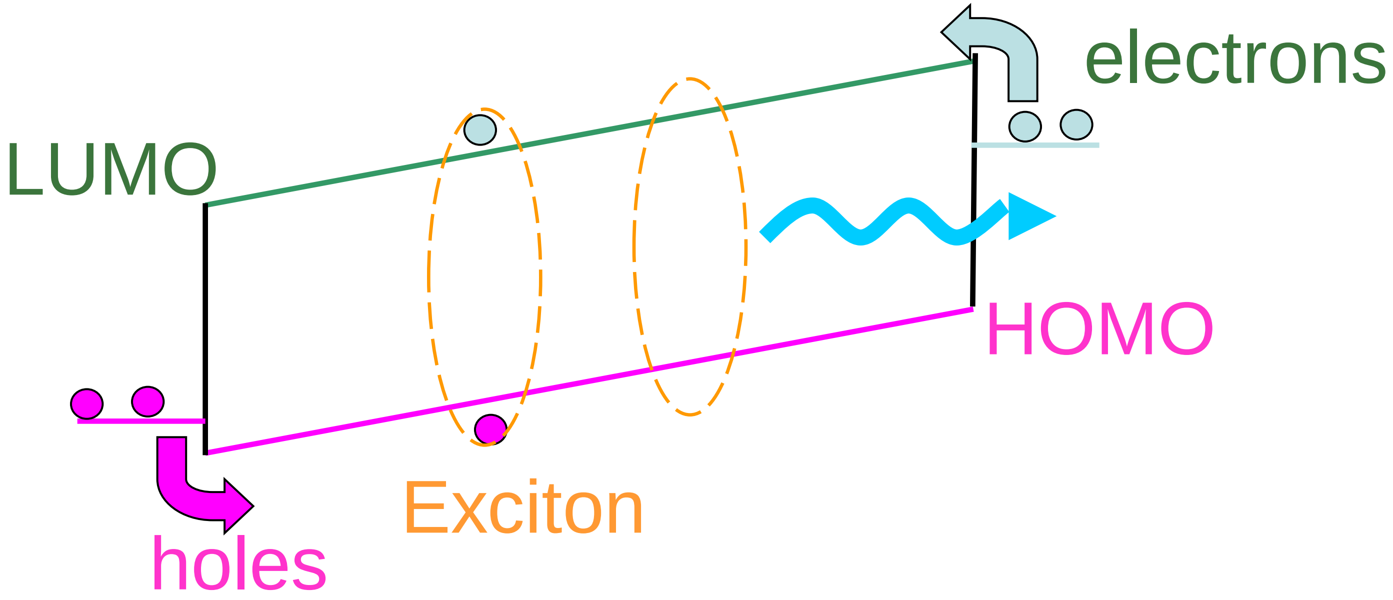
──	Experimental EQE	– – –	Experimental current density J
♦	KMC predicted EQE	■	KMC predicted J

R G E Kimber et al Phys Rev B (2012) **86**, 235206

Display Devices

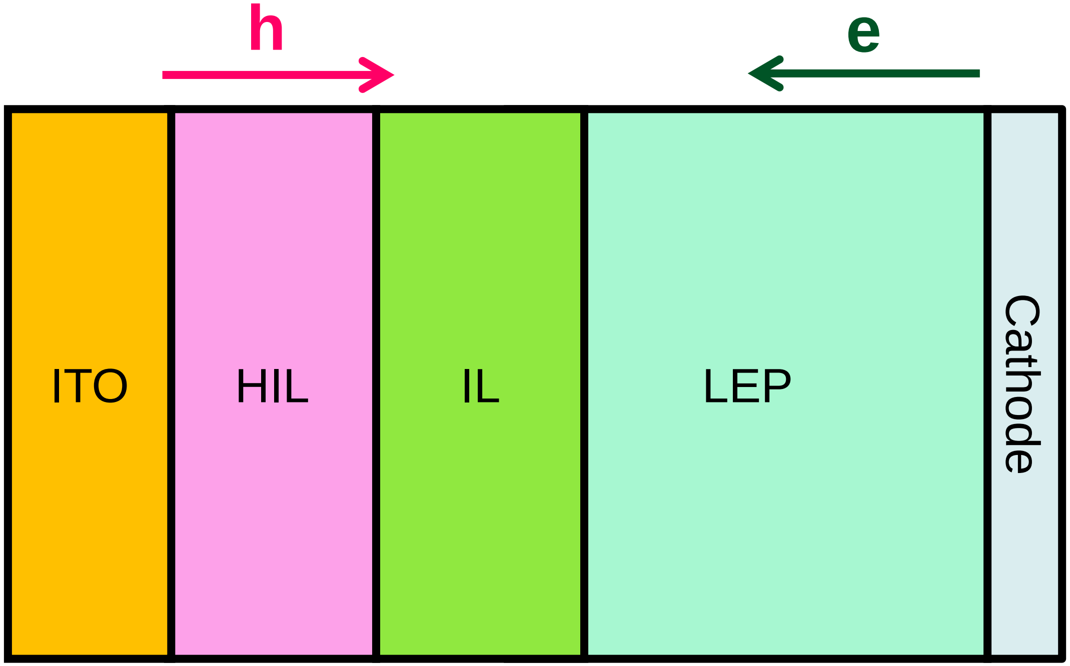
Fashion vibrating Bluetooth bracelet

OLED: Organic Light Emitting Device



Interlayers in OLEDs

Michael Cass (CDT), Je-Seon Kim (Imperial)



