Design of organic semiconductors
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Examples and Abbreviations

Processing: small molecules – vacuum deposited conjugated polymers: processed from solution

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(p-phenylenevinylene)</td>
<td>PPV</td>
</tr>
<tr>
<td>polyfluorene</td>
<td>PFO</td>
</tr>
<tr>
<td>poly(3-alkylthiophene)</td>
<td>P3AT, P3HT</td>
</tr>
<tr>
<td>tris(8-hydroxyquinoline)aluminium</td>
<td>Alq3</td>
</tr>
<tr>
<td>fullerene</td>
<td>C60</td>
</tr>
<tr>
<td>Phenyl C61 Butyric Acid Methyl Ester</td>
<td>PCBM</td>
</tr>
<tr>
<td>Cu-phtalocyanine</td>
<td>CuPc</td>
</tr>
</tbody>
</table>

Takeaway message

Google it
Problem: excitons generated within 10 nm of the interface dissociate. The rest decays prior to the dissociation.

Bulk heterojunction solar cell

Domains should be of the order of the exciton diffusion length

Efficiency versus domain size

Competition between the interfacial area and the length of the percolation path

Example: a mixture of a soluble polymer (P3HT) and fullerene derivatives (PCBM). Alternatively, mixed layers of small molecules (CuPc and C60)

Need: low band gap materials (more light absorption)

Bulk heterojunction soar cell

Excitons are generated close to the interface
There are uninterrupted pathways to the electrodes
The phases are connected to the appropriate electrode


Block copolymer solar cell, 3 times increase in efficiency
Motivation

To relate charge carrier mobility to the chemical structure

Mobility $\mu(F, \rho, T, \text{material, processing})$ is an important parameter entering Maxwell equations

Microscopic pathways of charge carriers influence device stability
Compound design: problems

NMR, WAXS: averaged quantities, no distribution functions

Is the improvement due to electronic structure or morphology?
Theoretical Challenges

a. Large-scale morphology (topology of the charge percolating network)
b. Local mutual orientations/positions of molecules
c. Electronic structure (reorganization energy, driving force, electronic coupling)
Workflow

Morphology
Atomistic force-fields (molecular dynamics)
Coarse-graining with back-mapping
SCF Hamiltonians

Electrostatics and polarization
Partial charges
Distance-dep dielectric constant (fast)
Atomic polarizabilities (polarizable FF)

Electronic coupling
Semi-empirical (fast)
DFT (10,000 pairs max)

Rates
Marcus – classical vibrational mode
Jortner – quantum vibrational modes
\[
\omega = \frac{J^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp \left[-\frac{(\Delta G - \lambda)^2}{4\lambda k_B T}\right]
\]

Master equation
Small systems, one charge carrier - ME
Large systems, different types - KMC
Versatile Object-oriented Toolkit for Charge transport Applications

Votca.org
Apache license
C++, scripting
Test suite
Hg, Google code
Wiki pages
Bug tracker

Compound design

What core shape and side chains are optimal for charge transport?

H. J. Raeder et. al. Nat. Mat. 2006; M. Van der Auweraer, F. C. De Schryver Nat. Mat. 2006

Triphenylenes, hexabenzocoronenes, phthalocyanines ...
Transfer integrals

Maximum of the transfer integral is in a face-to-face and in a 60 deg twisted arrangement of neighbors

Conjugated core

Triangularly-shaped core

60 deg twist due to steric repulsion of the side groups

Bulky side groups lock the azimuthal molecular motion

Alkyl side chains make the compound soluble

2DWAXS data

Conjugated core

Efficiency: large fraction of the excited states formed by charge recombination are triplets. Triplet-to-ground state transitions are forbidden (phosphorescence)

Injection: low energetic barriers at the metal-organic interfaces to inject equal amounts of electrons and holes, for balanced charge flow

High currents: low mobilities of amorphous materials require high current densities

Stability: lifetime is short compared to inorganic LEDs (< 1000 hours)
Phosphorescence-based Light Emitting Diode

ITO: transparent anode. Holes are injected from this side
HTL: allows a well-balanced hole transport to EML
ETL: metal cathode injects electrons in this layer
LiF reduces the injection barrier and protects ETL from chemical reactions with the cathode
Hole blocking layer: between EML and ETL: balances the hole and electron currents
Electron blocking layer: between HTL and the EML prevent holes/electrons from crossing and leaving the ENL without electron-hole recombination

