Blue Organic Electrophosphorescence Diodes using Diarylamino-substituted Heterocyclic Compounds as Host Material

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Diarylamino-substituted heterocyclic compounds (DHCs), 2,6-dicarbazolo-1,5-pyridine (PYD2) and 2,4,6-tricarbazolo-1,3,5-pyrimidine (PYM3), possess a high triplet energy level (T₁) of T₁ = 2.93 eV (PYD2) and T₁ = 2.89 eV (PYM3), respectively, in their solid state films. 6wt% Ir(ppy)₃(pic) and 6wt% Flrpic.PYM3-doped films showed high photoluminescence (PL) efficiencies of Φel = 88 ± 2 % and Φel = 80 ± 1 %, indicating near perfect confinement of Flrpic triplet excitons. By increasing the Flrpic concentration in DHC hosts, lower driving voltage and higher external electroluminescence (EL) quantum efficiencies (ηEL) were observed, indicating enhancement of electron injection and transport (electron current) in these emitting layers.

Keywords: Electrophosphorescence, Diarylamino-substituted heterocyclic compound, Flrpic

1. Introduction

With the introduction of heavy metal complexes such as fac tris[2-phenylpyridine] iridium (Ir(ppy)₃) and bis(2-phenylpyridine)Ir(III) acetylacetonate [(ppy)_2Ir(acac)], organic light emitting diodes (OLEDs) have achieved high external electroluminescence (EL) efficiencies (ηEL) approaching the theoretical limitation [1-5]. To obtain high EL efficiency, the triplet energy levels of host layers must be higher than those of the guest molecules so they can induce efficient radiative decay from guest triplet excitons [6].

The first blue electrophosphorescence in blue electrophosphorescence diodes was demonstrated using Iridium(III)bis[(4,6-di-fluorophenyl)pyridinato-N,C]picolinate (Flrpic) as an emitter and 4,4'-N,N'-dicarbazole-biphenyl (CBP) as a host material [6]. However, since CBP can not perfectly confine the Flrpic triplet excitons due to the endothermic energy transfer from Flrpic to CBP triplet levels, novel host materials with a higher triplet energy level are needed [7-12]. Recently, we reported that 2,4,6-tris(diarylamino)-1,3,5-triazine derivatives (TRZ1-TRZ4) are useful host materials in green electrophosphorescence diodes [13]. In this study, to achieve efficient Flrpic triplet emission, we used the diarylamino substituted heterocyclic compounds (DHC), including pyridine and pyrimidine, in their core units as a host layer.

2. Experimental

Absorption and photoluminescence (PL) spectra of DHC deposited films were measured with UV-2550 (SHIMADZU Co.) and FP-6500 (JASCO Co.) spectrometers, respectively. Absolute PL quantum efficiency (Φel) was measured with an
integrating sphere (Is-060, Labsphere Co.) [14]. Transient fluorescence and phosphorescence spectra were measured using a streak camera (Hamamatsu C4334). The highest occupied molecular orbital (HOMO) levels of organic layers were measured with an ultraviolet photoelectron spectroscopy (Riken Keiki, AC-1) and the lowest unoccupied molecular orbital (LUMO) levels were calculated by subtracting the energy gap (E_g) values from their HOMO levels. 50-nm-thick organic films were deposited by high-vacuum (\( \sim 1.0 \times 10^{-3} \) Pa) thermal evaporation onto pre-cleaned silicon and quartz substrates. The OLEDs were fabricated according to the following steps. Indium tin oxide (ITO) coated glass substrates were degreased with solvents and cleaned in a UV-ozone chamber for 20 min. Then, organic layers and metal electrodes were deposited by high-vacuum (\( \sim 1.0 \times 10^{-3} \) Pa) thermal evaporation onto pre-cleaned ITO-coated glass substrates. First, 40-nm-thick 4,4'-bis [N(1-naphthyl)-N-aminobiphenyl (\( \alpha \)-NPD) was deposited as a hole injection layer (HIL). Second, 10-nm-thick N, N'-dicarbazolyl-3,5-benzene (mCP) was deposited as a hole transport layer (HTL). 6, 12, 25wt%-Flrpic-doped PYD2 and PYM3 were deposited as an emitting layer (EML) in Device A and B, respectively. Finally, a 40-nm-thick 4,7-diphenyl-1,10-phenanthroline (BPhen) was deposited as an electron transport layer (ETL). A MgAg layer with an atomic ratio of 10:1 and 10-nm-thick Ag were deposited through a 1-mm-diameter opening in a shadow mask as the cathode and capping layers, respectively. J-V characteristics were measured using a semiconductor parameter analyzer (E5250A, Agilent Technologies), and EL spectra were obtained using a multichannel spectrometer (Ocean Optics, UBS2000).

