Long-range Correlations, Finite-size Effects, and Intrinsic Defects in Organic Semiconductors

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Conjugated Molecules

dithienothiophene
thienothiophene
thienopyrazine
carbazole
fluorene
thienopyrimidine
carbazole
thienothiophene
benzothiadiazole
cyclopentadithiophene
benzodithiophene
triphenylamine
polyaniline
tri phenylene
perylenediimide
porphyrin
hexabenzocoronene
pentacene
coronene
PCBM
Ir(ppy)$_3$
Organic Light Emitting Diodes

Lumiblade
Universal Display Corporation

luminous efficacy
100 lm / W

Organic Solar Cells

efficiency
14 %

Organic Electronics Saxony

Organic Field Effect Transistors

COPE center GaTech

mobility
20 cm² / V s
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**Experimental Workflow**

- X-ray diffraction
- Grazing incidence
- Absorption/emission spectra
- Solid-state NMR
- Cyclic Voltammetry
- Fast Transient spectroscopy
- Impedance spectroscopy
- Charge extraction
- Charge Extraction by Linearly Increasing Voltage
- Time of Flight measurements
- Microwave conductivity
- Terahertz spectroscopy
- Scanning tunneling microscopy
- Atomic force microscopy
- Kelvin probe microscopy

PCBM

Synthesized for anti HIV treatment
Excellent soluble acceptor

Computational Design

Quantum Chemistry
- Ground/Excited states
- Electrostatic multipoles
- Polarizabilities

Statistical Physics
- Advanced sampling techniques
- Master Equation solvers
- Long-range Interactions

Continuous Models
- Drift-diffusion solvers
- Light in-out-coupling

1nm
100nm
1μm

no fitting parameters, quantitative accuracy
Methods

Software package

Versatile Object-oriented Toolkit for Charge transport Applications

www.votca.org

2019: interfaced to Schrödinger

Typical OLED hosts

### Density of states

<table>
<thead>
<tr>
<th></th>
<th>2-TNATA</th>
<th>Spiro-TAD</th>
<th>NPB</th>
<th>TCTA</th>
<th>CBP</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>IE (eV)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>exp</td>
<td>5.0</td>
<td>5.3</td>
<td>5.4</td>
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<td>6.0</td>
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<td>sim</td>
<td>4.99</td>
<td>5.31</td>
<td>5.33</td>
<td>5.69</td>
<td>6.42</td>
</tr>
<tr>
<td><strong>σ (eV)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>exp</td>
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<td>0.09</td>
<td>0.09</td>
<td>0.10</td>
<td>0.10</td>
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<tr>
<td>sim</td>
<td>0.098</td>
<td>0.090</td>
<td>0.087</td>
<td>0.112</td>
<td>0.096</td>
</tr>
</tbody>
</table>

2-TNATA; Thickness: 210 nm

TCTA; Thickness: 240 nm

<table>
<thead>
<tr>
<th></th>
<th>2-TNATA</th>
<th>TCTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma$ (eV)</td>
<td>0.098</td>
<td>0.112</td>
</tr>
<tr>
<td>$\mu \times 10^{-8}$ (m$^2$/Vs)</td>
<td>0.185</td>
<td>1.01</td>
</tr>
<tr>
<td>$\alpha$ (nm)</td>
<td>1.31</td>
<td>1.34</td>
</tr>
</tbody>
</table>
Finite-size effects

\[ \mu(F, \rho, T, \text{material, processing}) \]

Simulation boxes

$512 = 8 \times 8 \times 8$
$2197 = 13 \times 13 \times 13$
$4096 = 16 \times 16 \times 16$
$13824 = 24 \times 24 \times 24$

Atomistic MD
- NPT ensemble
- Equilibration above glass T
- Quenching to room T
Finite size effects

Mobility does not converge with the increase of the box size?
Periodic boundary conditions

Average energy

\[
\frac{E_\infty}{\sigma} = -\frac{\sigma}{k_B T}
\]

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

Dispersive to non-dispersive transport

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

10,000 molecules max (ZINDO level)
30 $\times$ 30 $\times$ 30 lattice
Sampling of full DOS is not possible
Temperature-scaling

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

non-dispersive transport at high temperatures and use temperature dependence to extrapolate to the room temperature

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

K. Seki and M. Tachiya

After scaling

A. Lukyanov, D. Andrienko
P. Kordt et al, *PCCP* 2015
Intrinsic Defects
SCLC slope - test for trapped carriers
Space-charge Limited Currents

- Holes (IE) small molecules
- Holes (IE) polymers
- Electrons (EA) small molecules
- Electrons (EA) polymers [Nicolai et al.]

Slope $m$ (-)

IE or EA (eV)
IE$_{\text{H}_2\text{O}} = 12.65$ eV
Long-Range Effects
From molecule to molecular solid

Vacuum                         Bulk electrostatics                        Bulk polarization

$E_{A\,(\text{Vacuum})}$

$D_{\text{FT}}$

$\Delta^{(1)}$

$\Delta^{(2)}$

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Typical organic donors

Quadrupoles or dimerized dipoles
Charge-quadrupole interaction

\[ E_{q,Q} \sim \frac{qQ}{4\pi \varepsilon_0 r_{12}^3} \]

\[ E_{q,Q}^{\text{tot}} \sim \int dr r^2 \frac{qQ}{4\pi \varepsilon_0 r^3} \sim \log(r) \sim \infty \]

Recall the Madelung problem!
Saturated value is at -0.7 eV!

Ewald summation

Periodic boundary conditions

Periodic background
Aperiodic charge

Extension of the Ewald sum to
- aperiodic charges/excitons
- distributed multipoles
- induction effects

Band structure engineering

Intermixed systems
Unscreened interactions

\[ E_{q,Q} = \frac{qQ_1}{4\pi \varepsilon_0 r_{12}^3} + \frac{qQ_2}{4\pi \varepsilon_0 r_{13}^3} + \ldots \]
Long-range fields lead to continuous changes of IE and $V_{oc}$

Long-Range Effects in OPVs
Charge transfer state

acceptor (C60)

Polaron (-)

CT exciton

Polaron (+)

Frenkel exciton

donor (DCV4T)
Binding energy at a flat interface

Rough interfaces

Electrostatics at rough interfaces

Barrier-free splitting of CT states

\[ B(c) = \Delta h_A - \Delta h_D(c) \]

\( B > 0 \) = CT splitting

\( \Delta h_A \)- donor molecule in the acceptor phase
Design coordinates

\[ \Delta \Gamma = \Gamma - \Gamma_0 \text{ [eV]} \]

\[ \Delta G_e + \Delta G_h [\text{eV}] \]
Blue OLED
Phosphor-sensitized fluorescence
Phosphor-sensitized fluorescence

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Phosphor-sensitized fluorescence

MD simulations of ternary mixtures
$k_{\text{FRET}} = k_{\text{ph}} \left( \frac{R_{\text{FRET}}}{r} \right)^6$

I just don't have the energy to go out at night ever since I switched from being vegan to being solar.