LEP is Light Emitting Polymer layer,

IL is interlayer

HIL is hole injection layer i.e. PEDOT:PSS layer

$\mu_{hLEP} < \mu_{eIL} < \mu_{eLEP} < \mu_{hIL}$

Low LEP hole mobility μ_{LEP} contains 5% PFB
Low iL electron mobility μ_{eiL} to prevent electrons reaching HIL
High iL hole mobility μ_{hiL} to reduce hole build up and keep photon generation zone in IL
iL blocks excitons

M Roberts et al SPIE (2010) can be downloaded from CDT website
L P Lu, D Kabra, R H Friend Adv Func Mat **22** 4165 (2012)

Exciton reactions

Excitons generated when holes and electrons are on adjacent sites

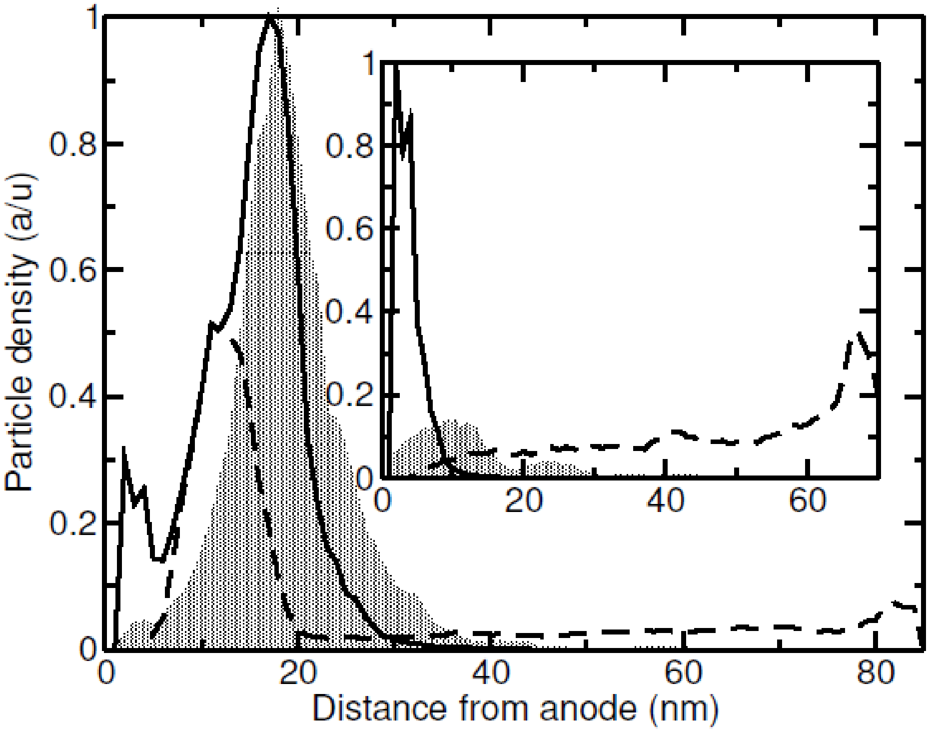
25% are singlets, 75% are triplets

- Triplet-triplet annihilation
  $^3D^* + {}^3A^* \rightarrow {}^1D + {}^3A^*$ or $^1D + {}^1A^*$ (ratio 75%:25%)
- Triplet-singlet annihilation
  $^3D^* + {}^1A^* \rightarrow {}^1D + {}^3A^*$
- Triplet-polaron quenching
  $^3D^* + A^+ \rightarrow {}^1D + A^{+*}$

Singlets hop by Förster, Triplets hop by Dexter

Y Zhang, S Forrest PRL **108** 267404 (2012)
S Reineke et al PRB **75** 125328 (2007)

