Development of High Performance OLED materials and Current Progress

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1. Approach for enhancing OLED performance

2. Materials for highly efficient fluorescent blue

3. Further improvement of device performance
   3-1 Triplet – Triplet Fusion
   3-2 Capping Layer

4. Development of Phosphorescent host

5. Summary
1. Approach for enhancing OLED performance

2. Materials for highly efficient fluorescent blue

3. Further improvement of device performance
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4. Development of Phosphorescent host

5. Summary
1. Approach for Enhancing OLED Performance

Application of OLEDs need to improve their power consumption much more. ⇒ Efficiency of a blue pixel would control whole efficiency of OLEDs.

TV specification by EnergyStar

Performance Improvement Curves for OLED by EnergyStar

http://www.energystar.gov/index.cfm?c=revisions.television_spec

1. Approach for Enhancing OLED Performance

General approach to improve power of OLED

Efficacy (lm/W) \( \eta = \frac{[IQE] \times [\text{Outcoupling Efficiency}]}{[\text{Driving Voltage}]} \)
1. Approach for enhancing OLED Performance

High efficiency with keeping long lifetime is important.

Device simulation results of typical blue device

ITO / HI / HT / BH:BD / ET / LiF / Al

60    20    40;5%   20      1  (nm)

- Thermal and electro-chemical stability of materials
- Excitation stability of emitting materials
- Material combination to optimize carrier balance in emitting layer
1. Approach for enhancing OLED performance

2. Materials for highly efficient fluorescent blue

3. Further improvement of device performance
   3-1 Triplet – Triplet Fusion
   3-2 Capping Layer

4. Development of Phosphorescent host

5. Summary
BD-7 was achieved the CIEy of 0.08 for NTSC blue.
## Materials for Highly Efficient Fluorescent Blue Device Structure

### 2008

<table>
<thead>
<tr>
<th>Dopant</th>
<th>CIE(x,y)</th>
<th>L/J(cd/A) @10mA/cm²</th>
<th>LT50 (hrs) @L₀=1000cd/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>BD-4</td>
<td>(0.14, 0.13)</td>
<td>6.5</td>
<td>11,000</td>
</tr>
<tr>
<td>BD-5*</td>
<td>(0.13, 0.21)</td>
<td>8.4</td>
<td>50,000</td>
</tr>
</tbody>
</table>

### 2009

| BD-6   | (0.15, 0.12) | 7.1                 | 8,000                    |
## Materials for Highly Efficient Fluorescent Blue Device Structure

Device Structure: ITO / HI-2 / HT-2 / BH-1: **BD-7* / ET-6 / LiF / Al**

<table>
<thead>
<tr>
<th>2011</th>
<th>Dopant</th>
<th>CIE(x,y)</th>
<th>L/J(cd/A) @10mA/cm²</th>
<th>LT50 (hrs) @L₀=500cd/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>BD-7*</td>
<td>(0.14, 0.08)</td>
<td>5.5</td>
<td>11,000</td>
<td></td>
</tr>
</tbody>
</table>

**NTSC Blue**
1. Approach for enhancing OLED performance

2. Materials for highly efficient fluorescent blue

3. Further improvement of device performance
   3-1 Triplet – Triplet Fusion
   3-2 Capping Layer

4. Development of Phosphorescent host

5. Summary
3. Further Improvement of Fluorescent Device

Recombination Process of Fluorescent Devices

Cathode → Electron → Recombination → Hole → Anode

Fluorescent device

25% → Singlet exciton → Fluorescence 25%

75% → Triplet exciton → Heat (vibration, rotation) 75%
3. Further Improvement of Fluorescent Device

**Approach**

- Cathode → Electron → Hole → Anode
- Recombination
- Exciton
  - Singlet exciton (25%)
  - Triplet exciton (75%)

**Fluorescent device**

- High efficiency to exceed the theoretical limit
  - Triplet-Triplet Fusion

- Improvement of out-coupling (Top emission OLED)
  - Capping Layer
Typical External Quantum Efficiency of fluorescence

\[ \eta_{ex} = \frac{1}{2\pi} \int_{\theta_c}^\infty d\Omega = \frac{1}{2\pi} \int_0^{2\pi} \int_0^{\theta_c} \sin \theta d\theta d\varphi = \frac{1}{2\pi} \cdot 2\pi \int_0^{\theta_c} \sin \theta d\theta \]

\[ = 1 - \cos \theta_c = 1 - \sqrt{1 - \frac{1}{n^2}} \]

\( \eta_{ex} = 0.15 \sim 0.20 \) (if \( n = 1.7 \sim 2.0 \))

IQE = 100% (Phosphorescence) \( \rightarrow \) EQE = 20%

IQE = 25% (Fluorescence) \( \rightarrow \) EQE = 5%
3-1. Triplet-Triplet Fusion

What is TTF?

