Advances in Organic Materials for White OLEDs

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0.33, 0.63
0.17, 0.38
0.16, 0.37
0.16, 0.29
0.15, 0.22
0.14, 0.13
0.16, 0.10

1931 CIE chart

sRGB
NTSC

0.35, 0.61
0.42, 0.57
0.62, 0.38
0.65, 0.35
0.67, 0.33
0.68, 0.32
Color Mixing to Achieve White Emission

- Color mixing
- Side-by-side arrangement of RGB elements
- Transparent devices can be stacked
  - Pixels on top of pixels with a common substrate
  - Large sheets of transparent R, G and B OLEDS can be stacked to achieve white
- Mixed emitters in a single device
  - Simplifies device
  - Color balance achieved automatically
  - Several possible architectures
- In all cases the White OLED lifetimes are limited by the blue components
Efficiency and Operational Lifetime of PHOLEDS

Phosphorescent dopants

<table>
<thead>
<tr>
<th>Color</th>
<th>CIE</th>
<th>LE (cd/A)</th>
<th>(t_{50}) (hrs)</th>
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<tbody>
<tr>
<td>Red</td>
<td>[0.64, 0.36]</td>
<td>30</td>
<td>900,000</td>
</tr>
<tr>
<td>Green</td>
<td>[0.31, 0.63]</td>
<td>85</td>
<td>400,000</td>
</tr>
<tr>
<td>Blue</td>
<td>[0.14, 0.12]</td>
<td>High</td>
<td>short</td>
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Universal Display Corp.

Commercial lighting panels use sky-blue dopant to extend lifetime, but the WOLED lifetime is still limited by blue.
Efficiency and Operational Lifetime of PHOLEDs

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Triplet exciton lifetime – $\mu$s

Is there enough energy in the $T_1$ exciton to break bonds?

<table>
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<tr>
<th>Color</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Energy (eV / kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red</td>
<td>600</td>
<td>2.07 / 48</td>
</tr>
<tr>
<td>Green</td>
<td>520</td>
<td>2.40 / 56</td>
</tr>
<tr>
<td>Blue</td>
<td>460</td>
<td>2.70 / 63</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy (eV / kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>3.6-4.1 / 85-100</td>
</tr>
<tr>
<td>C-C</td>
<td>3.0-4.0 / 70-95</td>
</tr>
<tr>
<td>C-N</td>
<td>3.0-4.0 / 70-95</td>
</tr>
<tr>
<td>Ir-C</td>
<td>3.4 / 80</td>
</tr>
</tbody>
</table>

Make emitters with bonds at the upper ends of the ranges. Is that good enough?
Degradation Routes

- Energetically Driven
  - Lifetime: R>G>B
- Two particle interactions lead to luminance loss
  - Exciton on phosphor, polaron on host
  - Exciton-exciton also possible

Fitting kinetic data through several half-lives suggests that bimolecular process (TTA and TPA) are the most important.

\[ \text{Rate}_{\text{annihilation}} = k[T_1][T_1,P^-] \]

Spreading the recombination zone: Dopant/Host Grading

\[ Rate_{\text{annihilation}} = k[T_1][T_1, P^-] \]

Stacked devices reduce the current in each PHOLED by 2X.
Can we be more proactive about preventing bimolecular decay pathways?

Y. Zhang, et al., *Nature Comm.* (2014), DOI: 10.1038/ncomms6008
The Problem of TTA or TPA

- Desirable blue emission
  1. Electrical excitation
  2. Blue Emission
  3. TTA / TPA
  4. Vibronic relaxation
  5. Dissociative reaction (Bond cleavage)
  6. Non-radiative/radiative decay

- Dissociative reaction (degradation)
  1. → 3 → 4

- High-energy states management
  1. → 3 → 4' → 5'

- To increase lifetime: decrease bimolecular collisions/processes
  - Lower [exciton] and [polaron], but this increases voltage

- Grading is good, but how do we improve on it?
  - New, more stable blue phosphors and host materials (on going)
  - Relax the hot-polaron before it decays (managers)
Blue PHOLED measured at initial luminance of 1,000 cd/m²