Recombination profiles



LEP width 70 nm
Interlayer width
15 nm

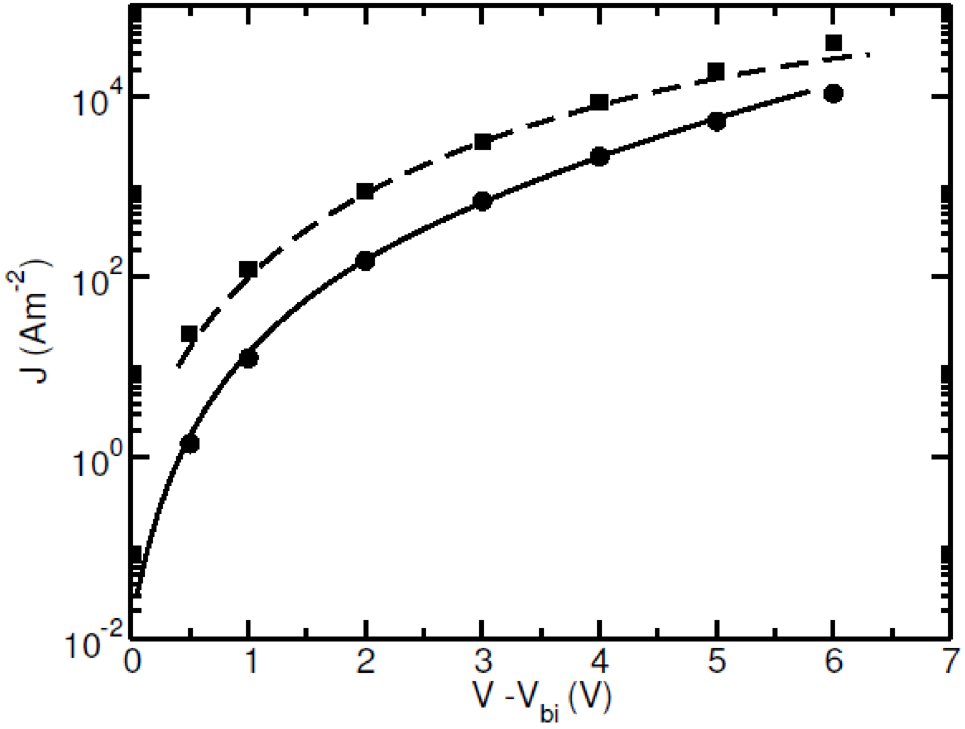
— Electron density

- - - Hole density

▨ Recombination profile

Main graph: With interlayer
Inset: Without interlayer

Total Current Density



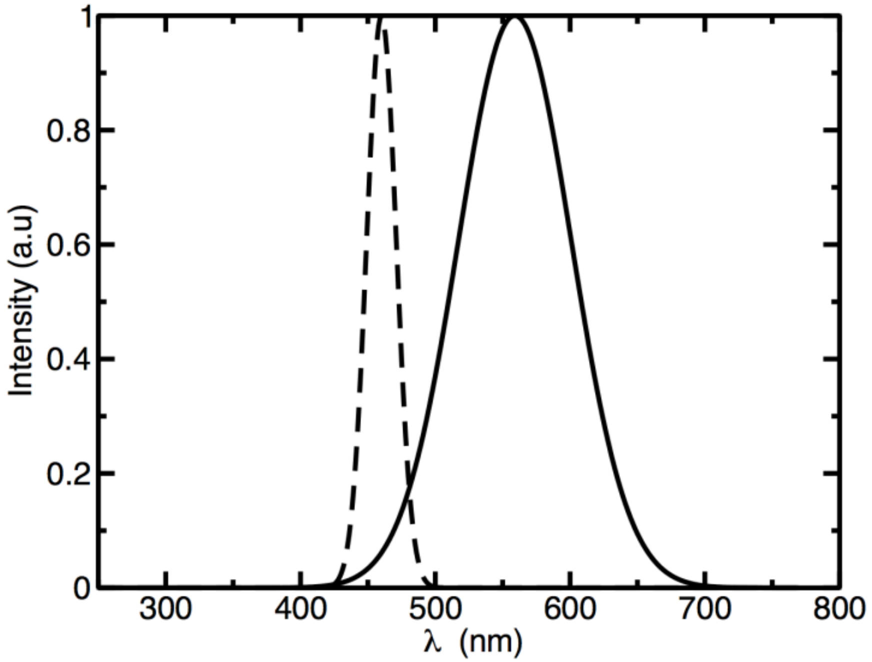
—— With interlayer

- - - - Without interlayer

Lines: experiment
Symbols: KMC

Fewer electron hopping sites in interlayer than in LEP

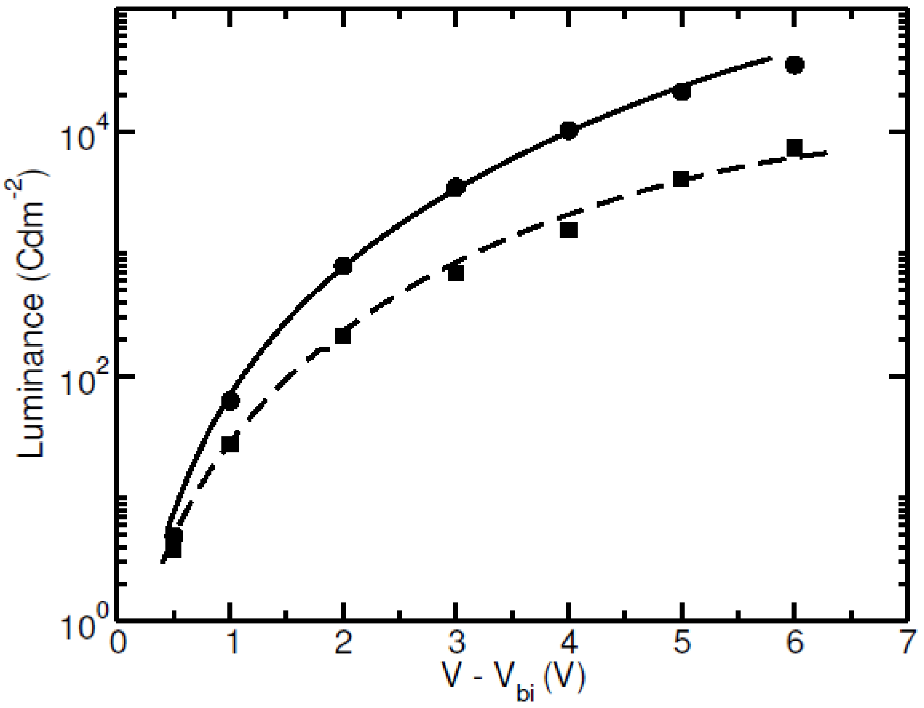
Optical Model



Solid line Photopic luminosity function (PLF)
Dashed line predicted emission spectrum

