Metallated and Metal-free Molecular Materials for Energy Conversion in OPVs and OLEDs

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Photovoltaic Cells (Solar Cells): *Electricity from Light (Sunlight)*

Organic Light-Emitting Diodes (OLEDs): *Light from electricity*
Conjugated (Metal)-organic Materials for OPVs
Introduction

Energy level diagram for a photoluminescence system.
The triplet states in light-emitting diodes can be utilized in metal-organic compounds through light-harvesting techniques.
Di-, Oligo- and Polymetallaynes

- Variation of metal centers (M)
- Variation of spacer groups (R)
- Variation of auxiliary ligands (L)

Transition Series

<table>
<thead>
<tr>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh</td>
<td>Pd</td>
<td>Ag</td>
<td>Cd</td>
</tr>
<tr>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
<td>Hg</td>
</tr>
</tbody>
</table>

Tuning of $E_g$ for polyplatinyines with different D-A combinations.
Why organic solar cells?

- Low fabrication cost
- Large area
- Improved coverage of solar spectrum
- Flexible substrates

Silicon solar cell (left) and plastic film solar cell (right)

Any alternative to organic polymers?

Organometallic polymers
Metallated conjugated polymers as a new avenue towards high-efficiency polymer solar cells

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\[
\text{Dark purple } E_g = 1.85 \text{ eV}
\]

\(P1\)

Absorption and Photophysics

Strong absorption in the visible region
Phase separation occurs for films with a 1:4 blend ratio, whereas films with a 1:1 ratio are smooth.
Effect of Metallation

Metal-free Polymers

![P1 MF](image1)

![P1](image2)

PCE ~ 0.13%
PCE ~ 4.1%

better overlap with the solar spectrum → MLCT at ~600 nm for P1
electron and hole transport is more balanced in P1

Tuning of Polymer Solar Cell Efficiency and Charge-transport Properties


Absorption and Photophysics

Absorption spectra in CH$_2$Cl$_2$ at 293 K

PL spectra at 293 K
Photovoltaic Behavior

$J$-$V$ curves of solar cells with $P6$-$P9$:PCBM (1:5) active layers under simulated AM1.5 solar irradiation

Max. PCE $\sim 2.9\%$

EQE wavelength dependencies of solar cells with $P6$-$P9$:PCBM (1:5) active layers
Hole and electron mobilities in P6-P9:PCBM blends obtained by the SCLC modeling
Improvement of Open-Circuit Voltage and Photovoltaic Properties of 2D-Conjugated Polymers by Alkylthio Substitution

R = 2-Ethylhexyl
Effect of substitution

PBDTT-TT

PBDTT-O-TT
Optical properties

Normalized absorption spectra of PBDTT-TT, PBDTT-O-TT and PBDTT-S-TT in (a) o-dichlorobenzene solution and (b) thin films on quartz.

W.-Y. Wong et al., *Energy Environ. Sci.*, 2014, 7, 2276
The red-shifted absorption and down-shifted HOMO level of PBDTT-S-TT are desirable for its application as the donor material in PSCs.
SCLC Measurements

Plot of \( \ln(JL^3/V^2) \) vs. \((V/L)^{0.5}\) of the polymers

The hole mobility values of the PBDTT-TT, PBDTT-O-TT and PBDTT-S-TT films are 2.83 \( \times 10^{-3} \), 1.50 \( \times 10^{-3} \) and 4.08 \( \times 10^{-3} \) \( \text{cm}^2 \text{ V}^{-1} \text{ s}^{-1} \), respectively.

Substitution with alkylthio side chains in PBDTT-S-TT increased hole mobility of the polymer.
The enhanced $V_{oc}$ value of 0.84 V for the PSC based on PBDTT-S-TT arise from the down-shifted HOMO energy level of the polymer.

high open-circuit voltage ($V_{oc}$) of 0.84 V, leading to a high PCE of 8.42% for PBDTT-S-TT (vs. 7.38% for PBDTT-TT and 6.68% for PBDTT-O-TT)
Metal-free Organic Dyes for DSSCs
Simple Phenothiazine-based Dyes

PCE up to 6.72% for PT1

*J. Power Sources, 2013, 243, 253.*

PCE up to 8.18% for PT-C6

Absorption spectra of the new dyes in CH$_2$Cl$_2$ solution (left) and on TiO$_2$ films (right)
Photocurrent-voltage ($J-V$) plots

PCE up to 8.18% for PT-C6

Incident photon-to-current efficiency (IPCE) curves
Co-sensitization of PT-C6 with porphyrin dye

Absorption spectra of (a) ZnP and PT-C6 in THF solution and (b) ZnP, PT-C6 and ZnP + PT-C6 on TiO2 films (ca. 3 μm).

Photovoltaic Performance

Table 1. Duration and sequence of dye uptaking, $J_{sc}$, $V_{oc}$, fill factor (FF) and PCE ($\eta$) and electrochemical parameters of device 1 to 9. The TiO$_2$ films for all the anodes consist of 12 µm transparent layer and 6 µm scattering TiO$_2$ layer. The photovoltaic performance was measured under simulated AM 1.5G illumination (power 100 mW cm$^{-2}$).

