Organic Electronics: Opportunities and Challenges in Solid-State Lighting

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Outline

• Introduction to organic semiconductors & devices

• Organic light emitting diodes
  - Processing and patterning
  - Charge injection and transport
  - Mobile ions
  - Degradation

• Organic thin film transistors
  - Morphology of organic films
  - Contact effects
  - Structure of organic films

• Organic photovoltaic cells
  - Influence of morphology
  - Energy vs. charge transfer

• Conclusions
Organic electronics: The big three

- OLEDs: Kodak
- OTFTs: DuPont
- OPVs: Siemens

Sony
U. of Linz
Organic electronics: a booming field
Organic semiconductor families

Molecularly Doped Polymers (MDP)

Functional Polymers

Small Molecules
Common organic semiconductors

TPD

Alq$_3$

PPV

Pentacene
Carbon as a semiconductor

• Hybridization: sp² and pₓ

\[ CH₂=CH₂ \]

• Particle in a box:

\[ E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2 \]

\[ n=1,2,3,... \]

\[ E_G \approx \frac{\hbar^2 \pi^2}{2maN} \]
Tuning of optical properties

Blue

Red

Table 1. Chemical structures and molecular weight characteristics of regio- and di-olefinic polychromenes.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n\times 10^3$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.7</td>
<td>2.3</td>
</tr>
<tr>
<td>II</td>
<td>0.89</td>
<td>1.6</td>
</tr>
<tr>
<td>III</td>
<td>4.2</td>
<td>2.7</td>
</tr>
<tr>
<td>IV</td>
<td>8.5</td>
<td>2.1</td>
</tr>
</tbody>
</table>

[a] R is n-decyl. [b] Relative in polymer quantity.

Tuning of electrical properties
Opportunities and challenges

(+ ) Ease of processing

(+ ) Tunability of electronic properties

(+ ) Integration with biological systems

(+/-) Significant ionic mobility

(- ) Low-end performance

(- ) Stability in devices

Will complement Si, not replace it
Organic light emitting diodes (OLEDs)
OLEDs vs. liquid crystals
GE OLED Vision

“Lighting Wallpaper”

- Energy Efficient
- Low Cost
- Thin and Flexible

New design possibilities could change the way we think about lighting!
Early Progress

2001 – Illumination-Quality Light Possible

2002 – Scalable Large Area Architectures.

2003 – Incandescent Milestone
Current GE Focus

Developing Low Cost Manufacturing Infrastructure
Effects of widespread adoption of 50% efficient SSL

- SSL has the potential, by 2025, to:
  - decrease electricity consumed by lighting by 62%
  - decrease total electricity consumption by 13%

<table>
<thead>
<tr>
<th>Projected Year 2025 Savings</th>
<th>US</th>
<th>World</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity used (TW-hr)</td>
<td>620/yr</td>
<td>1,800/yr</td>
</tr>
<tr>
<td>$ spent on Electricity</td>
<td>42B/yr</td>
<td>120B/yr</td>
</tr>
<tr>
<td>Electricity generating capacity (GW)</td>
<td>70</td>
<td>~200</td>
</tr>
<tr>
<td>Carbon emissions (Mtons)</td>
<td>100</td>
<td>~300</td>
</tr>
</tbody>
</table>
Efficiency of white OLEDs

Kido group, Yamagata U.
From Science to Deployment – a map for Solid-State Lighting

Discovery Research
- Rational design of SSL lighting structures
- Control of radiative & non-radiative processes in light-emitting materials
- New functionalities through heterogeneous nanostructures
- Innovative photon management
- Enhanced light-matter interactions
- Precision nanoscale characterization, synthesis, and assembly
- Multi-scale modeling – quantum excitations to light extraction

Use-inspired Basic Research
- Unconventional light-emitting semiconductors
- Photon conversion materials
- Polar materials and heterostructures for SSL
- Luminescence efficiency of InGaN
- Managing and exploiting disorder in OLEDs
- Understanding degradation in OLEDs
- Integrated approach to OLED fundamentals

Applied Research

Technology Milestones:
- By 2025, develop advanced solid state lighting technologies with a product system efficiency of 50 percent with lighting that accurately reproduces sunlight spectrum.
- Materials and components for inorganic and organic light-emitting diodes research for improved efficiency and cost reduction
- Strategies for improved device light extraction
- Low-cost fabrication and patterning techniques and tools & manufacturing R&D
- Product degradation and reliability issues

Technology Maturation & Deployment
- Developing national standards and rating systems for new products
- Commercial adoption and support
- Industrial partnership
- Legal, health, market, and safety issues
- Cost reduction
- Prototyping