- Find emission from an oscillating dipole in a stacked structure of micro-cavities.
- Luminance from product of overlap between the PLF and the emission spectrum and the rate of photon outcoupling

Luminance



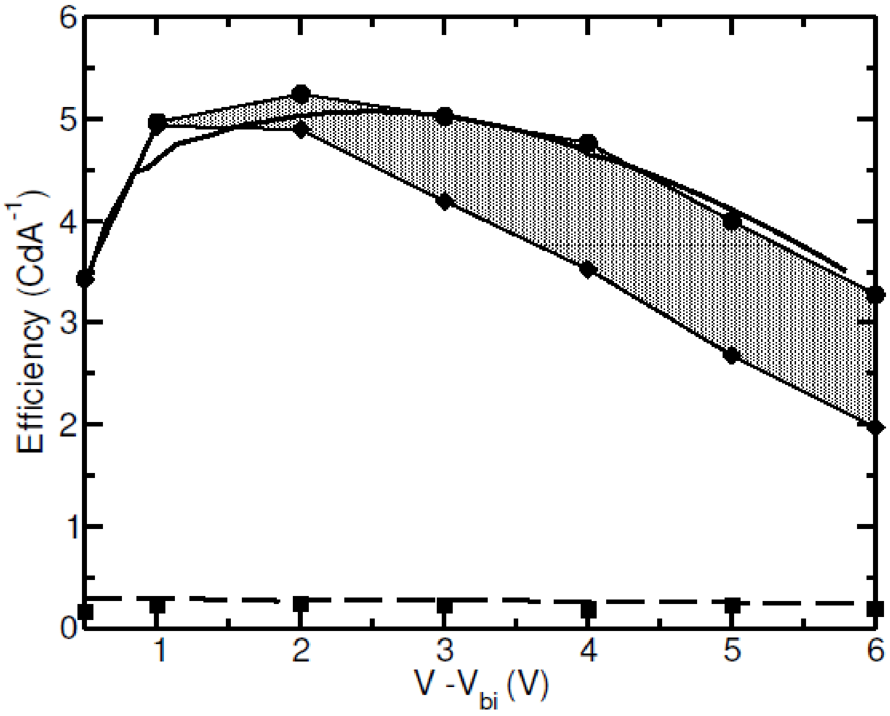
— With interlayer

- - - Without interlayer

Lines: experiment
Symbols: KMC

Optical model accounts for microcavity effects
Random exciton orientation
Have compared normal with parallel orientation