<table>
<thead>
<tr>
<th>Device</th>
<th>Driving J [mA/cm²]</th>
<th>EQE [%]</th>
<th>LT80 [hr]</th>
<th>ΔV [V]</th>
<th>CIE @5 mA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONV</td>
<td>6.7±0.1</td>
<td>8.0</td>
<td>93±9</td>
<td>0.4±0.1</td>
<td>[0.15,0.28]</td>
</tr>
<tr>
<td>GRAD</td>
<td>5.7±0.1</td>
<td>8.9</td>
<td>173±3 (+86%)</td>
<td>0.9±0.1</td>
<td>[0.16,0.30]</td>
</tr>
<tr>
<td>M3</td>
<td>5.3±0.1</td>
<td>9.0</td>
<td>334±5 (+260%)</td>
<td>1.5±0.2</td>
<td>[0.16,0.30]</td>
</tr>
</tbody>
</table>
Need lots of new stuff to extend lifetime:
- Stable emitters, hosts, blockers, transporters
- Managers to help protect the hosts and emitters
- New device structure ideas to maximize external efficiency
Phosphorescent OLED Efficiency:

$$\Phi_{EL} = \Phi_{PL} \chi \eta_r \eta_e$$

- **$\Phi_{EL/PL}$** luminescent quantum efficiencies
- **$\chi$** fraction of usable excitons
- **$\eta_r$** carrier recombination efficiency
- **$\eta_e$** out coupling efficiency

- Good devices: $\Phi_{PL}$, $\chi$, $\eta_r \rightarrow 1$
- **$\Phi_{EL}$** limited by $\eta_e$:
  - $\eta_e \uparrow$ mA/cm$^2$ ↓ lifetime ↑
Non-Isotropic Emitter Orientation

Consider the orientation of the transition dipole relative to the substrate.

- Anisotropy factor:

\[
\Theta = \frac{p_z}{p_x + p_y + p_z} = \frac{p_\perp}{p_{\parallel} + p_\perp}
\]

$p_z$ strongly couples to plasmon modes, $p_x$ and $p_y$ do not couple to plasmon modes.

Orientation and EQE

Isotropic
Ir(ppy)$_3$

Non-isotropic
Ir(ppy)$_2$(acac)

$\eta_{EQE}$

PL Quantum Yields ($q_{PL}$)

Orientation factor ($\Theta$)

Alignment of emitters in doped films

• Linear fluorescent molecules

\[
\text{BDASBi}
\]

in CBP, $\Theta = 0.09$

W. Bruetting, et. al, APL (2010)

• TADF emitters

\[
\text{Cis-BOX2}
\]

in CBP, $\Theta < 0.05$, $\eta_{\text{EXT}} = 33\%$

C. Adachi, et. al, APL (2016)

• Square planar platinum complexes

$\Theta = 0.59$

$\Theta = 0.67$

## Oriented Emitters: tris-ligand Ir based emitters

<table>
<thead>
<tr>
<th>Emitter</th>
<th>Host</th>
<th>Orientation (% vertical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir(dhfpy)$_2$(acac)</td>
<td>NPD</td>
<td>25%</td>
</tr>
<tr>
<td>Ir(ppy)$_2$(acac)</td>
<td>CBP</td>
<td>23%</td>
</tr>
<tr>
<td></td>
<td>TCTA/ B3PYMPM</td>
<td>23%</td>
</tr>
<tr>
<td>Ir(ppy)$_2$(tmd)</td>
<td>TCTA/ B3PYMPM</td>
<td>22%</td>
</tr>
<tr>
<td>Ir(MDQ)$_2$(acac)</td>
<td>NPD</td>
<td>24%</td>
</tr>
<tr>
<td></td>
<td>NPD/ B3PYMPM</td>
<td>20%</td>
</tr>
<tr>
<td>Ir(bt)$_2$(acac)</td>
<td>NPD</td>
<td>24%</td>
</tr>
<tr>
<td>Ir(chpy)$_3$</td>
<td>BPhen</td>
<td>22%</td>
</tr>
<tr>
<td>Ir(mphmq)$_2$(tmd)</td>
<td>NPD/ B3PYMPM</td>
<td>18%</td>
</tr>
<tr>
<td>Ir(mphq)$_2$(acac)</td>
<td>NPD/ B3PYMPM</td>
<td>23%</td>
</tr>
<tr>
<td>Ir(phq)$_3$</td>
<td>NPD/ B3PYMPM</td>
<td>30%</td>
</tr>
<tr>
<td>Ir(piq)$_3$</td>
<td>NPD</td>
<td>22%</td>
</tr>
<tr>
<td>Ir(bppo)$_2$(acac)</td>
<td>CBP</td>
<td>22%</td>
</tr>
<tr>
<td>Ir(ppy)$_3$</td>
<td>CBP</td>
<td>31%</td>
</tr>
<tr>
<td></td>
<td>CBP</td>
<td>33%</td>
</tr>
</tbody>
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Why do dopant align in an isotropic matrix?

- Electrostatic interactions between host and guest
- Dopant aggregations induced by high dopant dipole moment
- Vacuum/Organic boundary induces molecular orientation with aliphatic (acac) groups directed toward vacuum.

- Chemical anisotropy can drive alignment
- Near horizontal alignment is possible for linear molecules
- Can we achieve the same high degree of alignment for high performance Ir based phosphors?