Office of Science
BES

Technology Offices
EEERE
# OLEDs vs. LEDs

<table>
<thead>
<tr>
<th></th>
<th>LEDs</th>
<th>OLEDs</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Transport</strong></td>
<td>Extended states give rise to mobilities of $1000 \text{ cm}^2/\text{Vsec}$ or higher</td>
<td>Hopping among localized states results in low mobilities – typically in the range of $10^{-6}$-$10^{-3} \text{ cm}^2/\text{Vsec}$</td>
</tr>
<tr>
<td><strong>Doping</strong></td>
<td>$n$- or $p$-doped, with substitutional dopant densities of $10^{15}$-$10^{20} \text{ cm}^{-3}$</td>
<td>Usually undoped. Doping requires loading in the % range.</td>
</tr>
<tr>
<td><strong>Excited states</strong></td>
<td>Weak electron-phonon coupling and weakly bound excitons</td>
<td>Strong electron-lattice coupling, exciton binding energies of 0.5 eV</td>
</tr>
<tr>
<td><strong>Purity</strong></td>
<td>Well-controlled and characterized.</td>
<td>Impurities mostly unknown.</td>
</tr>
</tbody>
</table>
OLED structure and operation

Ca

e⁻

Anode

LUMO

Cathode

HOMO

ITO

h⁺
OLED characteristics

Au/MEH-PPV/Ca

Current (A)

Radiance (W)

Voltage (V)
Need for low work function cathode

Low work function cathode required for efficient electron injection
Bilayer devices

- Anode
  - Hole-transport layer
- Cathode
  - Electron-transport layer
Other architectures

Emissive Layer

Dopants
Small molecules for OLEDs

**Commonly used acronyms and chemical names**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alq or Alq₃</td>
<td>(emitter, electron transport material)</td>
</tr>
<tr>
<td>Cs₂</td>
<td>(3-(8-hydroxyquinolino)aluminum)</td>
</tr>
<tr>
<td>Bphen</td>
<td>(EEM, ETM)</td>
</tr>
<tr>
<td>φ-tol</td>
<td>(1-10-oxybenzen[(8)quinolino]herylum)</td>
</tr>
<tr>
<td>F8T2Fl</td>
<td>(EEM, ETM)</td>
</tr>
<tr>
<td>8-cis</td>
<td>(2,2-diphenylvinyl)phenylfluorine</td>
</tr>
<tr>
<td>DiPyBi</td>
<td>(EEM, bipolar transport)</td>
</tr>
<tr>
<td>1,5-bis-(2,2-diphenylvinyl)phenylfluorine</td>
<td></td>
</tr>
<tr>
<td>PBD</td>
<td>(EEM, ETM)</td>
</tr>
<tr>
<td>2-(2-(2-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole)</td>
<td></td>
</tr>
<tr>
<td>TTD or TMD</td>
<td>(hole transport material)</td>
</tr>
<tr>
<td>NN'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-bi-phenyl-4,4'-diamino</td>
<td></td>
</tr>
<tr>
<td>NPhB</td>
<td>(EEM)</td>
</tr>
<tr>
<td>NN'-diphenyl-N,N'-diphenyl-1,1'-bi-phenyl-3,3'-diamino</td>
<td></td>
</tr>
</tbody>
</table>
Conjugated polymers for OLEDs

PPP

PPV

PEDOT

P3HT

PFO
Multilayer devices from small molecules

Energy transfer from B→G→R

Multilayer devices from small molecules

Stacked OLEDs

(+ ) High brightness and efficiency
(+ ) Long operational stability due to reduced heat and charge
(- ) Highly transparent charge generation layer
(- ) Carrier balancing in each sub-pixel
(- ) Tuning optical path for white emission

Kido labs, Yamagata U.
Stacked OLEDs

Stacked OLEDs

Multilayer devices from polymers

Heeger group, UCSB
RGB schemes

Patterned emitters

Microcavities

Color filters

Fluorescent converters

Stacked
Shadow Mask Patterning

- Alignment is difficult
- Features widen causing shorts
- Complex shapes impossible
- Evaporation only
Inkjet Printing

- Serial process
- Inks must be specially formulated
- Polymer performance lagging

The Cambridge Research Laboratory of Epson

Xerox PARC

Cornell University
Efficiency

External quantum efficiency of an OLED

\[ \eta = b \cdot \Phi \cdot (1/2n^2) \]

- Fraction of charge that forms excitons
- Fraction of excitons that decay radiatively
- Fraction of photons that escape waveguiding (22%)

Depends on photophysics:
- Singlet: \( \Phi = (1/4) \cdot \Phi_{PL} \)
- Triplet: \( \Phi = \Phi_{PL} \)
Outcoupling efficiency


Electron-hole recombination

External Quantum Efficiency:  \( \eta = b \cdot \Phi / 2n^2 \)
Energetics of semiconductors

