Electronic properties of organic semiconductors and their interfaces

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Devices of "Organic & Hybrid Electronics"
Devices of "Organic & Hybrid Electronics":
There are interfaces

Organic Field-Effect Transistors (OFET)

Organic Light Emitting Diodes (OLED)

Organic Photovoltaic Cells (OPVC)

e.g.: Energy levels in an excitonic PV cell

selection of materials for optimized device design:

→ reliability of published IE / EA / $\phi$ values ?
→ influence of electrodes ?
→ reliability of predicted energy level diagrams / internal field distribution ?
Measured energy levels in an OPVC: Photoelectron spectroscopy

e.g., Frisch, Schubert, Preis, Rabe, Neher, Scherf, Koch, J. Mater. Chem. 22 (2012) 4418

Heterojunction energy levels found in literature
(based on photoemission experiments)

Vacuum level alignment  Interface dipole  Band bending

E_{\text{vac}}  E_{\text{vac}}  E_{\text{vac}}

CB/LUMO  VB/HOMO

No charge carriers  Maybe charge carriers  Certainly charge carriers

?  ?
photoelectron spectroscopy - PES

(inverse) photoelectron spectroscopy - (I)PES
Challenge of photoemission (UPS/IPES/XPS) studies with organics: Radiation-induced sample damage & charging

"... your sample may be damaged (and the measurement flawed) before you can record the first spectrum ..."

(Unnoticed) sample damage gives wrong energy levels

 photon flux difference: ca. x 80

Today's Topics

- organic semiconductors @ electrodes
  - Fermi-level pinning induced charge transfer
  - limits of charge injection barriers
  - interface dipoles vs. band bending
  - orientation dependent IE/EA

- organic semiconductor heterojunctions
  - Fermi-level pinning induced remote charge transfer
  - long range CT, band bending & electric fields

- organic semiconductor doping
  - ion pairs and CT complexes
  - doping efficiency

Organic Field Effect Transistor (OFET): channel semiconductor properties

\[ \sigma = n q \mu \]
Charge Transport in Organic Materials

**OFET: high mobility $\mu$ required**

![OFET Diagram]

**Band transport**
- low temperature
- high structural order

**Hopping transport**
- high temperature or poor structural order

**Source-Drain current:***

$$I_{SD,lin} = \frac{W}{L} C\mu \left( V_G - V_T - \frac{V_D}{2} \right) V_D$$

**Typical carrier mobilities ($\mu$):**

<table>
<thead>
<tr>
<th>Material</th>
<th>Structural order</th>
<th>Mobility (cm$^2$/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>single molecules (intra-molecular)</td>
<td>-</td>
<td>$10^3$</td>
</tr>
<tr>
<td>molecular solid</td>
<td>single crystal</td>
<td>$10^1$</td>
</tr>
<tr>
<td>molecular solid</td>
<td>polycrystal</td>
<td>$10^0$</td>
</tr>
<tr>
<td>molecular solid</td>
<td>amorphous</td>
<td>$10^{-7}$</td>
</tr>
<tr>
<td>inorganic solid (GaAs 2DEG)</td>
<td>single crystal</td>
<td>$&gt;10^6$</td>
</tr>
<tr>
<td>inorganic solid (Si)</td>
<td>amorphous</td>
<td>$10^0$</td>
</tr>
</tbody>
</table>

**Outline:**

ultraviolet photoelectron spectroscopy (UPS) to probe electronic structure

1. electron-vibron coupling [$\mu$]
2. band dispersion [$\mu$]
3. doping [$n$]

$$\sigma = n q \mu$$
Conjugation and many building blocks (monomers)

“organic” benzene: C atoms sp² hybridized → electrons in p₂ orbital

overlap of neighboring p₂-orbitals → formation of molecular π-orbitals in addition to σ-bonds

poly(para-phenylene)

intradmolecular overlap:
Linear Combination of Orbitals

ψ = \sum_i c_i \Psi_i

Conjugation in linear molecules

Hückel-Approximation:

\[ \alpha = \int \Psi_A^* H \Psi_A \, d\tau \quad \text{Coulomb-Integral} \]
\[ \beta = \int \Psi_A^* H \Psi_B \, d\tau \quad \text{Resonance-Integral} \]

Degenerate e₁g orbitals of benzene

Localised π-orbitals

\[ A \quad B \]

No p₂-p₂ overlap

De-localised π-orbitals

\[ p₂-p₂ \text{ overlap} \]

\[ \frac{2|\beta|}{3\alpha} \quad \frac{4\alpha}{4\alpha} \quad \frac{5\alpha}{5\alpha} \quad \frac{6\alpha}{6\alpha} \]

Energy levels:

\[ \text{E}_1, \text{E}_2, \text{E}_3, \text{E}_4, \text{E}_5, \text{E}_6 \]

n = 3 \quad n = 4 \quad n = 5 \quad n = 6
Molecular-Orbital derived Density of States: Oligomers (measured by Photoelectron Spectroscopy)

HOMO = (highest occupied molecular orbital)

monomer type and overlap $\beta$ determine splitting of levels

Change of intramolecular orbital overlap $\beta$: Substrate-induced molecular planarization