Triplet-Triplet Fusion
- Phosphorescence ➢ Decrease efficiency
- Fluorescence ➢ Increase efficiency

⇒ Triplet-Triplet Fusion

Excitons

Singlet Excitons

Ground State

Delayed fluorescence

Intersystem Crossing
3-1. Triplet-Triplet Fusion

**Study of TTF ~ Transient EL**

**Measurement system**

```
PG : Pulse Generator
OSC : Oscilloscope
PMT : Photo-multiplier
EL : OLED device
```

**Rate equation of TTF**

\[
\dot{n}_T = -\alpha \cdot n_T - \gamma \cdot n_T^2
\]

- **Simple Triplet decay**
- **Decay by T-T collision**

\[
n_T = \frac{\alpha \exp(-\alpha(t + t_0))}{\gamma(1 - \exp(-\alpha(t + t_0)))}
\]

\[
\approx \frac{1}{\gamma(t + t_0)} \quad \text{for small } t
\]

\[
\begin{align*}
I_s & \propto \int n_s \, dx \\
I_{T-T} & \propto \int n_T^2 \, dx
\end{align*}
\]

\[
\frac{1}{\sqrt{I_{T-T}}} \propto A + \gamma \cdot t
\]
3-1. Triplet-Triplet Fusion

**Discovery of Triplet-Triplet Fusion (TTF)**

Device Structure: ITO / HI / HT / RH-1: RD-2 / ET-1 / LiF / Al

**EQE = 8.4% > 5%**

The pattern is almost a Lambertian.

High efficiency originates in the red materials.

2006
3-1. Triplet-Triplet Fusion

**Discovery of Triplet-Triplet Fusion (TTF)**

Device Structure: ITO / HI / HT / RH-1: RD-2 / ET-1 / LiF / Al

**Transient EL decay**

- Ordinary EL decay
- Delayed EL

**Voltage Off**

\[
\frac{1}{\sqrt{I_{T-T}}} \propto A + \gamma \cdot t
\]

**IQE = 34% >> 25%**
3-1. Triplet-Triplet Fusion

Application of TTF to Blue

Efficiency Enhancement Layer (EEL) for Blue

\[ 3A^* + 3A^* \rightarrow (4/9)1A + (1/9)1A^* + (13/9)3A^* \]

⇒ One Singlet-exciton \((^1A^*)\) regenerates from Five Triplet-excitons \((^3A^*)\).


The Confinement of Triplet excitons can enhance TTF in EML
3-1. Triplet-Triplet Fusion

Efficiency Enhancement Layer (EEL) for Blue

Feature of EEL materials
- High electron mobility, suitable electron affinity (for lower voltage)
- Durability against hole and electron (for longer lifetime)
3-1. Triplet-Triplet Fusion

Blue devices with EEL

Device Structure: ITO / HI-2 / HT-2 / BH-1: BD / ET-6 / LiF / Al

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Voltage(V)</th>
<th>CIE(x,y)</th>
<th>L/J(cd/A)</th>
<th>EQE(%)</th>
<th>LT50 (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BD-6</td>
<td>3.8</td>
<td>(0.15, 0.12)</td>
<td>7.1</td>
<td>6.8</td>
<td>8,000</td>
</tr>
<tr>
<td>BD-7*</td>
<td>3.9</td>
<td>(0.14, 0.08)</td>
<td>5.5</td>
<td>7.1</td>
<td>10,000</td>
</tr>
</tbody>
</table>

Inserting EEL

Device Structure: ITO / HI-2 / HT-2 / BH-1: BD / EEL-2 / ET-6 / LiF / Al

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Voltage(V)</th>
<th>CIE(x,y)</th>
<th>L/J(cd/A)</th>
<th>EQE(%)</th>
<th>LT50 (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BD-6</td>
<td>3.8</td>
<td>(0.15, 0.12)</td>
<td>9.0</td>
<td>8.7</td>
<td>11,000</td>
</tr>
<tr>
<td>BD-7*</td>
<td>3.8</td>
<td>(0.14, 0.08)</td>
<td>6.5</td>
<td>8.7</td>
<td>9,000</td>
</tr>
</tbody>
</table>
Blue devices with EEL