Luminous efficiency



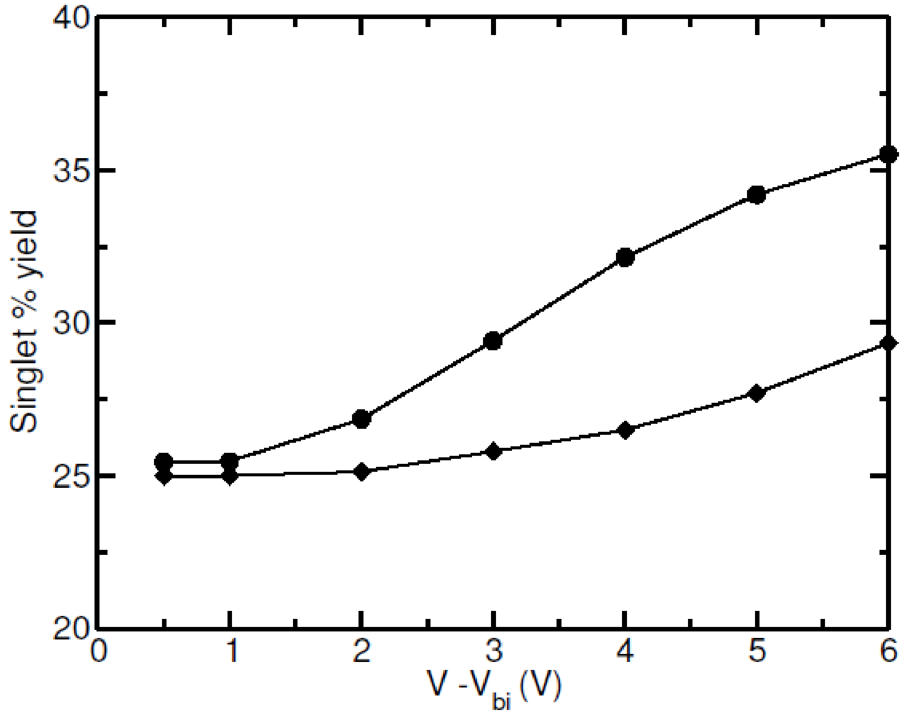
— With interlayer

- - - Without interlayer

▨ Increase due to triplet-triplet interactions

Lines: experiment
Symbols: KMC

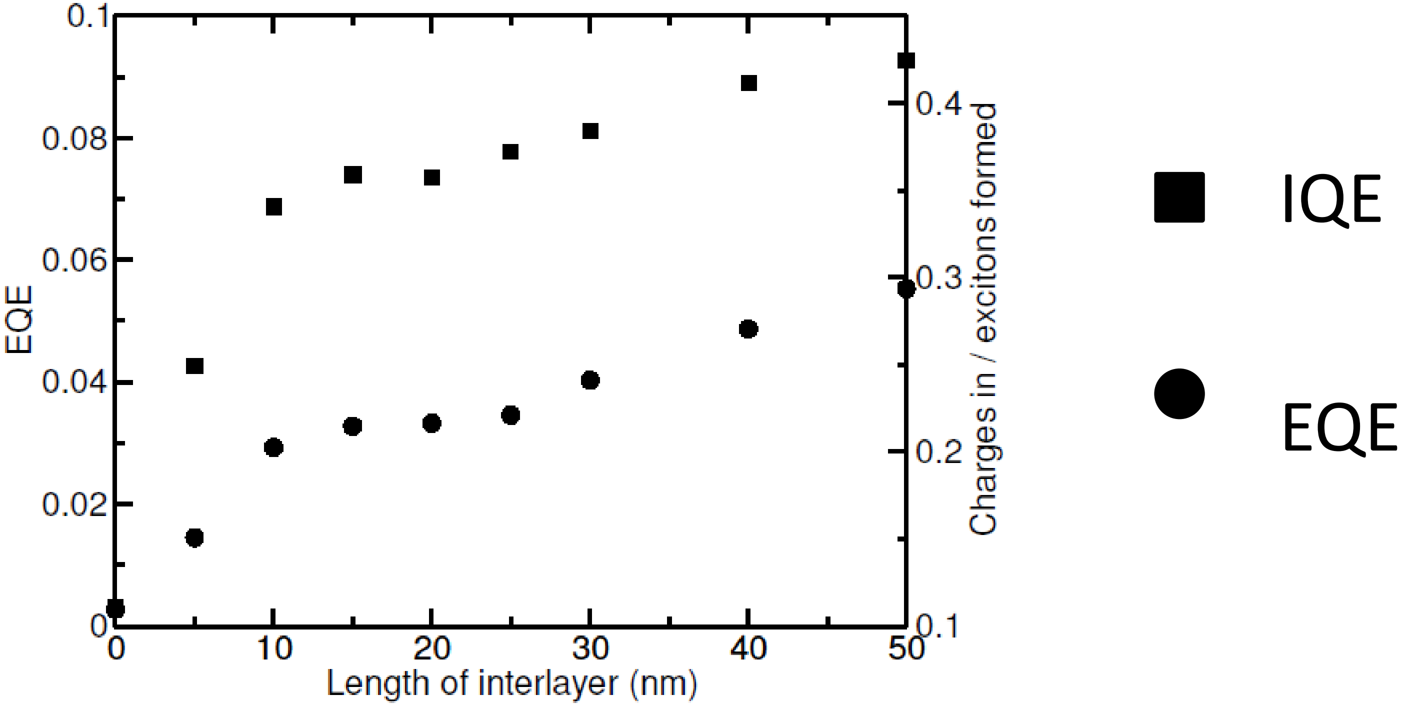
Singlet yield change with bias voltage



