OLED Emissive Materials Beyond Phosphorescence

Jian Li

Arizona State University
Progress of organic emitters in OLEDs

1987~
1st Generation
Fluorescence
IQE~25%

2000~
2nd Generation
Phosphorescence
IQE~100%

2012~
3rd Generation
Delayed Fluorescence (TADF)
IQE~100%

2014~
3.5th Generation
TADF Assisted Fluorescence (TAF)
IQE~100%

Singlets → Triplet

1987~
Alq_3
Fluorescence

2000~
Ir(ppy)_3
Phosphorescence

2012~
4CzIPN
Delayed fluorescence

2014~

TADF Material Intro - Courtesy of Prof. Adachi
### Basis for TADF molecular design

**Small: \( \Delta E_{ST} \)**

- \( E_S = (E_H - E_L) + K \)
- \( E_T = (E_H - E_L) - K \)

**\( \Delta E_{ST} = 2K \)**

- \( E_H : \text{HOMO Energy} \)
- \( E_L : \text{LUMO Energy} \)
- \( K : \text{Exchange Energy} \)

- **Large \( \Delta E_{ST} \)**

- **Small \( \Delta E_{ST} \)**

**Moderate Oscillator Strength:** \( f \propto \mu^2 \)

**Transition dipole moment**

\[
\begin{align*}
  f & \propto \mu^2 \\
  = & \\
  & HOMO |e_r| LUMO d
\end{align*}
\]

**Donor:**

- **Acceptor backbone**

- **\( X: \text{Introduction of steric hindrance} \)**

**Moderate radiative decay rate with small \( \Delta E_{ST} \)**
**Unlimited Molecular Design for TADF**

### Molecular Design
- Separation of HOMO and LUMO, but rather gentle decrease of HOMO and LUMO distribution for large transition dipole moment.
- Use of molecular units having a high localized triplet state ($^3\text{LE}$)
- Small $\Delta E_{ST}$ for short transient time $\sim \mu\text{s}$ order

<table>
<thead>
<tr>
<th>Molecular Design</th>
<th>4CzIPN</th>
<th>4CzPN</th>
<th>4CzTPN</th>
<th>PIC-TRZ</th>
<th>PIC-TRZ2</th>
<th>CC2TA</th>
<th>PXZ-TRZ</th>
<th>DMAC-DPS</th>
<th>ACRFLCN</th>
<th>Spiro-AN</th>
<th>Spiro-CN</th>
<th>HAP-3TPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E_{ST}$</td>
<td>0.01 eV</td>
<td>0.12 eV</td>
<td>0.06 eV</td>
<td>0.17 eV</td>
<td>0.10 eV</td>
<td>0.025 eV</td>
<td>0.06 eV</td>
<td>0.08 eV</td>
<td>0.10 eV</td>
<td>0.025 eV</td>
<td>0.06 eV</td>
<td>0.17 eV</td>
</tr>
<tr>
<td>$\lambda_{max}$</td>
<td>513 nm</td>
<td>531 nm</td>
<td>544 nm</td>
<td>610 nm</td>
<td>493 nm</td>
<td>495 nm</td>
<td>522 nm</td>
<td>465 nm</td>
<td>485 nm</td>
<td>495 nm</td>
<td>540 nm</td>
<td>610 nm</td>
</tr>
<tr>
<td>EQE</td>
<td>18%</td>
<td>19%</td>
<td>17%</td>
<td>17.5%</td>
<td>11%</td>
<td>15.5%</td>
<td>17%</td>
<td>20%</td>
<td>10%</td>
<td>16.5%</td>
<td>4.4%</td>
<td>17.5%</td>
</tr>
</tbody>
</table>