Figure of merit:

mobility, $\mu$ (cm$^2$/V·sec)
Space charge effects

Low voltages: Ohm’s law
\[ J_{\text{OHM}} = e \cdot N_0 \cdot \mu \cdot \frac{V}{L} \]

High voltages: Space charge limited current
\[ J_{\text{SCL}} = \frac{9}{8} \epsilon \epsilon_0 \mu \cdot \frac{V^2}{L^3} \]

\[ V_0 = \frac{8}{9} \cdot e \cdot N_0 \cdot \frac{L^2}{\epsilon \epsilon_0} \]

Energetics of amorphous semiconductors

N. Mott, Nobel Lecture (1977)
Time-of-flight (TOF)

\[
\mu = \frac{L^2}{t_{TR} \cdot V}
\]

Non-dispersive hole transport in TFB

ITO/PEDOT:PSS(CH8000)/TFB(6.4 μm)/Al

Electric field dependence of mobility
Gaussian disorder model

- Energetic disorder
- Positional disorder
Physical Models for Analysis of Electrical Characteristics for Organic Devices

- **Hopping Model**
  - **Effective Transport Energy**
    - The effective carrier transport energy ($E_{tr}$) is calculated from\textsuperscript{1,2}:

\[
E_{tr} \int g(E)(E_{tr} - E)^3 dE = \frac{6\beta}{\pi} (\gamma kT)^3
\]

\[
g(E) = \frac{N_i}{\sqrt{2\pi\sigma_i}} \exp\left(-\frac{E^2}{2\sigma_i^2}\right) + \frac{N_d}{\sqrt{2\pi\sigma_d}} \exp\left(-\frac{(E + E_d)^2}{2\sigma_d^2}\right)
\]

Where $g(E)$ is the DOS distribution, $N_i$ is the total intrinsic state density, $N_d$ is the total dopant state density, $\sigma_i$ is the intrinsic Gaussian DOS width, $s_d$ is the dopant Gaussian DOS width, $E_d$ is the energy shift, $\gamma$ is $1$/carrier localization radius, $\beta$ is the percolation constant, $E$ is the band energy, $k$ is Boltzmann’s constant and $T$ is the lattice temperature.


Device characteristics well understood

\[ J_{SCL} \approx \left( \frac{9}{8} \right) \varepsilon \varepsilon_0 \mu_0 V^2 \exp \left[ 0.89 (V/E_0 L)^{0.5} \right] / L^3 \]
Injection vs. transport

Water hose and valve

Is the flow limited by the valve or the hose?

Semiconductor contacts

Is the current limited by injection or transport?
Thermionic emission and tunneling

Energetics of conjugated polymers

Energetics at the contact

Ionization energy (IE) and electron affinity (EA) measured from HOMO and LUMO edges w.r.t vacuum level

* Work function of PEDOT:PSS substrate measured on separate sample produced in same batch.
Hole injection barriers for TFB contacts

\[ E_{\text{vac}} \]

\[ \text{Au} \quad 4.75\text{eV} \]

\[ 5.5\text{eV} \]

\[ \text{TFB} \]

\[ \text{ITO} \quad 4.85\text{eV} \]

\[ 5.5\text{eV} \]

\[ \text{TFB} \]

\[ E_{\text{vac}} \]

\[ \text{PEDOT:PSS} \]

\[ 5.15\text{eV} \]

\[ 5.5\text{eV} \]

\[ 0.6\text{eV} \]

\[ 0.25\text{eV} \]
Hole injection in TFB

![Graph showing hole injection in TFB](image-url)
MEH-PPV energetics

HOMO

LUMO

ITO

Ca

Al

Au

E (eV)

3.0

3.5

4.0

4.5

5.0

5.5
Degradation of the cathode

(a) 2 min  (b) 10 h  (c) 20 h
(d) 30 h  (e) 40 h

Courtesy of Dr. Homer Antoniadis
CsF/Al cathodes

![Graphs showing current and radiance vs. voltage for ITO/MEH-PPV/CsF(2Å)/Al and ITO/MEH-PPV/Al]
Thicknesss dependence
Degradation of the organic

Layered device

Mixed emission layer

Devices with laminated contacts

Structural changes

Films show intermediate range order

Structural changes

Structure evolves upon exposure to moisture

As prepared

20% RH

44% RH

\( d = 3.3 \text{ nm} \)

\( d = 10 \text{ nm} \)

\( d = 21 \text{ nm} \)
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Conclusions

- Organic semiconductors offer facile processing and tuning of electronic properties through chemical synthesis

- Organic light emitting diodes show excellent potential for applications in solid-state lighting

- Biggest challenge: lifetime