Controlling Charge Carrier Concentration in Organic Semiconductors

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Outline

- Basics of organic semiconductors

- Charge carrier control: Doping of organic semiconductors
  - Electrical Characterisation
  - UPS/XPS Spectroscopy: space charge layers

- Application in devices:
  
  Organic light-emitting diodes
  Organic solar cells
What is an organic semiconductor...

Why organic semiconductors...

Photovoltaic cells
Light emitters
Integrated circuits

Organic Semiconductors: a new class of materials
Conjugated $\pi$-electron systems

$\text{Sp}_2$-hybridised Carbon:

• Spatially extended electron systems:
  • Large dipole moments
  • Tunability of energy levels
  • Good coupling between molecules in solid state
Molecules with conjugated π-electron system

- saturated π-electron systems
- VdW crystals
- small π–π-overlap, narrow bands

\[
\begin{align*}
6 \times p_z & \\
18 \times sp_z & \\
\text{LUMO (π*)} & \Rightarrow E_C \\
\text{HOMO (π)} & \Rightarrow E_V
\end{align*}
\]

Film preparation technology:
- vapor deposition
Polymers with conjugated $\pi$-electron system

- broad bands
- transport limited by interchain hops

Film preparation technology:
solution processing
**Inorganic vs. Organic Semiconductors**

<table>
<thead>
<tr>
<th>Inorganic Semiconductor</th>
<th>Organic Semiconductor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band</td>
<td>Transport Mechanism</td>
</tr>
<tr>
<td>$10^2$-$10^3$</td>
<td>RT mobility (cm²/Vs)</td>
</tr>
<tr>
<td>$10^{15}$-$10^{18}$ (doping controlled)</td>
<td>Charge carrier concentration</td>
</tr>
<tr>
<td>$&lt;10^{15}$</td>
<td>Electr. Active impurit. (cm⁻³)</td>
</tr>
</tbody>
</table>

**Diagram: Inorganic vs. Organic Semiconductors**

- CB: Conduction Band
- VB: Valence Band
- LUMO: Lowest Unoccupied Molecular Orbital
- HOMO: Highest Occupied Molecular Orbital
- $E_D$: Energy Depth
- $E_A$: Energy Activation
- Electr. Active impurit. (cm⁻³): Electrical Active Impurities
• Basics of organic semiconductors

• **Charge carrier control: Doping of organic semiconductors**
  - Electrical Characterisation
  - UPS/XPS Spectroscopy: space charge layers

• Application in devices:
  Organic light-emitting diodes
  Organic solar cells
Basics of the doping mechanisms: p-type doping

Inorganic

- broad bands
- small correlation energies \((e-h \approx 4\text{meV})\)
- hydrogen model works

Organic

- hopping transport
- large correlation \((e-h \approx 1\text{ eV})\)
- polaron effects important
Co-evaporation of doped films

- Dopant Matrix
- Quartz monitors
- Substrate

- \( p \approx 10^{-4} \text{ Pa} \)
- \( T_{\text{evap}} = 100..400^\circ\text{C} \)
- \( T_{\text{Subs}} = -50..150^\circ\text{C} \)
- \( d = 25..1000 \text{ nm} \)
- \( r_m \approx 1 \text{ Å/s} \)

**Dopant/Matrix ratio of 1:2000 achieved**
Model system for p-doping: ZnPc:F4-TCNQ

**Organic Matrix:**
Zinc-Phthalocyanine (ZnPc)
monoclinic
\[a = 26.3 \text{ Å}, \quad b = 3.8 \text{ Å}, \quad c = 23.9 \text{ Å},\]
\[\gamma = 94.6^\circ, \quad Z = 4\]
HOMO \(\approx -5.3\text{eV}\)

**Organic Acceptor:**
Tetrafluoro-tetracyano-quinodimethane
(F4-TCNQ)
LUMO \(\approx -5.0\text{eV}\)

\(-\)
ZnPc-F₄-TCNQ charge transfer by FTIR

IR-spectra of a F₄-TCNQ -KBr- sample

Degree Z of the charge-Transfer:

\[ Z = \frac{\nu_0 - \nu_x}{\nu_0 - \nu_1} \]

\( \nu_0 \) : neutral molecule  
\( \nu_1 \) : charged molecule  
\( \nu_x \) : doped layer

Result in Pc films: \( Z=1 \)!
Nominally undoped ZnPc:
\( \approx 10^{-10} \text{ S/cm in vacuo} \)

\[ \Rightarrow \text{Doping increases conductivity by orders of magnitude} \]

- Superlinear behavior?
- Shallow acceptors? Coulomb energy too large…. 