Transmit EL of blue devices

BH-1:BD-6 devices

- Increase of delayed fluorescence by inserting EEL
  → Higher efficiency

EL emission originated from triplet excitons increased in the device with EEL

3-1. Triplet-Triplet Fusion
### 3-1. Triplet-Triplet Fusion

**Current Status of Fluorescent Blue**

<table>
<thead>
<tr>
<th>Device Structure</th>
<th>ITO / HI-2 / HT-2 / BH-1: BD-7* / EEL-2 / ET-6 / LiF / Al</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>2011</strong></td>
<td></td>
</tr>
<tr>
<td>Dopant</td>
<td>BD-7*</td>
</tr>
<tr>
<td>CIE(x,y)</td>
<td>(0.14, 0.08)</td>
</tr>
<tr>
<td>L/J(cd/A)</td>
<td>6.5</td>
</tr>
<tr>
<td>EQE(%)</td>
<td>8.7</td>
</tr>
<tr>
<td>LT50 (hrs)</td>
<td>9,000</td>
</tr>
<tr>
<td>LT50 (hrs)</td>
<td>@L_0=500cd/m^2</td>
</tr>
<tr>
<td>@10mA/cm^2</td>
<td></td>
</tr>
<tr>
<td>*Under development</td>
<td></td>
</tr>
<tr>
<td><strong>2012</strong></td>
<td></td>
</tr>
<tr>
<td>Dopant</td>
<td>BD-8*</td>
</tr>
<tr>
<td>CIE(x,y)</td>
<td>(0.14, 0.08)</td>
</tr>
<tr>
<td>L/J(cd/A)</td>
<td>7.1</td>
</tr>
<tr>
<td>EQE(%)</td>
<td>9.3</td>
</tr>
<tr>
<td>LT50 (hrs)</td>
<td>11,000</td>
</tr>
</tbody>
</table>

A newly developed material BD-8 showed high efficiency with good CIEy.
3-2. Capping Layer

**Function of the capping layer**

- **Top emission device**
  - **Merits**
    a. Peak intensity and high color purity by Micro-cavity structure
    b. High aperture ratio
  - **Issues**
    Surface Plasmon coupling by metal electrode causes a Quenching seriously.

To avoid the quenching, the application of a capping layer was demonstrated.
IK focused on the material for capping layer which has the function of suppressing SPP mode.
3-2. Capping Layer

Newly developed capping layer CL-1

Efficiency of the TE device was dramatically improved with using CL-1.
### 3-2. Capping Layer

#### Newly developed capping layer **CL-1**

<table>
<thead>
<tr>
<th>Device Structure</th>
<th>Anode / HI-2 / HT-4 / Blue / EEL / ET-4 / LiF / Mg:Ag / CL-1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Device</strong></td>
<td><strong>Initial Lumin. (cd/m²)</strong></td>
</tr>
<tr>
<td>Flu. Blue</td>
<td>500</td>
</tr>
</tbody>
</table>

The device capped by CL-1 showed much enhanced L/J value of 8.8 and CIEy of 0.06.
### RGB device with common layer

**Device Structure:** Anode / HI-2* / HT / Green / EEL / ET / LiF / Mg:Ag / CL-1 (Common Layers)

<table>
<thead>
<tr>
<th>Device</th>
<th>Initial Lumin. (cd/m²)</th>
<th>Voltage (V)</th>
<th>CIEy</th>
<th>CIEy</th>
<th>L/J (cd/A)</th>
<th>LT95 (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flu. Blue</td>
<td>500</td>
<td>3.8</td>
<td>0.13</td>
<td>0.061</td>
<td>8.8</td>
<td>750</td>
</tr>
<tr>
<td>Phos. Green**</td>
<td>5,000</td>
<td>3.5</td>
<td>0.24</td>
<td>0.72</td>
<td>105</td>
<td>&gt;1,000</td>
</tr>
<tr>
<td>Phos. Red**</td>
<td>2,500</td>
<td>3.5</td>
<td>0.67</td>
<td>0.33</td>
<td>40</td>
<td>&gt;2,000</td>
</tr>
</tbody>
</table>