$\rho$-sexiphenyl 6P

inter-ring twist angles $\alpha$: 25°-35° in bulk (steric hindrance of –H)

UPS: non-rigid shift of molecular levels
monolayer conformation ≠ bulk conformation

Density Functional Theory: orbital energies as function of $\alpha$:

→ substrate-induced planarization of 6P $\alpha = 10^\circ$-15°

Intramolecular Energy Bands in Polymers

\[ E = \alpha + 2\beta \cos\left(k\pi / (N + 1)\right), \quad k = 1,2,\ldots,N \]

Oligomer (orbitals) \[ \Rightarrow \]
Polymer (intramolecular bands)

Local disorder:
charge carrier scattering & charge traps

\[ \frac{1}{\mu_{\text{eff}}} = \frac{1}{\mu_{\text{int}}} + \frac{1}{\mu_{\text{GB}}} + \ldots \]

charge carrier mobility reduced by grain boundary (GB)

Puntambekar, Dong, Haugstad, Frisbie
1. Charge Carrier Hopping $[\mu]$

Closer Look at Photoemission from Molecular Frontier State: Estimation of Hopping Mobility

hopping mobility from electron transfer rate $k_{ET}$:

$$
\mu = \frac{e a^2}{k_B T} k_{ET}
$$

$$
k_{ET} = \frac{2\pi}{\hbar} t^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left[-\frac{\lambda}{4k_B T}\right]
$$

$$
\tilde{\lambda} = \lambda_{\text{rel}}^{(1)} + \lambda_{\text{rel}}^{(2)} \approx 2\lambda_{\text{rel}}^{(2)}
$$

$k_{ET}$ electron transfer rate

$a$ intermolecular distance

$t$ intermolecular transfer integral

$\lambda$ charge reorganization energy

Kera, Yamane, Ueno, Prog. Surf. Sci. 84 (2009) 135
Estimation of $\lambda$ for holes

Gas phase UPS of pentacene

![Graph showing ionization energy vs. intensity](image)

From analysis of vibronic sidebands in photoemission from HOMO:

- Huang-Rhys factor $S$
- $h\nu_k$ energy of vibration $k$
- $S$ from fit to intensity distribution of vibrational sidebands:

$$I_n = \frac{S^n}{n!} e^{-S}$$

$$\lambda_{rel}^{(2)} = \sum S_k \cdot h\nu_k \approx \frac{1}{2} \lambda$$

Localization of charge carriers at electrodes:
increased electron-vibron-coupling

Charge reorganization energies: $\lambda \approx 2 S \cdot h\nu$

<table>
<thead>
<tr>
<th>Material</th>
<th>$\lambda_{gas}$</th>
<th>$\lambda_{HOPG}$</th>
<th>$\lambda_{Au(111)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEN</td>
<td>99 meV$^1$</td>
<td>118 meV$^2$</td>
<td>174 meV</td>
</tr>
<tr>
<td>PFP</td>
<td>$\approx 200$ meV</td>
<td>-</td>
<td>214 meV</td>
</tr>
</tbody>
</table>


$\lambda_{metal} > \lambda_{gas}$: stronger electron-vibron-coupling
stronger charge localization (lower $\mu$)

2. Electron bands $[\mu]$
Single Crystals, Polymorphs, and Thin Films

abundance & morphology dependent on:
• substrate
• substrate temperature
• evaporation rate

Band dispersion = \( f \) (sample ↔ structure)

Pen on HOPG
Pen on Bi(001)
Pen on \( \sqrt{3} \times \sqrt{3} \) Bi–Si(111)
Pen SC

190 meV (RT) - 240 meV (120 K)
330 meV
400 meV
~ 0 meV

Krause, et al., unpublished
New opportunity for band structure determination: The ARTOF 10k

**Angle-Resolved Time Of Flight**

Scienta 4-lens system + flight tube =

- High resolution
- Full cone detection
- 250 times higher transmission
- Needs pulsed source

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**Tetracene and Rubrene**

Organic field-effect transistors based on tetracene and rubrene single crystals:

- Hole mobility of over 2 cm²/Vs and 15 cm²/Vs at room temperature#
- Better than that of micro-crystalline Si-based transistors*

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Tetracene HOMO, chemical structure, crystal structure, and Brouillin zone

Rubrene HOMO, chemical structure, crystal structure, and Brouillin zone

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Rubrene single crystal

first report of angle-resolved photoemission of an organic single crystal by Machida et al.


measurement time < 1 hour

@10^7 photons per second


organic semiconductors @ electrodes
Electrode/organic semiconductor contacts: Efficiency of OLEDs

Systematic tuning of energy levels

metal surface potential $\phi$ changes as (linear) function of acceptor coverage due to metal→adsorbate charge transfer (CT). CT creates localized dipoles $\vec{\mu}$

Helmholtz-Equation:
$$\Delta \phi = \frac{eN\mu}{\varepsilon_0\varepsilon}$$
for $\varepsilon$ ... effective diel. const. equiv. to Topping-model

mechanism works in general:

predictable tuning of HIB for any subsequent organic layer by up to 1.4 eV