<table>
<thead>
<tr>
<th>Devices$^{[1]}$</th>
<th>Dye-loading strategy</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
<th>$R_{ct}$ (Ω)</th>
<th>$f$ (Hz)</th>
<th>τ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ZnP</td>
<td>15.78</td>
<td>0.699</td>
<td>67.5</td>
<td>7.44</td>
<td>55.70</td>
<td>34.53</td>
<td>4.61</td>
</tr>
<tr>
<td>2</td>
<td>PT-C6</td>
<td>14.70</td>
<td>0.778</td>
<td>71.3</td>
<td>8.16</td>
<td>371.2</td>
<td>5.43</td>
<td>29.32</td>
</tr>
<tr>
<td>3</td>
<td>10h in ZnP + 1h in PT-C6$^{[2]}$</td>
<td>18.46</td>
<td>0.707</td>
<td>69.1</td>
<td>9.02</td>
<td>69.84</td>
<td>26.51</td>
<td>6.00</td>
</tr>
<tr>
<td>4</td>
<td>10h in ZnP + 2h in PT-C6</td>
<td>18.93</td>
<td>0.715</td>
<td>72.1</td>
<td>9.76</td>
<td>88.08</td>
<td>21.99</td>
<td>7.24</td>
</tr>
<tr>
<td><strong>5</strong></td>
<td>10h in ZnP + 3h in PT-C6</td>
<td><strong>19.20</strong></td>
<td><strong>0.726</strong></td>
<td><strong>72.0</strong></td>
<td><strong>10.04</strong></td>
<td><strong>116.47</strong></td>
<td><strong>17.23</strong></td>
<td><strong>9.24</strong></td>
</tr>
<tr>
<td>6</td>
<td>10h in ZnP + 4h in PT-C6</td>
<td>19.36</td>
<td>0.735</td>
<td>71.0</td>
<td>10.10</td>
<td>139.45</td>
<td>15.91</td>
<td>10.01</td>
</tr>
<tr>
<td>7</td>
<td>10h in ZnP + 10h in PT-C6</td>
<td>19.61</td>
<td>0.739</td>
<td>69.6</td>
<td>10.08</td>
<td>145.12</td>
<td>14.01</td>
<td>11.36</td>
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<tr>
<td>8</td>
<td>10h in PT-C6 + 4h in ZnP</td>
<td>17.05</td>
<td>0.713</td>
<td>70.6</td>
<td>8.58</td>
<td>81.11</td>
<td>30.49</td>
<td>5.22</td>
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<tr>
<td>9</td>
<td>2h in ZnP + 10h in PT-C6</td>
<td>17.48</td>
<td>0.748</td>
<td>69.7</td>
<td>9.11</td>
<td>205.15</td>
<td>10.75</td>
<td>14.81</td>
</tr>
</tbody>
</table>
Heavy Metal Electrophosphors Derived from Multifunctional Chromophores for High-Efficiency Monochromatic and White Light Light OLEDs

Why we need OLEDs?

- Low power consumption
- High contrast and high brightness
- Flexible
- Large viewing angle
Organic Light Emitting Diodes (OLEDs)
Organic light-emitting diodes (OLEDs)

Applications:
- Flat-panel displays and flexible screens
- Solid state lighting
聖誕燈飾碳排404噸
改LED燈可省電八成

璀璨的聖誕燈飾，倍添節日氣氛，但現時本港多棟的大廈仍使用傳統燈泡，有環保團體估計，在聖誕期間將會產生逾四百○四噸的二氧化碳，相等於一千六百輛巴士的排放量。團體建議大廈的燈飾可改用發光二極管（LED）燈泡，既可省電八成，亦符合環保。

大會環保會實地觀察了鰂魚涌兩岸及尖東一帶共十七棟外牆設有聖誕燈飾的大廈，結果發現，大部份的燈飾均以傳統燈炮製作，該會主席邱榮光以其中一棟大廈用的燈炮數目共用五千多個燈炮推算，十七座大廈便共用了八萬五千多個傳統燈炮，並以開啓四十晚，每晚開五至六小時進行估算，本港在聖誕期間便會產生約四百○四噸二氧化碳排放量。

邱榮光表示，雖然燈飾可以增加節日氣氛，但也要顧及環保，他建議大廈可改用光度相若，但可省電八成的LED燈泡取代。

另外，該會又發現，不少家庭會將燈飾通宵開着，但若市民在睡覺前，將家中的燈飾關掉，每年聖誕也可以減少約二百一十二噸的二氧化碳，約等於八百輛巴士的排放量。
Iridium(III) Complexes

- One of the best phosphorescent dyes at present
- Effective intersystem crossing by spin-orbit coupling
- High phosphorescence efficiency at room temperature
Molecular Design

