Current Status and Future Prospect of TADF Emitters

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Classification of light-emitting materials

- **Fluorescence**
  - $S_1 \rightarrow T_1 \rightarrow S_0$
  - 25% ns

- **Phosphorescence**
  - $S_1 \rightarrow ISC \rightarrow T_1 \rightarrow S_0$
  - μs 100%

- **Thermally Activated Delayed Fluorescence**
  - $S_1 \rightarrow RISC \rightarrow T_1 \rightarrow S_0$
  - μs 100%
Thermally Activated Delayed Fluorescence

- 100% internal quantum efficiency
- ~30% external quantum efficiency in RGB colors
- Up-conversion of triplet excitons into singlet excitons (RISC)
- Small singlet-triplet energy gap ($\Delta E_{ST}$)
- Purely organic emitting materials
- Long triplet exciton lifetime (a few $\mu$s)
- Various applications as host, assistant dopant, and emitter
Molecular Design of TADF Emitter

**Donor-Acceptor type TADF**

- **Free Rotation**
- **Large Stokes Shift**
- **Broad Emission (FWHM > 50 nm)**

- Easy control of $\Delta E_{ST}$ by strong charge transfer (CT) character caused by HOMO-LUMO separation
- Broad emission & Large Stokes shift by strong CT character
  - Inefficient energy transfer & Poor color purity

**Multi-Resonance type TADF**

- **Small Stokes Shift**
- **Narrow Emission (FWHM < 30 nm)**

- Polycyclic aromatic hydrocarbon (PAH) structure with short-range CT character by alternating HOMO-LUMO distribution
- Small Stokes shift & Narrow emission by rigid structure
  - Efficient energy transfer process & High color purity

Nat. Photonics 2019, 13, 678
Molecular Design of TADF Emitter

Singlet-triplet energy gap

\[ E_0 - J \rightarrow E_s - 2K \rightarrow E_T \]

Singlet exciton  Triplet exciton

LUMO
HOMO

작은 K  큰 K
Molecular Design of TADF Emitter

**Spin-orbit coupling**

Forbidden transition by El-Sayed rule

- $S_1$ (LE)
- $S_1$ (CT)
- $T_1$ (CT) $>$ $T_1$ (LE)
- $S_0$
- $T_1$ (CT) $>$ $T_1$ (LE)

Allowed transition by El-Sayed rule

- $S_1$ (LE)
- $S_1$ (CT)
- $T_1$ (CT) $>$ $T_1$ (LE)
- $S_0$
- $T_1$ (LE) $>$ $T_1$ (CT)
- $T_1$ (LE) $\approx$ $T_1$ (CT)

TADF

Low probability

High probability

El-Sayed rule

Forbidden transition

Allowed transition
Molecular Design of TADF Emitter

**Oscillator strength**

\[
k_{if} = \frac{2\pi}{\hbar} \left| \langle \psi_f | e \mathbf{r} | \psi_i \rangle \right|^2 \rho(E_{if})
\]

\[
f = \left( \frac{8 \pi m_e \bar{v}}{3 \hbar e^2} \right) \langle \Psi_1 | \mathbf{P} | \Psi_2 \rangle^2
\]

Large oscillator strength: probability of absorption of radiation between energy levels

- depends on orbital overlap
Molecular Design of TADF Emitter

✓ Large separation of HOMO and LUMO

✓ Weak overlap of HOMO and LUMO
Recent Progress of TADF OLEDs

Red TADF Emitters

![Chemical structure of 4CzTPN, 4CzTPN-Me, and 4CzTPN-Ph]

Nature 492, 234 (2012)

![Graph showing external electroluminescence quantum efficiency and external quantum efficiency against luminance for PzTDBA and PzDBA]

Adv. Mater 33, 2007724 (2021)
Recent Progress of TADF OLEDs

Green TADF Emitters

Nature 492, 234 (2012)

Recent Progress of TADF OLEDs

**Blue TADF Emitters**

![Blue TADF Emitters](image)

EQE (%) vs Luminance (cd m\(^{-2}\))

Nat. Photonics 13, 540 (2019)

![SpiroAC-TRZ](image)

Recent Progress of TADF OLEDs

**Blue TADF Emitters**

- **DDCzTrz**
- **5TCzBN**
- **BDpyInCz**
- **3Ph₂CzCzBN**

*Adv. Mater. 2015, 27, 2515*

*Mater. Horiz. 2016, 3, 145*

*Adv. Sci. 2017, 4, 1600502*

*Nat. Commun. 2018, 9, 5036*
Recent Progress of MR-TADF OLEDs

Red TADF Emitters

J. Am. Chem. Soc. 142, 19468 (2020)
Recent Progress of MR-TADF OLEDs

Green TADF Emitters

AZA-BN

Ang. Chemie. 59, 17499 (2020)
Recent Progress of MR-TADF OLEDs

Blue TADF Emitters

DABNA

DOBNA-OAr

Normalized intensity

Wavelength (nm)