*Cavity lengths for each color were controlled by thickness of HI.*

**Phosphorescent emitters provided by Universal Display Corp under the joint development program.**

![Common Layers](image)
3-2. Capping Layer

Simulated Power of 4.0” WVGA OLED

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of pixels</td>
<td>800 x 480 x RGB</td>
</tr>
<tr>
<td>Pixel pitch</td>
<td>0.11 mm x 0.11 mm</td>
</tr>
<tr>
<td>Brightness</td>
<td>350 cd/m²</td>
</tr>
<tr>
<td>CIE coordinates (White)</td>
<td>(0.29, 0.30)</td>
</tr>
<tr>
<td>Driving conditions</td>
<td>Duty = 1</td>
</tr>
<tr>
<td></td>
<td>100% on</td>
</tr>
</tbody>
</table>

Assumption:
4.0” WVGA panel (Top Emission)

- 3-color side-by-side configuration, polarizer (transparency 42%) is used.
- Power Consumption:
  Voltage of TFT = 3.5V
- Display gamma:
  \( \gamma = 2.0 \)
- Picture source:
  IEC 62087 Edition 2.0 (2008-10)
  (Average Y level = 23%)

Power consumption (100% Full white) : 750 mW
Power consumption (Picture image ave.) : 167 mW
1. Approach for enhancing OLED performance

2. Materials for highly efficient fluorescent blue

3. Further improvement of device performance
   3-1 Triplet – Triplet Fusion
   3-2 Capping Layer

4. Development of Phosphorescent host

5. Summary
In phosphorescent devices with metal complex dopants, the emission from $T_1$ is observed. Allowing $S_1$ to $T_1$ energy transfer through intersystem crossing, a theoretical internal quantum efficiency is 100%!
4. Development of Phosphorescent Host

Host materials for Green phosphorescent devices

### 2010

<table>
<thead>
<tr>
<th>Host</th>
<th>ETL</th>
<th>Voltage(V)</th>
<th>CIE(x,y)</th>
<th>L/J(cd/A)</th>
<th>EQE(%)</th>
<th>LT50 (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGH-2*</td>
<td>ET-4</td>
<td>3.5</td>
<td>(0.33, 0.63)</td>
<td>63.9</td>
<td>17.2</td>
<td>200,000</td>
</tr>
</tbody>
</table>

*Phosphorescent emitter, PGD kindly provided by Universal Display Corporation under the joint development program.

### 2011

<table>
<thead>
<tr>
<th>Host</th>
<th>ETL</th>
<th>Voltage(V)</th>
<th>CIE(x,y)</th>
<th>L/J(cd/A)</th>
<th>EQE(%)</th>
<th>LT50 (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGH-3*</td>
<td>ET-4</td>
<td>3.3</td>
<td>(0.33, 0.63)</td>
<td>73.9</td>
<td>19.8</td>
<td>230,000</td>
</tr>
</tbody>
</table>

*Under development
4. Development of Phosphorescent Host

Host materials for Green phosphorescent devices

PGH-3 reduces efficiency drop in the high luminance region.

![Graph showing L/J (cd/A) vs. Luminance (cd/m²)]

- PGH-3:PGD
- PGH-2:PGD

Δ9%
Δ15%
1. Approach for enhancing OLED performance

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   3-1 Triplet – Triplet Fusion
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4. Development of Phosphorescent host

5. Summary
1. A newly developed material BD-8 showed a CIE1931 coordinate of (0.14, 0.08) for NTSC compatible blue. It also showed a high current efficiency of 7.1 cd/A with using a new efficiency-enhancement layer which can make triplet-triplet fusion process effectively inside of an emitting layer.

2. We applied the blue materials to top-emission OLEDs. By depositing a new organic capping layer CL-1 on a top cathode, we successfully achieved CIEy of 0.061 and a current efficiency of 8.8 cd/A.

3. We developed a host material PGH-3 for phosphorescent green device that showed a EQE of 19.8% at 1mA/cm$^2$ and long LT50 of 230,000hrs at an initial luminance of 1,000cd/m$^2$. 
Idemitsu Kosan Co., Ltd. would like to gratefully acknowledge the contributions of:

- Universal Display Corp.
- Mitsui Chemicals Inc.