Charge transport physics of high-mobility organic semiconductors

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## Organic electronics – Status and opportunities

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<td>Phones, MP3, camera $475 million (2006)</td>
<td>OLED</td>
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Solution processible, organic semiconductors

- Synthesized by controlled organic chemistry
- Semiconductors with band gap of 1.5 - 2 eV
- Solution processible in common organic solvents through side chain attachment.
Charge transport in organic semiconductor thin films

\[ I_{sd} = W \cdot \mu_{FET} \cdot C_i \cdot (V_g - V_T) \cdot \frac{V_{sd}}{L} \]
Organic field-effect transistors

[Graph showing mobility cm²/V.s for different materials over time from 1984 to 2008.]

Materials:
- PolySi
- α-Si
- Pentacene
- Oligothiophenes
- Polythiophenes
- Single x-tal rubrene
- pBTIT
- PQT-12
- P3HT

Key:
- Source-drain electrodes
- Gate
- Organic semiconductor
- Dielectric

Companies:
- PolyIC
- Plastic Logic
- Logic
- OLED displays
- Sony
- Flexible E-paper displays

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Materials as a source of innovation

- Performance enhancement resulting from exploration of rich organic materials chemistry.

- Sustainability benefits: Low-temperature materials; Only naturally abundant elements
Organic field-effect transistors

![Graph showing the evolution of transistor mobility from 1984 to 2008 with various organic materials such as PolySi, a-Si, Oligothiophenes, Polythiophenes, Pentacene, and Single x-tal rubrene, along with related companies PolyIC, Plastic Logic, Sony, and OLED displays.](image)

- Source-drain electrodes
- Organic semiconductor
- Gate electrode
- Dielectric

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**Hopping or band-like, extended state transport?**

\[ \Psi(\vec{r}) = \Phi^1_{RC}(\vec{r}-\vec{r}_0) \]

\[ \Psi(\vec{r}) = \frac{1}{\sqrt{N}} \sum_j \Phi(\vec{r}-\vec{r}_j) e^{i \vec{k} \cdot \vec{r}_j} \]

\( \Phi(\vec{r}_j) \) : molecular orbital wavefunction localized on site \( \vec{r}_j \)
Factors governing charge transport in organic semiconductors

- Bandwidth $W$
  - Due to overlap between nearest-neighbour molecular orbitals in perfect crystal

- Energetic disorder $\sigma$
  - Broadening of electronic density of states by disorder

- Reorganisation energy $\lambda$
  - Consequence of strong electron-electron and electron-ion interaction

\[ \langle \varepsilon \rangle = -\frac{\sigma^2}{kT} \]
Bandwidth

- Bandwidth in tight binding approximation for molecular orbitals:

\[ H_e = \sum_m \varepsilon_m a_m^+ a_m + \sum_{m,n} t_{mn} a_m^+ a_n \]

\[ t_{mn} = \left< \phi_m \left( r - R_m \right) \bigg| e^{-i e \tau / m^*} \bigg| \phi_n \left( r - R_n \right) \right> \]

- Bandwidth on the order of several 100 meV.

- Mobility limited by scattering: \( \mu = \frac{e\tau}{m^*} \)
  - Increasing with decreasing temperature
Evidence for “band-like” charge transport in single crystals

• Mean free path $\lambda$ needs to be larger than the molecular distance $a$:

$$\lambda = \frac{\mu}{e} \left(3m^* k_B T\right)^{\frac{1}{2}}$$

$$m^* = \frac{2\hbar^2}{W a^2}$$

• With $W = 100$ meV, $a = 4 \text{ Å}$ and $\mu = 1 \text{ cm}^2/\text{Vs}$: $m^* = 9m_e$ \hspace{1cm} $\lambda = 0.2 \text{nm}$

• At RT band-description seems borderline even in molecular single crystals.
Energetic disorder

- Density of states broadened by disorder; complete localisation of states if disorder strong

- Origin of energetic disorder:
  - Coulomb traps; on the order of exciton binding energy (0.5 eV)
  - Variation in conjugation length, torsional defects
  - Dynamic lattice fluctuations
  - Dipolar disorder in bulk / at interface

- Thermally activated hopping transport

\[
\mu(\sigma, \Sigma, E) = \mu_0 \exp\left(-\frac{2}{3} \frac{\sigma}{kT}\right)^2 \exp\left(C(\dot{\sigma}^2 - \Sigma^2)E^{1/2}\right)
\]
Reorganisation energy

- Internal reorganisation energy

\[ \lambda_{\text{reorg}}^{\text{int}} = \sum_k \lambda_k^{\text{int}} (D2) + \lambda_k^{\text{int}} (A1) = \sum_k S_k \hbar \nu_k \]

- Contribution of similar magnitude from relaxation of surrounding medium

- Marcus rate for electron transfer:

\[ \mu = \frac{e a^2}{k_B T} \cdot \frac{i^2}{h} \left( \frac{\pi}{\lambda_{\text{reorg}} k_B T} \right)^{1/2} \exp \left( - \frac{\lambda_{\text{reorg}}}{4k_B T} \right) \]

- Reorganization energy on the order of 100-200 meV

\[
\begin{array}{cccc}
\text{ionization energy (eV)} & 15 & 13 & 11 & 9 & 7 \\
\lambda_1^{(1)} & 94 & 68 & 56 & 48 & 48 \\
\lambda_2^{(1)} & 93 & 69 & 57 & 49 & - \\
\lambda_3^{(1)} & 187 & 137 & 113 & 97 & - \\
\lambda_1^{(2)} & 98 & 66 & 57 & 51 & 51 \\
\lambda_2^{(2)} & 91 & 70 & 56 & 49 & 49 \\
\lambda_3^{(2)} & 189 & 136 & 113 & 100 & 100 \\
\end{array}
\]

Transport in conjugated polymers

Transport even in semicrystalline polymers limited by energetic disorder

Light-emitting polymer FETs
Zaumseil et al., Nat. Mat. 5, 69 (2006)

Clean ambipolar transport

- Mobility thermally activated with typical activation energies of 50-120 meV for both electron and holes.