400 500 600 700 800

0 0.5 1.0

469 nm

18 nm

CIE = (0.12, 0.11)

ECE (%)

Luminance (cd m⁻²)

34.4 32.8 26.0

10 100

Nat. Photon. 13, 678 (2019)
Recent Progress of MR-TADF OLEDs

**Blue TADF Emitters**

- **DABNA-1**
  - EQE = 13.5% CIEy = 0.09

- **B2**
  - EQE = 18.3% CIEy = 0.11
  - J. Am. Chem. Soc. 2018, 140, 1195

- **ν-DABNA**
  - EQE = 34.4% CIEy = 0.11
  - Nat. Photonics 2019, 13, 678

- **DABNA-NP-TB**
  - EQE = 19.5% CIEy = 0.11
  - Angew. Chem. 2021, 133, 2918–2922

- **ν-DABNA-O-Me**
  - EQE = 29.5% CIEy = 0.10
  - Angew. Chem. 2021, Accepted Articles

✓ Several Boron-based MR-TADF emitters with deep-blue emission with y color coordinate of ~ 0.10
Recent Progress of MR-TADF OLEDs

Blue TADF Emitters

![Diagram showing blue TADF emitters with EQE, FWHM, and wavelength values](image-url)
Recent Progress of MR-TADF OLEDs

Boron free blue TADF Emitters

tPBisICz

Recent Progress of Hyperfluorescence OLEDs

Hyperfluorescence Mechanism

Sensitizer

- high efficiency
- fast RISC
- Dexter energy transfer management

Emitter

- high PLQY
- small Stokes shift
- Dexter energy transfer management
- Charge trapping management

✓ Dominant emission of final emitter by Förster energy transfer: ~100% internal quantum efficiency
Recent Progress of Hyperfluorescence OLEDs

**Blocking group effect**

- **PAD**
- **MePAD**
- **tBuPAD**
- **PhBuPAD**

![Chemical structures](image)

- **p4TCPbBN**
- **t-DABNA**

![Graphs](image)


✓ Dexter energy transfer management by blocking group: improved EQE

**Adv. Mater. 32, 1908355 (2020)**
Recent Progress of Hyperfluorescence OLEDs

- **TADF assisted TADF**: high EQE and long lifetime

![Diagram showing TADF assisted TADF](image)

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Nat. Photon. 15, 203 (2021)
Recent Progress of Hyperfluorescence OLEDs

TADF assisted TADF

✓ TADF assisted TADF: high EQE and long lifetime

Nat. Photon. 15, 208 (2021)
### Recent Progress of Hyperfluorescence OLEDs

**Device data from industry**

<table>
<thead>
<tr>
<th>Color</th>
<th>( \lambda_{\text{peak}} ) (nm)</th>
<th>FWHM (nm)</th>
<th>CIE xy</th>
<th>Efficiency (cd/A)</th>
<th>LT95@1000nit (hours)</th>
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</thead>
<tbody>
<tr>
<td>Red</td>
<td>BE 617</td>
<td>43</td>
<td>0.65, 0.35</td>
<td>32</td>
<td>&gt;37,000</td>
</tr>
<tr>
<td></td>
<td>TE 618</td>
<td>23</td>
<td>0.68, 0.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Green</td>
<td>BE 522</td>
<td>34</td>
<td>0.24, 0.70</td>
<td>81</td>
<td>&gt;20,000</td>
</tr>
<tr>
<td></td>
<td>TE 523</td>
<td>17</td>
<td>0.14, 0.79</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blue</td>
<td>BE 471</td>
<td>21</td>
<td>0.12, 0.13</td>
<td>43</td>
<td>280</td>
</tr>
<tr>
<td></td>
<td>TE 469</td>
<td>16</td>
<td>0.12, 0.06</td>
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<td></td>
</tr>
</tbody>
</table>

Kyulux, SID (2021)
Recent Progress of Hyperfluorescence OLEDs

Summary of RGB OLEDs
## Issues and Outlook

<table>
<thead>
<tr>
<th></th>
<th>Phosphorescent OLED</th>
<th>TADF OLED</th>
<th>Hyperfluorescence OLED</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Theoretical maximum internal quantum efficiency</strong></td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td><strong>External quantum efficiency</strong></td>
<td>&gt;20%</td>
<td>&gt;20%</td>
<td>~20%</td>
</tr>
<tr>
<td><strong>Device lifetime</strong></td>
<td>○○○○○</td>
<td>○○</td>
<td>○○○</td>
</tr>
<tr>
<td><strong>Color purity</strong></td>
<td>○○○○</td>
<td>○○</td>
<td>○○○</td>
</tr>
</tbody>
</table>
| **Key issues**                       | Blue device lifetime | Red efficiency
R/G/B device lifetime
Color purity
High driving voltage | Red efficiency
R/G/B device lifetime
High driving voltage
Complicated fabrication process |