● With interlayer

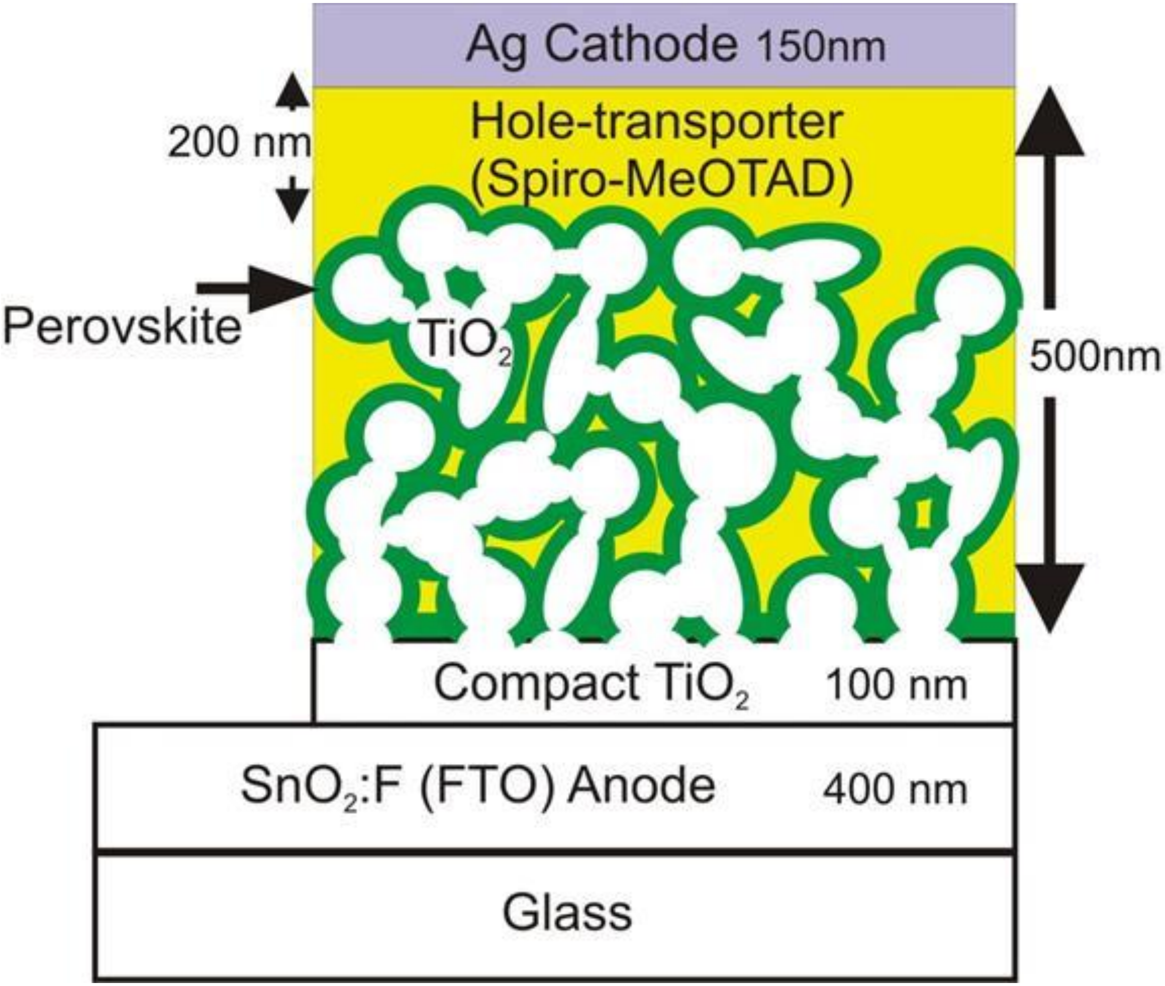
◆ Without interlayer

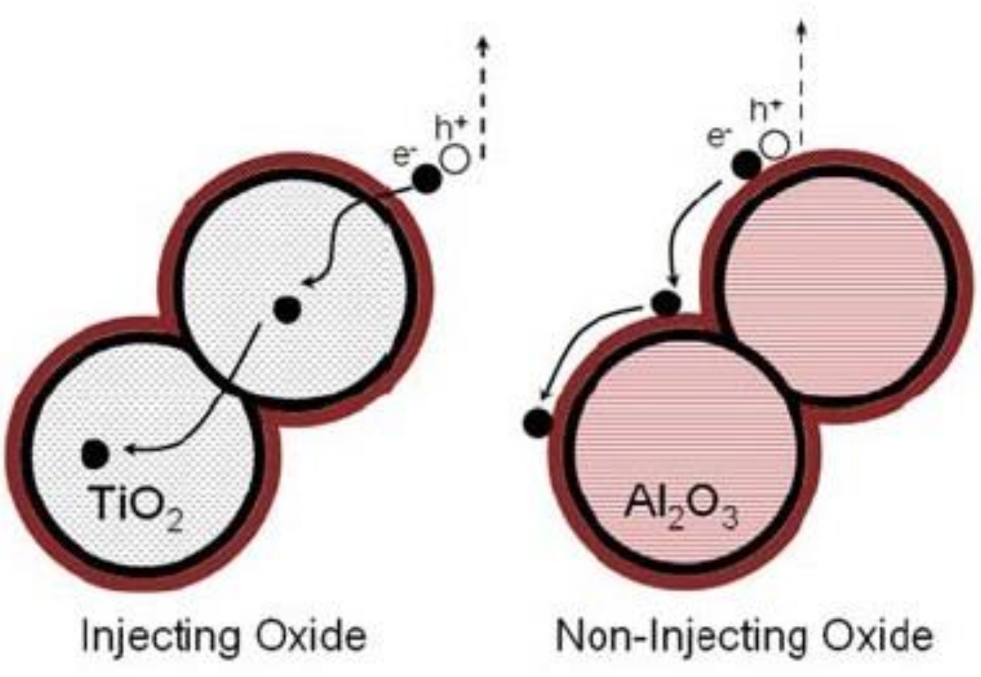
EQE variation with interlayer length



As iL layer width increases, improvement in exciton formation efficiency is reduced by worse out-coupling efficiency.