Zhao, Adv. Mat 21, 3759 (2009)
Hallam PRL 103, 256803 (2009)
Soluble molecular semiconductors - TIPS pentacene

Anthony et al.

- High solubility and crystallinity

**Mobility > 1 cm²/Vs**

What is the nature of charge transport in this molecular semiconductor?

- Temperature and electric field-dependence of field-effect mobility
- Hall effect measurements
- Optical spectroscopy of charges as a function of temperature and electric field
FET characteristics at room temperature

Mobility = 1.5 cm²/Vs
Temperature dependence of mobility in long channels

- Weak “band-like” temperature dependence near room temperature
- Below 200 K: Shallow trap, activation energy of 14 meV
Temperature dependence in short channels

$L = 5 \ \mu m$

$V_g = -15V$

$V_d = -15V$
Temperature dependence in short channels

$L = 5 \, \mu m$

$V_g = -15V$
$V_d = -15V$

$V_g = -30V$
$V_d = -30V$

• Nonlinear charge transport at low temperatures
Mobility dependent on lateral electric field

- Mobility (at high field) determined by band-like, scattering physics.
- Energetic disorder reduced to $< 10^{-15}$ meV.
- Origin of field-dependence of mobility?
What is nature of charge carriers?

Charge modulation spectroscopy

Induced absorptions of charge carriers in accumulation at the interface are a measure of degree of molecular relaxation and degree of carrier localisation.
Chemical doping of TIPS pentacene in solution

TIPS pentacene solution (2x10^{-5} M) + Saturated FeCl_3 solution

2 TIPS pentacene + 2 FeCl_3 \rightarrow 2 \text{TIPS pentacene}^+ + 2 \text{FeCl}_2 + 2\text{Cl}^-

Isolated cation
CMS spectra of FETs at room temperature

- Room temperature charge induced absorption in FET is broader than absorption of isolated radical cation in solution.
Temperature dependence of CMS spectra

\[ L = 40 \, \mu m \]
Comparison of low T CMS and chemical doping spectrum

At low temperatures charges in FET are localized on single molecule

Existence of shallow trap states (10-15 meV deep)
Origin of the nonlinear transport at low temperatures

- With increasing lateral field low T CMS spectrum of charges in shallow trap evolves towards room temperature spectrum without lateral field.

- Mechanism for nonlinearity at low temperatures - Electric field-induced detrapping from shallow traps.
Electric field dependence of low T mobility

Fowler Nordheim tunneling

\[ \mu = \mu_0 \cdot \exp \left( - \frac{E_0}{E} \right) \]

\[ E_0 = \frac{4}{3} \sqrt{2m^* e \hbar} \Delta^{3/2} \]

- Trap depth \( \Delta = 13 \text{ -} 17 \text{ meV} \) extracted from Fowler-Nordheim fit is consistent with low field activation energy of the mobility.
Time scales for molecular reorganisation

• Time scale for Bloch electron formation due to bandwidth $J_0 = 100$ meV:
  
  \[ \tau_J \approx \frac{\hbar}{J_0} = 4 \cdot 10^{-14} \, s \]

• Interaction with intramolecular vibrations – governed by characteristic vibronic energy $E_v = 400$ – $3000 \, \text{cm}^{-1}$:
  
  \[ \tau_v \approx \frac{\hbar}{E_v} = 10^{-15} - 10^{-14} \, s \]

  – Fast $\rightarrow$ Leads to renormalization of transfer integrals

• Interaction with intermolecular vibrations – governed by characteristic optical and acoustic phonon energy $E_i < 50$ – $100 \, \text{cm}^{-1}$:
  
  \[ \tau_i \approx \frac{\hbar}{E_i} > 5 \cdot 10^{-14} - 10^{-13} \, s \]

  – Slow $\rightarrow$ Leads to dynamic disorder in transfer integrals and reorganisation energy

  – Localisation by dynamic disorder
Localisation by dynamic disorder

\[ t = t_1 + \Delta t^{(ps)} \]

Electric field
Model for dynamic disorder limited transport

\[ H = \sum_j \left[ -\tau + \alpha (u_{j+1} - u_j) \right] (|j\rangle\langle j+1| + |j+1\rangle\langle j|) + \frac{1}{2} m\dot{u}_j^2 + \frac{1}{2} K u_j^2. \]

- Band-like temperature dependence of mobility due to freezing of thermal lattice fluctuations.

Outlook

- Beginning to achieve understanding of charge transport on molecular scale

- Static energetic disorder < 10 meV – Potential of studying transport phenomena governed by energy scales of several meV.

- Emerging interest in better understanding of spin as well as thermal transport properties.

- Realisation of device functions relying on unique charge transport and optoelectronic properties of these molecular materials.
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