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

Ground state not planar: Intramolecular dihedral angle is 38°

Intermonomer distances in the smectic phase (Å)

31.5 Å
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 i.e. within a few hops.
Organic blend PV

Gyroids
Continuous charge transport pathways, no disconnected or ‘cul-de-sac’ features
First Reaction Method
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

<table>
<thead>
<tr>
<th>Islands</th>
<th>IQE</th>
<th>Optimum feature size</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>0.55</td>
<td>5.6 nm</td>
</tr>
<tr>
<td>1%</td>
<td>0.50</td>
<td>6.4 nm</td>
</tr>
<tr>
<td>5%</td>
<td>0.48</td>
<td>7.5 nm</td>
</tr>
</tbody>
</table>

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

KMC vs experiment OPV blend device

Building blocks approach to fitting data.

Experimental EQE
KMC predicted EQE
Experimental current density J
KMC predicted J

Display Devices

OLED: Organic Light Emitting Device

LUMO → HOMO

Exciton

holes → electrons

Fashion vibrating Bluetooth bracelet
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 \( \mu_{LEP} \) contains 5\% PFB

Low iL electron mobility \( \mu_{eIL} \) to prevent electrons reaching HIL

High iL hole mobility \( \mu_{hIL} \) 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

Exciton reactions

Excitons generated when holes and electrons are on adjacent sites
25% are singlets, 75% are triplets

• Triplet-triplet annihilation
  \[ ^3D^* + ^3A^* \rightarrow ^1D + ^3A^* \text{ or } ^1D + ^1A^* \] (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

Main graph: With interlayer
Inset: Without interlayer

LEP width 70 nm
Interlayer width 15 nm

- Electron density
- Hole density
- Recombination profile
Total Current Density

Fewer electron hopping sites in interlayer than in LEP

Lines: experiment
Symbols: KMC
• 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

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

Lines: experiment
Symbols: KMC
Singlet yield change with bias voltage

![Graph showing singlet yield change with bias voltage. The graph compares singlet yield with and without interlayer, with the y-axis representing singlet % yield and the x-axis representing \( V - V_{bi} \) in volts. The graph shows an upward trend for both conditions, with the line for with interlayer being higher than the line for without interlayer.]

- With interlayer
- Without interlayer
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$_4$N-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
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$_4$N-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$_4$N-TFSI, blue triangles)  
inset 0.7\sqrt{3}$ nm (pink crosses).  
Lines show fits to the simulated data

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

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Pete Watkins
Michael Cass

DyE Sensitized solar cells with enhanced stability