Takeaway message
Don’t be scared. This is the simplest design
Light Emitting Diode: energy levels and materials

<table>
<thead>
<tr>
<th>LUMO</th>
<th>HOMO</th>
</tr>
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<tbody>
<tr>
<td>4.7 eV</td>
<td>2.3 eV</td>
</tr>
<tr>
<td>5.6 eV</td>
<td>2.6 eV</td>
</tr>
<tr>
<td>3.0 eV</td>
<td>3.3 eV</td>
</tr>
<tr>
<td>3.7 eV</td>
<td>6.0 eV</td>
</tr>
</tbody>
</table>

ITO | HMTPD | TAZ +12% Ir(ppy)$_2$(acac) | Alq$_3$ | MgAg

HTL | EML | ETL

HMTPD (solid line) | TAZ (dashed line) | Ir(ppy)$_2$(acac) (dashed line) | Alq$_3$
Tris(8-hydroxyquinolinato)aluminium (Alq3)

- Green light emitter
- Hole and electron conductor
- Pronounced Poole-Frenkel behaviour

Dipole moment \( D = 5 \) Debye

Changes the direction in ions

Phase: amorphous
Isomer: meridional

Hole reorganization energy \( \lambda = 0.23 \) eV

Tris(8-hydroxyquinolinato)aluminium
Alq3: Force Filed and Morphology

21 unknown angle and dihedral potentials
[scans and fits using B3LYP/6-311+g(d,p)]
partial charges (CHELPG)
van der Waals parameters – OPLSaa
Ligands - rigid

Box of 512 molecules

\[ \rho = 1.5 \text{ g/cm}^3 \]
\[ T_g = 425 \text{ K} \]
\[ T_g = 448 \text{ K} \]

Alq3: Electronic couplings

Charge is localized on molecules
Hopping sites – centers of mass
Neighbor list – cutoff for ligands

\[ J_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle \]

\( \phi_{i,j} \) - frontier orbitals
\( \hat{H} \) - Hamiltonian of a dimer

\( J_{ij} \) depend on positions, orientations
Distributions are not Gaussian
Span several orders of magnitude
Are qualitatively similar for semi-empirical and DFT-based methods
Electrostatic contribution

- Electrostatic contribution
- Polarization contribution

Partial charges
Polarizable force-field

5 neighbors
6 neighbors

Graph showing normalized counts from neighborhood vs. electrostatic energy difference (eV) with different curves representing different parameters:
- \( \epsilon = 1, \sigma = 0.299 \text{ eV} \)
- \( \epsilon(\epsilon_{\infty} = 3, s = 3 \text{ nm}^{-1}), \sigma = 0.148 \text{ eV} \)
- \( \text{SCF}, \sigma = 0.232 \text{ eV} \)
- \( \epsilon(\epsilon_{\infty} = 3, s = 1.3 \text{ nm}^{-1}), \sigma = 0.236 \text{ eV} \)
Energetic Disorder: correlations

\[
C(r_{ij}) = \frac{\langle (E_i - E)(E_j - E) \rangle}{\langle (E_i - E)^2 \rangle}
\]

\[
C(r_{ij}) = 0 \quad \text{– decorrelated}
\]

\[
C(r_{ij}) = 1 \quad \text{– correlated}
\]

Electrostatics: long-ranged

Correlated disorder

Onset of the Poole-Frenkel behaviour
Electronic Coupling
Energetic Disorder

Shallow, deep, and very deep traps
Master Equation (single charge carrier)

\[ \frac{\partial p_i}{\partial t} = \sum_j \omega_{ij} p_j - \omega_{ji} p_i \]

\[ \nu = \sum_{ij} \omega_{ji} p_i (r_i - r_j) \]

\[ \nu = \mu E \]

kinetic Monte Carlo algorithm (direct solution of ME is often problematic)
Alq3: Occupation probabilities and currents

occupation probabilities
4096 molecules

current filaments
512 molecules

All sites are sampled (can be also checked using detailed balance)
Currents have preferred pathways (correlated disorder) – current filaments
Alq3: Poole-Frenkel behavior

Boxes of molecules

512 = 8 × 8 × 8
2197 = 13 × 13 × 13
4096 = 16 × 16 × 16
13824 = 24 × 24 × 24

Mobility does not converge with the increase of the box size?

