Electroluminescence Property of Highly Soluble Ir(III) Complex Utilized by Various Hole Blocking Layers in Polymer Light Emitting Diodes

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Abstract:
The tris(2-phenylpyridine)iridium(III) [Ir(ppy)$_3$] is a well known highly efficient green light-emitting phosphorescent guest dye dopant, but its relatively low solubility has been obstraining it to be used in polymer light-emitting diodes (PLEDs). According to our latest reports the solubility of Ir(ppy)$_3$ complexes with the carbazole ligands, i.e., Ir(Czppy)$_3$, was improved significantly in organic solvents, and was sufficient to be used in soluble process. This highly soluble Ir(Czppy)$_3$ complex showed remarkably higher photoluminescence characteristics than conventional Ir(ppy)$_3$, but it showed similar or comparably better electroluminescence (EL) characteristics, when the PLED was composed by widely used conventional hole blocking layer (HBL) and electron transport layer; 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline and tris(8-hydroxyquinoline) aluminum, respectively. In this report, we applied various HBLs to improve the EL characteristics of soluble Ir(III) complex based phosphorescent PLEDs. The PLEDs utilized by the wide band-gap 3-(4-biphenyl)-4-phenyl-5-tort-butyphenyl-1,2,4-triazole demonstrated highly improved the current and the external quantum efficiency of 17.61 cd/A and 6.42%, respectively.
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The tris(2-phenylpyridine)iridium(III) [Ir(ppy)3] is a well known highly efficient green light-emitting phosphorescent guest dye dopant, but its relatively low solubility has been obstructing it to be used in polymer light-emitting diodes (PLEDs). According to our latest reports the solubility of Ir(ppy)3 complexes with the carbazole ligands, i.e., Ir(Czppy)3, was improved significantly in organic solvents, and was sufficient to be used in soluble process. This highly soluble Ir(Czppy)3 complex showed remarkably higher photoluminescence characteristics than conventional Ir(ppy)3, but it showed similar or comparably better electroluminescence (EL) characteristics, when the PLED was composed by widely used conventional hole blocking layer (HBL) and electron transport layer; 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline and tris(8-hydroxyquinoline)aluminum, respectively. In this report, we applied various HBLs to improve the EL characteristics of soluble Ir(III) complex based phosphorescent PLEDs. The PLEDs utilized by the wide band-gap 3-(4-biphenylyl)-4-phenyl-5-tert-butylphenyl-1,2,4-triazole demonstrated highly improved the current and the external quantum efficiency of 17.61 cd/A and 6.42%, respectively.

Keywords: Highly Soluble Ir(III) Complex, Ir(ppy)3, Ir(Czppy)3, Phosphorescent, Hole Blocking Layer.

1. INTRODUCTION

The organic light-emitting diodes (OLEDs) has been widely researched in these days. Their fascinating theoretical potentials such as, flexibility, low power consumption, wide color gamut, thinner thickness, and environmentally friendliness, make them to be believed as a candidate for the not only the next generation light source, but also the flat panel display applications.1 The phosphorescent organic light-emitting diodes (PHOLEDs) are the most widely studied material due to their high potential to realize 100% internal quantum efficiency.2–5 However, its relatively low solubility has been obstructing it to be used in soluble process based fabrication of OLEDs.6,7 To overcome this issue, some of the highly soluble Ir(III) complexes; fac-tris[2-(4-octyl-phenyl)pyridine] [Ir(Ocppy)3],6 tris(2-(4-tolyl)phenylpyridine)iridium [Ir(mppy)3],7 fac-tris (2-p-xyllyphenyl)pyridine iridium(III) [TEG]8 have been reported. They have shown highly improved solubility, thus suffice them to be used in soluble process.

Most recently, we have reported another highly soluble Ir(III) complexes; Iridium(III) tris(9-(6-Phenyl-pyridin-3-ylmethyl)-9HCarbazole) [Ir(Czppy)3] and Iridium(III) tris (9- (4- (6- Phenyl-pyridin-3-ylmethoxy)-butyl)-9H-Carbazole) [Ir(BCzppy)3].9 They showed remarkably higher photoluminescence but similar or comparably better electroluminescence than Ir(ppy)3 with conventionally used device structure of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) as a hole blocking layer (HBL) and tris(8-hydroxyquinoline)aluminum (Alq3) as an electron transport layer (ETL), respectively.