3. Results and Discussion

Figure 1 shows the chemical structures of the \( \alpha \)-NPD, mCP, PYD2, PYM3, Flrpic, and BPhen used in this study. PYD2 is composed of two electron-donating carbazole substituents with a pyridine core unit, and PYM3 has three carbazole substituents with a pyrimidine core unit. Figure 2 shows phosphorescence spectra of PYD2 and PYM3 films at T = 6K and a 6wt%-Flrpic:PYD2 film at room temperature. These host materials possess high triplet energy levels of T_1 = 2.93 eV (PYD2) and T_1 = 2.89 eV (PYM3), which are substantially higher than the T_1 = 2.64 eV of Flrpic. Figure 3 shows the transient PL decay profiles in the 6wt%-Flrpic doped into the PYD2 and PYM3 hosts. Both deposited films showed single exponential PL decays, including nearly perfect confinement of Flrpic triplet excitons. In a separate experiment, we confirmed high PL efficiencies of

Fig. 1. Chemical structures of hole injection layer [(A):\( \alpha \)-NPD], hole transport layer [(B):mCP], host [(C):PYD2, (D):PYM3], guest [(E):Flrpic] materials and electron transport layer [(F):BPhen] used in this study.

\[ \Phi_{PL} = 88 \pm 2\% \text{ in 6wt\%-Flrpic:PYD2 and } \Phi_{PL} = 80 \pm 1\% \text{ in 6wt\%-Flrpic:PYD3, which are consistent with the transient decay characteristics.} \]

Figure 4 shows the OLED structures, Device A (PYD2 host) and Device B (PYM3 host) with their HOMO and LUMO levels including the work functions of the ITO and MgAg layers. Figure 5 shows the dependence of the J-V characteristics of Devices A and B on the Flrpic concentrations. The J-V curves shifted to a lower driving voltage as the doping concentration increased. Further, the devices
Fig. 3. Transient phosphorescence decay profiles of 6wt% Flrpic doped into PYD2 and PYM3 hosts.

with higher dopant concentration showed a higher $\eta_{EL}$, as shown in Fig. 6. This phenomenon can be understood as the enhancement of electron injection efficiency by increasing the Flrpic concentration. Here, we compare the dependence of PL and EL characteristics on Flrpic concentration (Table 1). The PL quantum efficiencies of X wt% Flrpic:PYD2 films with X = 6wt%, 12wt% and 25wt% showed $\Phi_{PL} = 88 \pm 2\%$, $79 \pm 1\%$, and $66 \pm 2\%$, respectively, and Xwt% Flrpic:PYM3 films with X = 6wt%, 12wt% and 25wt% showed $\Phi_{PL} = 80 \pm 1\%$, $73 \pm 1\%$, and $50 \pm 1\%$, respectively. These results indicate that the doping concentration of 6wt% provides the highest $\Phi_{PL}$, which gradually decreases as Flrpic concentration increases. Although the EL quantum efficiency should be

![Figure 4](image)

**Fig. 4.** OLED structures used in this study. HOMO, LUMO levels of hole injection layer (HIL) and hole transport layer (HTL), emitting layer (EML) and electron transport layer (ETL) with work functions of indium thin oxides (ITO) and metal electrode are indicated.