Solid-state sensitized solar cells

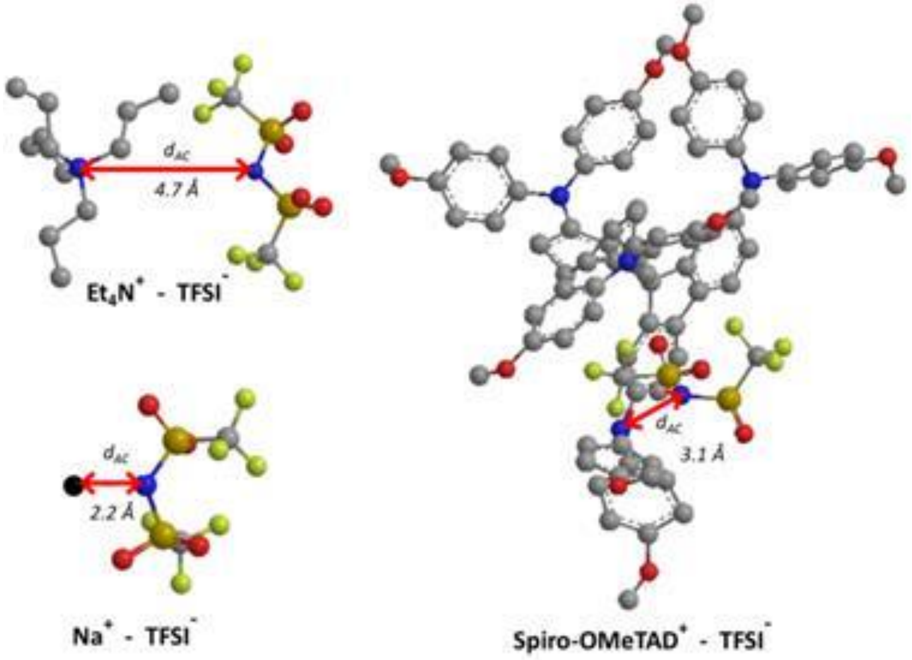


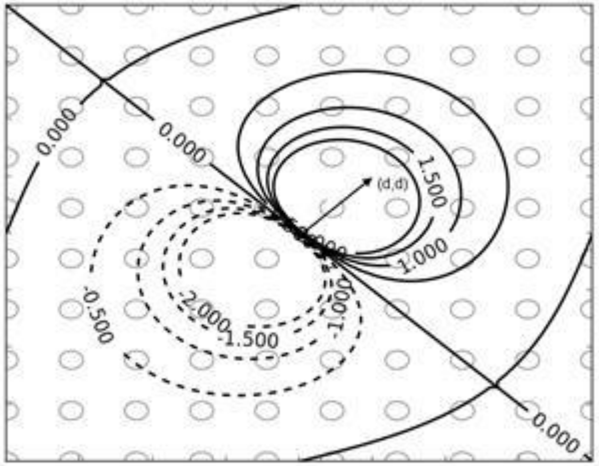


Left a solar cell with a titanium dioxide electrode (where excitons travel through the titanium dioxide)

Right a solar cell with an alumina electrode (where excitons travel more quickly through the thin perovskite layer)

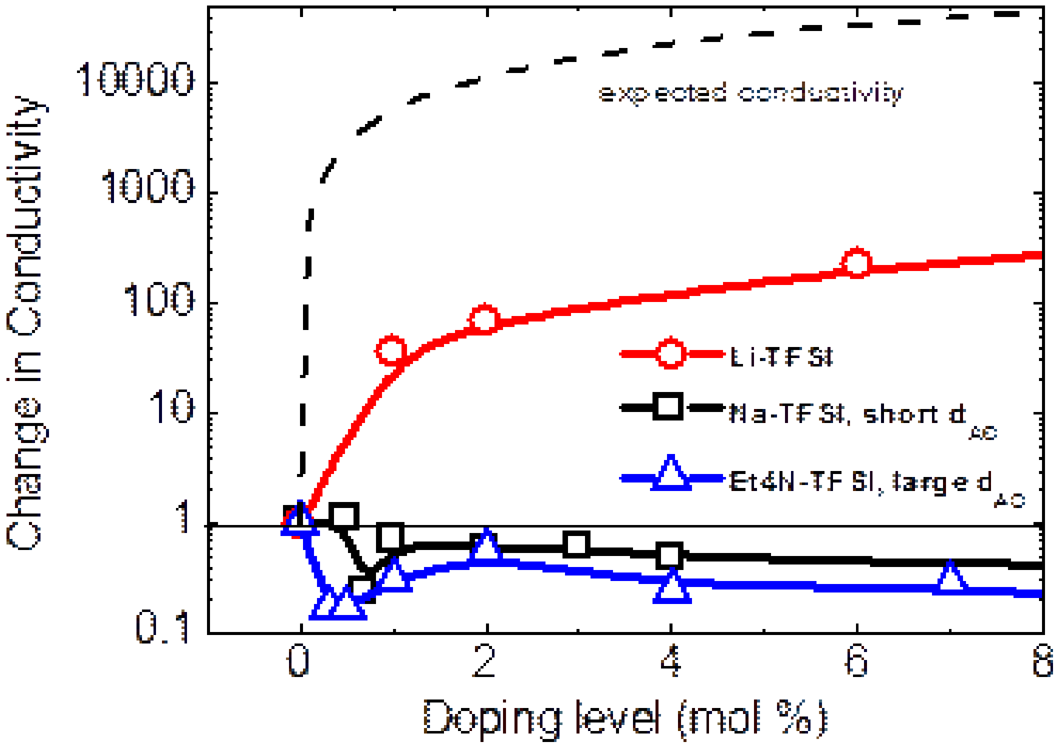
Doped organic semiconductors for solid state solar cells