Conductivity vs. Doping Concentration

\[ \text{T= 30°C} \]

- ZnPc series 1
- ZnPc series 2

Conductivity \( \sigma \) [
\text{S/cm}]
Hole densities of ZnPc:F4-TCNQ

\[ p(T) = N \frac{E_F - E_\mu}{kT} \]

Hole density is not thermally activated!

Conduction in exponential band tails: Explains superlinear doping efficiency

Density of states:
\[ g(E) = g_0 \exp\left(-\frac{E}{k_B T_c}\right) \]

Variable Range Hopping
\[ T < T_c \]
\[ E_F >> k_B T_c \]

Percolation model:
\[ \sigma = \sigma_0 Z_c^{-1} \]
with \( Z_c^{-1} \) threshold conductance

Assuming shallow acceptors
\[ \sigma \sim (N_A)^{T_0/T} ; \ T_0 > T \]
Application to field-effect and conductivity data:

![Graphs showing theoretical curves and experimental data for polycrystalline ZnPc.](image)

Basic parameters are independent of specific material:

<table>
<thead>
<tr>
<th>Material</th>
<th>$\sigma$ (S/cm)</th>
<th>$E_{\text{act}}$ (eV)</th>
<th>$\sigma_0$ ($10^5$S/m)</th>
<th>$T_0$ (K)</th>
<th>$\alpha$ (Å$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnPc (polycr.)</td>
<td>$5.8 \times 10^{-3}$</td>
<td>0.18</td>
<td>12 ± 3</td>
<td>485 ± 15</td>
<td>0.37 ± 0.01</td>
</tr>
<tr>
<td>ZnPc (amorph.)</td>
<td>$4 \times 10^{-4}$</td>
<td>0.23</td>
<td>11 ± 6</td>
<td>455 ± 15</td>
<td>0.64 ± 0.02</td>
</tr>
<tr>
<td>VOPc (polycr.)</td>
<td>$2.3 \times 10^{-5}$</td>
<td>0.32</td>
<td>6 ± 1</td>
<td>485 ± 15</td>
<td>1.00 ± 0.04</td>
</tr>
<tr>
<td>TDATA (amorph.)</td>
<td>$5.9 \times 10^{-7}$</td>
<td>0.34</td>
<td>3 ± 1</td>
<td>515 ± 15</td>
<td>1.39 ± 0.03</td>
</tr>
</tbody>
</table>

$\sigma$ and $E_{\text{act}}$ for dopant density 1% and $T=25°C$
N-type doping: conventional approach

Electron transfer from high-lying HOMO to matrix LUMO:

Donor: Bisethylendithio-tetrathiafulvalene (BEDT-TTF)

Matrix: Naphthalin-tetracarboxylic-dianhydride (NTCDA)

N-type doping: novel approach using cationic dyes

Pyronin B chloride

Donor precursor

charge transfer

LUMO

HOMO

dye radical created \textit{in situ} from cation

very strong organic donor

Conductivity [S/cm]

undoped NTCDA

$\sigma = 3.3 \times 10^{-8}$ S/cm

Molar doping ratio

UPS/XPS study of organic/inorganic interfaces

Interested in:

- Space charge layers at junctions and their influence on injection
- Barriers and their possible dependence on doping
- Direct observation of Fermi level shift

with N. Armstrong, D. Alloway, P. Lee, Tucson

J. Blochwitz et al., Organic Electronics 2, 97 (2001)
Creation of ohmic contacts by doping

undoped: blocking
doped: ohmic

J. Blochwitz et al., Organic Electronics 2, 97 (2001)
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OLED cooperation in Dresden

Institut für Angewandte Photophysik (www.iapp.de)
• Basic research on novel OLED device concepts
• Organic solar cells