![Figure 5](image)

**Fig. 5.** Current density and voltage (J-V) characteristics of Devices A and B with different Flrpic concentration.

![Figure 6](image)

**Fig. 6.** External electroluminescence (EL) quantum efficiency and current density ($\eta_{EL}$-J) characteristics of Devices A and B with different Flrpic concentration.
Table 1. Photoluminescence quantum efficiency ($\Phi_{PL}$), maximum electroluminescence quantum efficiency ($\eta_{EL}$) at $J$ = 0.2 mA/cm$^2$, and driving voltage at $J$ = 1mA/cm$^2$ with different Flrpic concentration in Device A and B.

<table>
<thead>
<tr>
<th>Concentration (wt %)</th>
<th>PYD2-host</th>
<th>PYM3-host</th>
<th>Device A</th>
<th>Device B</th>
<th>Device A</th>
<th>Device B</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>88±2</td>
<td>80±1</td>
<td>6.1</td>
<td>6.5</td>
<td>7.0</td>
<td>7.4</td>
</tr>
<tr>
<td>12</td>
<td>79±1</td>
<td>73±1</td>
<td>6.7</td>
<td>7.6</td>
<td>6.9</td>
<td>6.4</td>
</tr>
<tr>
<td>25</td>
<td>66±2</td>
<td>50±1</td>
<td>7.0</td>
<td>8.0</td>
<td>6.3</td>
<td>6.3</td>
</tr>
</tbody>
</table>

proportional to the PL efficiencies, the $\eta_{EL}$ characteristics showed the opposite tendency, as shown in Fig. 6. Here, we discuss the different behaviors of $\Phi_{PL}$ and $\eta_{EL}$ depending on Flrpic concentration. The strong electron accepting characteristics of the fluorine atoms in Flrpic enhance Flrpic's electron transport capabilities. Thus, at higher Flrpic concentrations, electrons are injected into the Flrpic LUMO level, and the carrier recombination site moves toward the mCP side. This shift in recombination site would escape Flrpic exciton quenching by the Bphen layers ($T_1 = 2.47$ eV), resulting in higher EL efficiency, even though the $\Phi_{PL}$ decreases.

A final phenomenon that should be noted is the improvement of in the roll-off characteristics of the Flrpic devices. Figure 7 shows $\eta_{EL}$ dependence on the thickness of the 25wt%-Flrpic:PYD2 layer in Device A. In low current density regions ($0.01$ mA/cm$^2$ $\sim 1$ mA/cm$^2$), all devices showed about the same $\eta_{EL}$. However, in the high current density region ($1$ mA/cm$^2$ $\sim 1000$ mA/cm$^2$), pronounced differences in $\eta_{EL}$ depending on the thickness of the emitting layer was observed. The roll-off characteristics are much better in devices with thicker emitter layers. With a 40nm-thick EML, an $\eta_{EL}$ of $\sim 3\%$ was maintained even at $J=1$A/cm$^2$. This can be explained by the lower exciton density in the thicker EML than in the 5nm-thick EML. The density is lower because the exciton formation region is larger, which reduces triplet-triplet annihilation.

4. Conclusion
We showed that PYD2 and PYM3 have triplet energy levels of $E_T = 2.93$ eV and $E_T = 2.89$ eV, respectively. We also demonstrated that PYD2 and PYM3 host layers confine the triplet excitation of Flrpic ($E_T = 2.64$ eV) well, which leads to high efficiency blue phosphorescence. Controlling the Flrpic concentration was found to improve $\eta_{EL}$ by enhancing electron current into the EML. Also, roll-off characteristics of $\eta_{EL}$ were greatly improved by controlling EML thickness, which suppresses triplet-triplet exciton annihilation at high current density.

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References