Dispersive versus non-Dispersive Transport

Mean energy of a charge carrier

\[ E_N = \left( \frac{\sum_{n=1}^{N} \epsilon_n e^{-\beta \epsilon_n}}{\sum_{n=1}^{N} e^{-\beta \epsilon_n}} \right) \]

\( \epsilon_n \) - Gaussian distributed

\[ \frac{E_\infty}{\sigma} = -\frac{\sigma}{k_BT} \]

Dispersive to non-dispersive transport

\( \left( \frac{\sigma}{k_BT} \right)^2 = -5.7 + 1.05 \ln N \)

10,000 molecules max (ZINDO level)

30 \times 30 \times 30 lattice

Sampling of full DOS is not possible

\[ \sigma/k_BT = 5.4 \]


\[
\left( \frac{\sigma}{k_B T} \right)^2 = -5.7 + 1.05 \ln N
\]

**Trick:**
simulate non-dispersive transport at high temperatures and use temperature dependence to extrapolate to the room temperature

\[
\mu(T) = \frac{\mu_0}{T^{3/2}} \exp \left[ - \left( \frac{a}{T} \right) - \left( \frac{b}{T} \right)^2 \right]
\]

Alq3: After scaling

Conclusions

Electrostatic – better treatment of polarization effects and in larger systems

Finite size effects are substantial (if PBCs are used it is not clear what to do)
Systems with large energetic disorder will always have higher mobilities (hot carriers). Extrapolation to larger systems is in general not possible [unless either \( \mu(\rho) \) or \( \mu(T) \) are known]. Periodic boundaries do not help.

Self-assembly of viscous systems (kinetically trapped morphologies)

Compound design: merit functions are too complicated to simulate directly
Compound design: donor-acceptor concept to reduce the band gap normally results in large dipole moments. Efficient absorption can lead to bad transport. Cure: molecular symmetry.
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Marcus Theory of Charge Transfer

\[ M_1^+ + M_2 \rightarrow M_1 + M_2^+ \]

\[ w \sim \exp \left( -\frac{\Delta U}{k_B T} \right) \]

Diabatic States

Reaction Coordinate

\[ \Delta U \]
\[ \Delta G \]
Reorganization Energy

\[ w \sim \exp \left( - \frac{\Delta U}{k_B T} \right) \]

How to calculate \( \Delta U \)?

\[ \lambda = E_2 - E_1 \]

\[ \Delta U = \frac{(\Delta G - \lambda)^2}{4\lambda} \]

Four calculations are required to obtain \( \lambda \)

- Energies of an optimized neutral and charged molecules
- Energy of a charged molecule in a neutral geometry
- Energy of a neutral molecule in a charged geometry

May, Kuhn “Charge and Energy Transfer Dynamics in Molecular Systems”
Reorganization energy: Examples

<table>
<thead>
<tr>
<th>Compound</th>
<th>hole, eV</th>
<th>electron, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triphenylene</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>Hexabenzocoronene</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Alq3</td>
<td>0.23</td>
<td>0.28</td>
</tr>
<tr>
<td>Perylenediimide</td>
<td>0.14</td>
<td>0.25</td>
</tr>
<tr>
<td>Carbazole</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Rubrene</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>Indolocarbazole</td>
<td>0.21</td>
<td></td>
</tr>
</tbody>
</table>

\[
\Delta U = \frac{(\Delta G - \lambda)^2}{4\lambda}
\]

\[
w \sim \exp \left( -\frac{\Delta U}{k_B T} \right)
\]

Method: B3LYP, 6-311g(d,p)

Reorganization energy can be different for electrons and holes. It can significantly change the rate (exponent)
Transfer Integrals

What happens at the crossing point?
Charge tunnels from one diabatic state to another

Fermi’s Golden Rule

\[
w = \frac{2\pi}{\hbar} \int dq f(q) |V_{DA}|^2 \delta(U_D(q) - U_A(q))
\]

\[
f(q) = Z^{-1} \exp \left( -\frac{\Delta U}{k_B T} \right)
\]

\[
J \equiv V_{DA} = \langle D | H_{DA} | A \rangle
\]

Electronic coupling element
(or)
Transfer Integral

\[
w = \frac{J^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp \left[ -\frac{(\Delta G - \lambda)^2}{4\lambda k_B T} \right]
\]

Assumptions: one promoting frequency, high temperatures, diabatic states, non-adiabatic regime

\[
J \ll \lambda
\]