In this work, various hole blocking materials were applied to the polymer light-emitting diodes (PLEDs) which are composed by the green light emitting highly
soluble Ir(ppy)_3 complex to improve the EL characteristics. 4,7-diphenyl-1,10-phenanthroline (Bphen), 3-(4-biphenylyl)-4-phenyl-5-tert-butylphenyl-1,2,4-triazole (TAZ), and BCP were used as a hole blocking layer (HBL) and Bphen and Alq3 were used as an electron transport layer (ETL).

2. EXPERIMENTAL DETAILS

In this work, five PLEDs with various HBL and ETL were examined. The device structure and energy band diagram are shown in Figure 1 and Table I which is similar to that of the reference. Indium tin oxide (ITO) was used as a transparent anode; poly(ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), as a hole injection and transport layer; poly(N-vinyl-carbazole) (PVK) doped with Ir(III) complexes, as an emissive layer (EML); BCP or TAZ, as a HBL, Alq3 or Bphen, as an ETL; lithium-fluoride (LiF), as a electron injection layer; aluminum as a cathode, respectively. The doping ratio of Ir(ppy)_3 and Ir(Czppy)_3 are 6 wt% and 10 wt%, respectively.

Devices were fabricated on the ITO coated glass which is purchased from the Samsung Corning Precision Glass. The BAYTRON-P AI4083 was used to form the PEDOT:PSS layer. Before using the ITO coated glass, it was finely cleaned by ultrasonication with organic solvents and deionized water. The active area of the device was 5 × 5 mm². The PEDOT:PSS layer was spin-coated onto the ITO-coated glass under air atmosphere. And the EML was spin-coated using the solution in monochlorobenzene. The organic and cathode layers were subsequently deposited by thermal evaporator at a base pressure of about 10⁻⁶ torr. The deposition rate of all organic materials and metal were ~1 Å/s and ~6 Å/s, respectively.

The electroluminescence (EL) was measured using the PR-670 SpectraScan Spectroradiometer (Photo Research, Inc.) and the Model 237 High-Voltage Source-Measure Unit (Keithley Instruments, Inc.). The devices were measured in dark box and air atmosphere.

3. RESULTS AND DISCUSSION

Figures 2 to 4 show the EL characteristics of fabricated PLEDs, and Table II shows the summarized device performances. Figure 2 shows the current density and the luminance as a function of the applied voltage. When the devices have the same HBL and ETL, the device 2 using the Ir(Czppy)_3 doped EML showed relatively higher peak luminance than device 1 using the Ir(ppy)_3 doped control device. The device 3 showed higher driving voltage than device 2 due to the higher highest occupied molecular orbital (HOMO) energy and lower electron mobility of TAZ (1.0E⁻⁷ cm²/Vs) than BCP (1.1E⁻³ cm²/Vs). On the other hand both of the device 2 and 3 showed relatively higher driving voltages than the device 1, thus the Ir(III) complexes doped EML seems to have the lower carrier mobility, which is not solved in this work. The increased driving voltage was reduced by applying Bphen (2.4E⁻⁴ cm²/Vs) for the ETL in device 4 and 5. The higher electron mobility of Bphen compared to Alq3 (4.7E⁻⁶ cm²/Vs) resulted the lower driving voltage. The device 3 using TAZ as a HBL showed the highest luminance, while the device 4 and 5 using Bphen HBL showed relatively lower luminance. This tendency is also shown in the EL efficiencies as in Figure 3.

Figures 3 shows the current and the power efficiencies (PE) as a function of the luminance. The device 2 and 3...
showed higher efficiencies than device 1. The device 3 showed the highest EL efficiencies at overall luminance.