Fraunhofer-IPMS Dresden (www.ipms.fraunhofer.de)
• Stability of doped organic LED
• OLED-Inline-deposition set-up (30x40cm Substrate)

Novaled GmbH (www.novaled.com)
• Holds University patents
• New Materials for stable doping systems
Organic Light Emitting Diodes

Device structure

Device energy diagram
OLED Benefits

- Thinness
- Brightness and colour
- Viewing Angle

Source: Kodak
OLED Performance

Cost

Thin

Light Weight

High Resolution

Lifetime

Contrast

Brightness

Color Quality

High Response

Wide View Angle

Power Consumption

Suitable for TV and Movies

Suitable for Mobile

a-Si TFT LCD

p-Si TFT LCD

p-Si TFT OLED

Further improvements expected

Source: Toshiba 2002
OLED products on the market

Passive Matrix

Active Matrix

- 2003 market: approx 250 mio US$
- 98% small molecule devices
Sony 13” full color display
Comparison: Inorganic vs. Organic LED

Inorganic LED (e.g., GaAs/AlGaAs)

- Exponential current-voltage relation
- Flat-band under operation
- Low work-function contacts not needed!

Organic LED

- Space charge limited currents
- Low work function metals needed
  ITO-preparation necessary

\[
\begin{align*}
\text{CB} & \quad \text{p} \quad \text{n} \quad \text{VB} \\
E_{Fh} & \quad E_{Fe} & \quad \text{Metal} \\
\end{align*}
\]
Ideal OLED: pin-heterostructure

Steps towards this design:

Step 1: p-type doping

Step 2: blocking layers for high efficiency

Step 3: n-type doping
Step 1: Doping of amorphous wide gap materials


Starburst = TDATA
4,4',4''-tris(N,N-diphenylamino) triphenylamin

Y. Shirota et al., APL 65, 807 (1994)

Dopant: F_4-TCNQ

- undoped TDATA: 10^{-10} S/cm
- doped TDATA: up to 10^{-5} S/cm
=> low ohmic losses: 0.1V/100nm@100mA/cm^2
Structure of pin-OLED

N-doping: Batho-Phenanthroline doped with Li (developed by Kido group)
Lowest voltages reported in literature for small-molecule devices


Performance of p-i-n structure

Current efficiency:
5.27 cd/A @1,400 cd/m²
(pure Alq3 emitter)
What determines OLED efficiency?

\[ \eta_{\text{external}} = b_1 \times \frac{h\nu}{eU} \times \eta_{\text{recomb}} \times \eta_{\text{optical}} \]

- \( b_1 \): Electron and hole current balance: 1 can be reached

- \( eU \): Operating voltage should be \( \approx \) photon energy

- \( \eta_{\text{recomb}} \): 75% Triplet, 25% Singlet excitons: 0.25 for fluorescent emitter
  Use phosphorescent (triplet) emitter

- \( \eta_{\text{optical}} \): about 20% in flat structure: 80% lost to wave guide modes:
  optimize optical outcoupling!
Highly efficient PIN Triplet OLED

- Luminance (cd/m$^2$) vs. Voltage (V)
  - 10000 cd/m$^2$ @ 3.79V
    - 52.4 cd/A; 43.5 lm/W
  - 10000 cd/m$^2$ @ 4.2V
    - 26 cd/A; 19 lm/W
  - 10000 cd/m$^2$ @ 3.4V
    - 35 cd/A; 33 lm/W
  - 10000 cd/m$^2$ @ 3.21V
    - 62.4 cd/A; 61.1 lm/W
  - 10000 cd/m$^2$ @ 3.1V
    - 65.3 cd/A; 69.4 lm/W
  - 10000 cd/m$^2$ @ 2.95V
    - 65.3 cd/A; 69.4 lm/W
  - 1000 cd/m$^2$ @ 3.21V
    - 44 cd/A; 44 lm/W

- Luminance (cd/m$^2$) vs. Voltage (V)
  - Standard
  - D-doping

- 100 cd/m$^2$ @ 3.1V
  - 44 cd/A; 44 lm/W

- 1000 cd/m$^2$ @ 3.1V
  - 65.3 cd/A; 69.4 lm/W

- 1000 cd/m$^2$ @ 2.95V
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Highly efficient PIN Triplet OLED

