SUPPORTING INFORMATION

Understanding Dispersive Charge-Transport in Crystalline Organic-Semiconductors

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Details of the Charge-transport simulations

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Calculate electronic-coupling between pairs

Calculate site-energy for each possible charge-transfer.

Calculate and map hopping sites/rates

Perform kMC simulation

Calculate mobility $\mu \sim d/T$
A. Transfer Rates

Here, we use the charge-transport simulations procedure implemented in the VOTCA package developed by Prof. Andrienko and co-workers. The simulations rely on the basis of the assumption that charges are localized on a single molecule and charge-transfer reactions take place via an intermolecular hopping. Then the charge-hopping rate can be evaluated by the non-adiabatic Marcus rate

\[
\begin{equation}
 k_j = \frac{J_{ij}^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_b T}} \exp \left[ -\frac{(\Delta E_{ij} - \lambda)}{4 \lambda k_b T} \right]
\end{equation}
\]

where \(T\) is the temperature, \(J_{ij}\) is the transfer integral between the initial and final states. \(\lambda_e\) is the electron-transfer reorganization energy and \(\Delta E_{ij} = \varepsilon_i - \varepsilon_j\) is called the site-energy difference of the transfer reaction. \(\varepsilon_i\) is the energy difference of the entire system when molecule \(i\) is charged or neutral.

In the next sections we will explain the parameters entering the Marcus rate, Eq. 1.

A. 1. Reorganization Energy:

The reorganization energy, \(\lambda\), has two contributions; intramolecular reorganization energy, \(\lambda_{in}\), due to non-adiabatic changes in the molecular geometry and the intermolecular reorganization energy, \(\lambda_{ext}\), due to reorganization of the surrounding molecules during the charge-transfer reaction:

\[
\lambda = \lambda_{in} + \lambda_{ext}
\]

Since for organic solids intermolecular reorganization is much slower than the intramolecular reorganization, \(\lambda_{ext}\) is often neglected. Thus, \(\lambda \approx \lambda_{in}\).

Intramolecular reorganization, \(\lambda\), is calculated from adiabatic potential energy surfaces (Figure S1) of neutral and cationic states of compounds, using the following expression:
\[ \lambda = \left( E_{q_c}^n - E_{q_n}^n \right) + \left( E_{q_n}^c - E_{q_c}^c \right) \]  

(3)

where \( E_{q_n}^n \) (\( E_{q_n}^c \)) is the energy of the neutral \( n \) (charged \( c \)) state of the molecule in its optimized neutral geometry, and \( E_{q_c}^n \) (\( E_{q_c}^c \)) is the energy of the neutral \( n \) (charged \( c \)) state of the molecule in its optimized charged geometry. We used B3LYP/6-311G(d,p)\(^{55-58}\), implemented in Gaussian09, to calculate \( \lambda \) for an isolated molecule.\(^{59}\)

Table S1. DFT calculated reorganization energies of five organic materials considered in this study.

<table>
<thead>
<tr>
<th>Material</th>
<th>Reorganization Energy, ( \lambda ) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DNTT</td>
<td>134</td>
</tr>
<tr>
<td>DCV4T</td>
<td>228</td>
</tr>
<tr>
<td>NTMTI</td>
<td>236</td>
</tr>
<tr>
<td>Pentacene</td>
<td>95</td>
</tr>
<tr>
<td>Rubrene</td>
<td>160</td>
</tr>
</tbody>
</table>

A. 2. Site-energies:

A charge-transfer reaction from molecule \( i \) and \( j \) is driven by site-energy. Here, we calculate site-energies of the electron transfer from polarizable force-fields with the help of \textit{ab initio} methods. Site-energies include contributions from electrostatic Coulombic interactions (with polarization effects) between atoms and the contributions from the external electric field. Thus, site energy difference is defined as follows:

\[ \Delta E_{ij} = \Delta E_{\text{elec.}} + \Delta E_{\text{ext.}} \]  

(4)

External electric field contributions are calculated using the expression \( \Delta E_{\text{ext.}} = q \vec{F} \cdot \vec{d}_{ij} \). Here \( \vec{F} \) is the field-vector and \( \vec{d}_{ij} \) is the position-vector between molecules \( i \) and \( j \). Polarized Coulombic contributions to site energies are calculated self-consistently using the Thole Model.\(^{52}\) Partial charges of neutral and charged states are generated via Merz−Singh−Kollman scheme\(^{510,511}\) using the HF/6-31G(d) method based on B3LYP/6-31G(d,p)\(^{55-58}\) optimized geometries, as implemented in Gaussian09\(^{59}\). Isotropic atomic polarizabilities of the neutral and charged states are reparameterized for each species as to reproduce the molecular polarizabilities obtained from the B3LYP/6-311G(d,p) method.\(^{55-59}\)

A. 3. Energetic disorder

Energetic disorder \( \sigma \) is calculated by fitting the histogram of \( \Delta E_{ij} \) site-energy differences to a Gaussian-distribution function

\[ f(\epsilon, \sigma) = \frac{1}{2\pi \sigma^2} e^{-\frac{\epsilon^2}{2\sigma^2}} \]  

(5)
B. kMC simulations and electron-mobility:

Charge dynamics is simulated using the kinetic Monte Carlo (kMC) technique using the VOTCA package. In this stochastic procedure, a Markov chain is constructed in site space. A charge-carrier is initially chosen randomly within the space with periodic-boundaries and propagated by hopping between sites, where hopping probabilities (thus the hopping times) from site $i$ to a generic site $j$ are defined by the Marcus rate, $k_{ij}$. The total “escape” rate from site $i$ to all possible $j$ sites is calculated from

$$k_i = \sum_j k_{ij}$$

(6)

from the neighborlist. Thus the probability of hopping from site $i$ to a particular site $j$ is $p_{ij} = k_{ij}/k_i$. During a kMC run, hopping will occur from $i$ to a certain $j$ with a higher probability, which is found according to

$$\frac{\sum_j k_{ij}}{k_i} \leq u_1$$

(7)

where, $u_1$ is a uniform random number between 0 and 1. Then the event is carried out and charge is moved from site $i$ to $j$ and the time is updated, $t = t + \Delta t$, where

$$\Delta t = \ln(1/u_2)/k_i,$$

(8)

where, $u_2$ is another uniform random number. The simulations are performed until the results are converged. Charge-carrier mobility is then calculated by
\[ \mu = \frac{\nu}{|F|}, \]

where \( \nu \) is the charge-carrier velocity and \( F (=10^7 \text{ V/m}) \) is the applied electric field. The reported mobilities are the averages over 10-100 stochastic realizations.

Table S2. References for the cif of the crystal structures.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Guidance to download</th>
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Table S2. High-quality images of supercells.

**DNTT**
NTMTI

Pentacene
Rubrene
References.