**References**
- **PIC-TRZ**: $\Delta E_{ST}: 0.1\text{eV}$, $\lambda_{max}: 466\text{nm}$, EQE: 5.3% (Appl. Phys. Lett., 98, 83302 (2011))
- **PIC-TRZ2**: $\Delta E_{ST}: 0.01\text{eV}$, $\lambda_{max}: 505\text{nm}$, EQE: 14% (Phys. Rev. Lett., 110, 247401 (2013))
- **CC2TA**: $\Delta E_{ST}: 0.07\text{eV}$, $\lambda_{max}: 493\text{nm}$, EQE: 11% (Appl. Phys. Lett., 101, 93306 (2012))
- **PXZ-TRZ**: $\Delta E_{ST}: 0.0084\text{eV}$, $\lambda_{max}: 522\text{nm}$, EQE: 15.5% (Chem. Com., 48, 11392 (2012))
- **DMAC-DPS**: $\Delta E_{ST}: 0.08\text{eV}$, $\lambda_{max}: 465\text{nm}$, EQE: 20% (Nat. Photo., 8, 826 (2014))
- **ACRFLCN**: $\Delta E_{ST}: 0.07\text{eV}$, $\lambda_{max}: 495\text{nm}$, EQE: 11% (Angew. Chem., 2012, 51, 11311)
- **Spiro-AN**: $\Delta E_{ST}: 0.025\text{eV}$, $\lambda_{max}: 495\text{nm}$, EQE: 16.5% (Chem. Comm., 49, 10385 (2013))
- **Spiro-CN**: $\Delta E_{ST}: 0.1\text{eV}$, $\lambda_{max}: 540\text{nm}$, EQE: 10% (Chem. Com., 48, 9580 (2012))
- **HAP-3TPA**: $\Delta E_{ST}: 0.17\text{eV}$, $\lambda_{max}: 610\text{nm}$, EQE: 17.5% (Adv. Mat., 25, 3319 (2013))
A new route to harvest triplets in OLEDs with fluorescence emitters

**TADF based OLEDs**

- High efficiency up to 100%
- Unlimited molecular design
- Broad spectra due to CT emission (not appropriate for display applications)


Intermolecular: K. Goushi et al., Nature Photo. 6, 253 (2012)

**Fluorescence based OLEDs**

- High color purity (narrow spectrum)
- Long lifetimes of operational stability
- Unlimited molecular design
- Theoretical limitation of $\eta_r$ 25% - 62.5% (even TTA process)

**TADF as assistant & Fluorescence as emitter**

- Long lifetimes of operational stability
- High color purity
- Flexibility of material design
- Theoretical limitation of $\eta_r$ - 100%

TADF: Exciton-generation

Fusion of two Functions

Fluo: Light-emission

A remarkable progress has been achieved for the performance and stability of TADF materials. With the better understanding of TADF mechanism and the incorporation of better suited host materials, the TADF device performance can be improved further.
Blue TADF OLEDs

- High EQE of **19.5%** with emission peak at 450nm

Q. Zhang, et al., Nature Photonics, 8, 326 (2014)

The choice of donor and accepter type materials will be less for blue TADF materials due to the high triplet energy requirement.
Metal-Assisted Delay Fluorescent Emitters

PdN3N devices can be efficient with improved device operational stability (EQE ~15%, LT90 >1000 hrs @ 1000 cd/m²).

Why MADF materials?

Magic of MADF?

77 K → RT

Blue-emitting MADF emitter with green triplet energy could be most energetically favorable.
Semiconductor Colloidal Quantum Dots

- Size- and composition-dependent tunable emission through visible spectrum (quantum confinement effect)
- Narrow emission peaks (minimum width ~20 nm)
- High luminescence quantum yield (~90%)
- Solution processible; good stability

Versatile for solid-state lighting; potential for high CRI and high efficacy

CRI=90, LER= 360 lm/W
Solution-Processed QD-LEDs

<table>
<thead>
<tr>
<th>Color</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>FWHM (nm)</th>
<th>Max. Lum. (cd/m$^2$)</th>
<th>$\eta_{\text{EQE}}$ (%)</th>
<th>$\eta_{P}$ (lm/W)</th>
<th>$\eta_{A}$ (cd/A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue</td>
<td>455</td>
<td>20</td>
<td>4,000</td>
<td>10.3</td>
<td>2.7</td>
<td>4.3</td>
</tr>
<tr>
<td>Green</td>
<td>537</td>
<td>29</td>
<td>14,000</td>
<td>14.3</td>
<td>58</td>
<td>62</td>
</tr>
<tr>
<td>Red*</td>
<td>625</td>
<td>28</td>
<td>21,000</td>
<td>12.0</td>
<td>17.4</td>
<td>15</td>
</tr>
</tbody>
</table>

- EQE > 10% achieved in QLEDs for all three colors
- QLEDs operate more efficiently at high luminances
- Low operation voltage $\Rightarrow$ good lm/W efficiency
- Possible lifetime improvement (PEDOT:PSS, HTL, etc.)

Future Outlooks

- The development of stable blue emitters is key;
- The choice of emissive materials should include phosphorescent materials, thermal activated delayed fluorescent (TADF) materials and metal-assisted delayed fluorescent (MADF) materials;
- The recent progress of QLEDs has demonstrated enough promise as a future solution for solution processed organic solid state lighting devices.