Compared to the device 2, the device 4 showed remarkably lower EL efficiency. This lower EL efficiency could be explained by the recombination zone shifted to the HTL/EML by the higher electron mobility of Bphen. The recombination zone shifting improved the energy transfer between the EML and the HTL, and followed by the non-radiative quenching occurred by the HTL. The overall trend of EL efficiencies (device 2, 3 > device 1 > device 4, 5) could also be explained by the triplet quenching at the EML/HBL interface depending on the triplet energy level of HBLs; the triplet energy levels are, BCP (2.6 eV),\(^1\), and Bphen (2.5 eV),\(^1\), respectively, while that of TAZ has not yet been reported precisely. When the triplet energy levels are lower, the more triplet quenching could be realized at the EML/HBL interface.

Figure 4 shows the external quantum efficiency (EQE) as a function of the current density. The EQE shows the same tendency like other EL efficiencies as in Figure 3. The inset shows the magnified view of EL spectra. As we have reported in our previous work, the peak intensity was shown at 512 nm and 526 nm for Ir(ppy)$_3$ and Ir(Czppy)$_3$, respectively.\(^9\) The EL spectra showed the clear broadening at the right tail as the HOMO energy of the HBL reduced; from 6.6 eV of TAZ to 6.5 eV of BCP and 6.3 eV of Bphen. These spectral broadening is the un-intentional emission from the direct emission of the ETL or the exciplex emission of the HBL/ETL. The reduced HOMO energy of the HBL results the smaller energy gap between the EML and the HBL and finally, the probability of hole carrier injection from the EML to the HBL is increased, causing representation of the un-intentional emission.

The PLED with TAZ as a HBL showed the highest EQE and PE, while its driving voltage was higher than the others. The highest HOMO energy level of TAZ resulted highly improved EL efficiencies of the PLED by efficiently blocking the majority carrier, the hole.\(^1\) Also TAZ as a HBL efficiently confined the excitons in the EML from the triplet–triplet energy transfer from the EML to the HBL by its highest triplet energy in this device structure whose recombination zone mainly placed at the EML/HBL interface.

### 4. CONCLUSION

The PLED utilized by the Ir(Czppy)$_3$ doped PVK as an EML and TAZ as a HBL showed the highest EL characteristics; peak luminance of 20,860 cd/m$^2$, current efficiency of 17.61 cd/A, and the peak EQE of 6.34%. The EL characteristics of the fabricated PLEDs showed remarkable dependence on the kind of HBL and ETL materials. The EL characteristics were improved following the increase

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**Table II. Summary: performances of PLEDs.**

<table>
<thead>
<tr>
<th>Device configuration</th>
<th>Luminance, cd/m$^2$ (at mA/cm$^2$)</th>
<th>EQE, % (at mA/cm$^2$)</th>
<th>EQE, %</th>
<th>PE, lm/W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Device 1</td>
<td>12,630 (202)</td>
<td>3.71 (2.68)</td>
<td>3.63</td>
<td>3.93</td>
</tr>
<tr>
<td>Device 2</td>
<td>16,670 (242)</td>
<td>5.33 (5.15)</td>
<td>4.48</td>
<td>4.72</td>
</tr>
<tr>
<td>Device 3</td>
<td>20,860 (253)</td>
<td>6.34 (4.57)</td>
<td>5.65</td>
<td>5.60</td>
</tr>
<tr>
<td>Device 4</td>
<td>8,013 (223)</td>
<td>1.55 (77.64)</td>
<td>0.70</td>
<td>0.73</td>
</tr>
<tr>
<td>Device 5</td>
<td>7,974 (186)</td>
<td>2.19 (36.58)</td>
<td>1.41</td>
<td>1.39</td>
</tr>
</tbody>
</table>

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**Fig. 3.** The current efficiency and power efficiency curve as a function of luminance.

**Fig. 4.** The external quantum efficiency as a function of current density. The inset is enlarged EL spectra from 475 nm to 625 nm.
of hole-blocking barrier and triplet energy of the HBL. In this work, TAZ was the most suitable HBL material for the highly soluble Ir(Czppy)$_3$ based PLED with widely used simple structure. While employing TAZ as the HBL, improved device performances would be expected by applying additional well known techniques as follows; $n$-type and $p$-type carrier doping, employing the novel material with high mobility, and the ITO surface treatment using UV-ozone or O$_2$-plasma.

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References and Notes


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