Quantum efficiency (%)

Power efficiency (lm/W)

Current density (mA/cm²)
LED performance vs. time: linear plot

- **Power Efficiency** vs. **Year**
- Key: Red Filtered, InGaN green, AlInGaP Red/Yellow, OLED, PLED, Tungsten Bulb (unfiltered), Red Filtered
What determines OLED efficiency?

$$\eta_{external} = b_1 \times \frac{h \nu}{eU} \times \eta_{recomb} \times \eta_{optical}$$

- $b_1$: Electron and hole current balance: 1 can be reached

- $eU$: Operating voltage should be $\approx$ photon energy

- $\eta_{recomb}$: 75% Triplet, 25% Singlet excitons: 0.25 for fluorescent emitter
  Use phosphorescent (triplet) emitter

- $\eta_{optical}$: about 20% in flat structure: 80% lost to wave guide modes:
  optimize optical outcoupling!
Three modes:

- External (≈ 20%)
- Substrate (≈ 35%)
- ITO/org (≈ 45%)

FIG. 2. Three radiative modes in OLEDs: (I) external modes, (II) substrate modes, and (III) ITO/organic modes.
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Problem I: Exciton Separation

- Absorption dominated by Frenkel excitons
- Large exciton binding energy: approx. 0.5eV
- Free carrier generation requires high fields (=> use in photocopiers)
Exciton diffusion

LUMO

hν

HOMO

Absorption and exciton formation

Exciton diffusion

Exciton separation at the interface

Carrier drift in the electric field of a pn-heterojunction

Solution: Donor-Acceptor-Heterojunction
Problem II: Exciton Diffusion

- Efficiency 1%
- Problems:
  - Too low exciton diffusion length
  - Low voltage, no controlled doping

C.W. Tang (Kodak) (1986)

Donor: p-type

Acceptor: n-type
Cells with interpenetrating network: $C_{60}$ as electron acceptor

ultrafast electron transfer
The pi-n-heterojunction concept with electron acceptor

- Photoactive interface between two i-layers
- Wide gap transport layers
- Highly doped layers to maximize $V_{bi}$
- Electron acceptor

$C_{60}$ energy levels

M. Pfeiffer
Evolution of the organic solar cell concept

Tang 86

photoactive region

p-i-n cell

Optical mode can be optimized as well

ZnPc\textsuperscript{C\textsubscript{60}}
Pin-structure solar cell

- ca. 80% internal quantum efficiency
- Fill factor has to be improved

\[
\begin{align*}
\text{p-i-n Zelle mit 60nm ZnPc*C}_{60} (1:2) \\
U_{oc} &= 0.51 \text{ V} \\
J_{sc} &= 16.7 \text{ mA/cm}^2 \\
\text{FF} &= 36.4 \% \\
\eta &= 2.3 \%
\end{align*}
\]
Tandem Solar Cell Structure

- Full sun spectrum can be used
- Higher voltage, lower current than single devices
Tandem solar cell: Doping is crucial for low losses
Tandem cell: influence of doping

- with Doping and Gold-Cluster: quasi-ohmic behavior
Tandem solar cell with 3.6% efficiency

Tandem:
- $U_{oc}$ = 0.99 V
- $J_{sc}$ = 10.4 mA/cm$^2$
- FF = 46.7%
- $\eta$ = 3.6%

Einzelzelle:
- $U_{oc}$ = 0.51 V
- $J_{sc}$ = 16.7 mA/cm$^2$
- FF = 36.4%
- $\eta$ = 2.3%
Next step: 3-layer cell

Simulation by H. Hoppe (Uni Linz)

\[ V_{OC} = 0.6 \text{ V} \quad 0.5 \text{ V} \quad 0.5 \text{ V} \]

\[ \sum = 1.5 \ldots 1.6 \text{ V} \quad ??? \]

\[ \eta = 5\text{-}6\% \]
Conclusions

• Organic semiconductors can be efficiently doped
• Microscopic physics not well understood
• Doping very useful for devices

Future work:
• Molecular n-doping
• Microscopic understanding of doping necessary
• Make solar cells as good as OLED already are
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