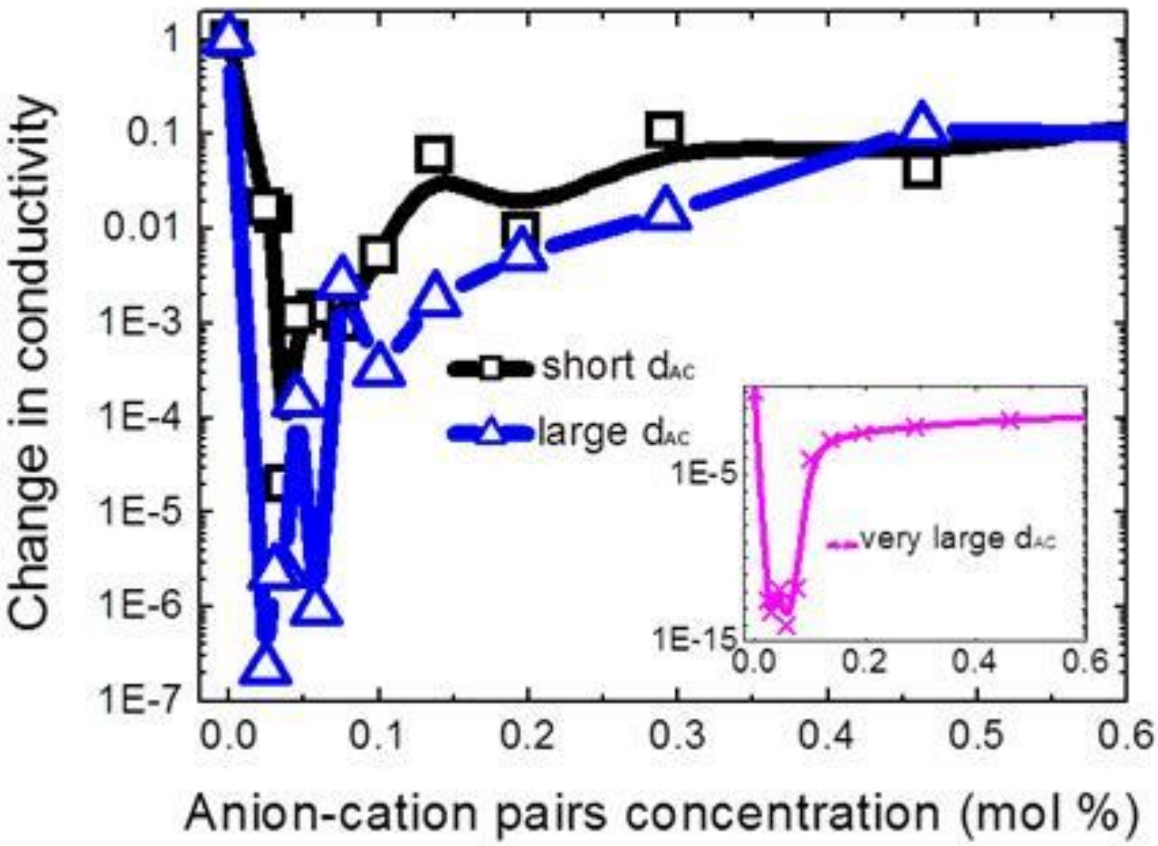
Inert salts Et_4N-TFSI and Na-TFSI, Anion-cation pair generated by Li doping in the Spiro-OMeTAD (Spiro-OMeTAD$^+$-TFSI$^-$). C grey, N blue, F yellow, O red, S orange, Na black

2D slice of hopping sites in the plane of a dipole from an anion-cation pair, with electrostatic interaction energy



conductivities scaled by the conductivity of undoped spiro-OMeTAD

Solid lines: measured conductivities for spiro-OMeTAD doped with Li-TFSI (circles), and the inert dopants Na-TFSI (squares, short anion-cation distance, d_{AC}) and Et_4N-TFSI (triangles, large anion-cation distance, d_{AC}). Dashed line: expected increase in conductivity assuming that only 1% of the lithium salt added in the Spiro-OMeTAD will generate extra mobile charges



d_{AC} = $0.5\sqrt{3}$ nm (Na-TFSI, black squares),
$0.6\sqrt{3}$ nm (Et_4N-TFSI, blue triangles)
inset $0.7\sqrt{3}$ nm (pink crosses).
Lines show fits to the simulated data

A Abate et al Phys. Chem Chem Phys submitted (2013)

Conclusions

- Multiscale modelling predicts exciton diffusion length changes with packing and hopping rates
- Dynamical Monte Carlo links morphology to device performance
- Building blocks approach to fitting data
- Can track singlet and triplet excitons
- Interlayer reduces electron leakage current and optimises recombination zone location
- Use the predictions for the recombination zones to look into degradation mechanisms.
- Useful tool to investigate reduction in mobility in doped organic semiconductors

Acknowledgements

Edward Wright
Robin Kimber
Pete Watkins
Michael Cass

MERCK

EPSRC

DESTINY

DyE SensiTIzed solar cells with eNhanced stabilitY

MARIE CURIE ACTIONS

SUPER*SOLAR*

SEVENTH FRAMEWORK PROGRAMME

UNIVERSITY OF BATH