HI/HT → EL → EI/ET
D → A

HI/HT

EI/ET

EL

Ar = (hetero)aryl moiety
White OLEDs
Red emitter
Green emitter
Blue emitter

WOLEDs as Low-Cost and Energy-Saving Lighting Sources

White OLEDs
Orange emitter
Blue emitter
Earth by Light

Electricity

~20% for lighting
Efficient Single-Layer White Polymer Light-emitting Devices for Solid-State Lighting

30:1

Maximum efficiencies

\[ h_L = 42.9 \text{ cd/A} \]
\[ h_p = 20.3 \text{ lm/W} \]
\[ h_{ext} = 19.1\% \]

Efficient Single-Layer White Polymer Light-emitting Devices for Solid-State Lighting

Maximum efficiencies

\[ h_L = 60.1 \text{ cd/A} \]
\[ h_p = 37.4 \text{ lm/W} \]
\[ h_{\text{ext}} = 28.8\% \]

Applying low conductivity PEDOT:PSS P8000

Extremely High-Efficiency Single Emissive Layer White Organic Light-Emitting Diodes Based on Solution-Processed Dendritic Host and New Orange-Emitting Iridium Complex

Device Configuration

Maximum efficiencies at 100 cd/m²
\( h_L = 70.6 \text{ cd/A} \)
\( h_P = 47.6 \text{ lm/W} \)
\( h_{\text{ext}} = 26.0\% \)

A Multifunctional Orange Phosphor for High-Performance Two-Element WOLED Exploiting Exciton-Managed Fluorescence/Phosphorescence

Luminance (■), power (●), and external quantum (▲) efficiencies as a function of current density for OLED devices
Maximum efficiencies

\[
h_L = 26.61 \text{ cd/A} \\
h_P = 13.46 \text{ lm/W} \\
h_{\text{ext}} = 8.91 \%
\]

[Ir(ppy-X)₂(acac)] with main group elements: Color tuning is achieved by shifting the charge-transfer character from the pyridyl ring to the electron-withdrawing main group moiety.
EL Spectra for OLEDs at 8 V

Metallophosphors of platinum with distinct main-group elements

Duplicating “sunlight” from simple WOLEDs for lighting application
EL Spectra of simple WOLEDs at 10 wt-% doping concentration

Pt-O

Pt-Ge

\[ h_L = 11.4 \text{ cd/A} \]
\[ h_P = 7.3 \text{ lm/W} \]
\[ h_{\text{ext}} = 5.1\% \]

The white-light quality of our simple single-dopant WOLEDs.

<table>
<thead>
<tr>
<th>WOLEDs</th>
<th>CIE</th>
<th>CRI</th>
<th>CCT /K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sunlight (CIE Standard Illuminant D65)</td>
<td>(0.313, 0.329)</td>
<td>90</td>
<td>6500</td>
</tr>
<tr>
<td>Incandescent bulb</td>
<td>(0.448, 0.408)</td>
<td>90</td>
<td>2854</td>
</tr>
<tr>
<td>Fluorescent, warm white</td>
<td>(0.440, 0.403)</td>
<td>72</td>
<td>2940</td>
</tr>
<tr>
<td>WOLED with Pt phosphorescent excimer</td>
<td>(0.340, 0.350)</td>
<td>75</td>
<td>--</td>
</tr>
<tr>
<td>Device with \textbf{Pt-Ge} as emitter</td>
<td>(0.337, 0.369)</td>
<td>90</td>
<td>5340</td>
</tr>
<tr>
<td>Device with \textbf{Pt-Ge} as emitter</td>
<td>(0.354, 0.360)</td>
<td>97</td>
<td>4719</td>
</tr>
<tr>
<td>Device with \textbf{Pt-O} as emitter</td>
<td>(0.320, 0.340)</td>
<td>94</td>
<td>6066</td>
</tr>
<tr>
<td>Device with \textbf{Pt-O} as emitter</td>
<td>(0.313, 0.339)</td>
<td>90</td>
<td>6428</td>
</tr>
</tbody>
</table>

Better efficiency/color quality/brightness trade-offs for WOLEDs.
Sunlight Duplicator

CIE (0.354, 0.360)  CRI = 97

White Organic Light-emitting Devices
The image of the objects with different perceived colors (blue-green-yellow-red) when illuminated under (a) our Pt-O doped WOLEDs and (b) the daylight, showing an excellent true color reproduction.
White Organic Light-Emitting Diodes with Evenly Separated Red, Green and Blue Colors for Efficiency/Color Rendition Trade-off Optimization

At 100 cd/m²

\[ h_L = 63 \text{ cd/A} \]
\[ h_P = 36.6 \text{ lm/W} \]
\[ h_{\text{ext}} = 16.3\% \]

Red-shifted spectrum from Ir(ppy)₃
At 100 cd/m²
\( h_L = 34.2 \text{ cd/A} \)
\( h_P = 18.5 \text{ lm/W} \)
\( h_{ext} = 13.2\% \)

Efficiency–luminance curves of the electrophosphorescent WOLEDs with different thickness of yellowish green/green emission layer.
EL spectra of the hybrid WOLEDs with (a) 1 and (b) Ir(ppy)$_3$ as emitter.
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The End
Thank You!