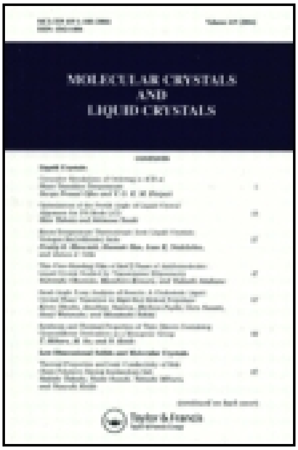

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Optimization of White Organic Electroluminescent Devices with Sensitized Heteroleptic Ir Complex

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In this study, the heteroleptic tris-cyclometalated iridium complex, bis(2-phenylquinoline)(2-phenylpyridine)iridium(III) [Ir(pq)$_2$(ppy)], used as red emitting dopant for white organic light-emitting diodes (WOLEDs) had higher maximum luminescence efficiency (13.80 cd/A) than that of the homoleptic tris-cyclometalated iridium complex, tris(2-phenylquinoline)iridium(III) [Ir(pq)$_3$], due to the presence of a sensitizing ppy ligand. Thus, WOLEDs combining the Ir(pq)$_2$(ppy) as a red emissive phosphorescent material and 4,4′-bis(9-ethyl-3-carbazovinylene)-1,1′-biphenyl (BCzVBi) as a blue emissive fluorescent material have been studied. The WOLEDs were optimized by adjusting the device structure, the optimized WOLED (device 10) had a maximum luminescence efficiency of 16.90 cd/A and CIE coordinates of (0.407, 0.337) at the applied voltage of 12 V.

Keywords: Heteroleptic tris-cyclometalated iridium complex; sensitizing ppy ligand; WOLEDs

1. INTRODUCTION

Recently, white organic light-emitting diodes (WOLEDs) have considerable research and interest commercially due to their demonstrated applications in the fabrication of full color displays with color filters [1]. Organic thin-film transistors (OTFTs) also have been extensively studied due to their application in organic light-emitting diodes (OLEDs) [2]. OLEDs offer the advantage of ease of fabrication, low operating voltages, and the possibility of a wide selection of emission colors through the molecular design of organic materials. OLEDs

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can be fabricated by vapor deposition of emissive dyes in a single or multilayer structure [3–7]. White-light emission requires the mixing of two compleimentary colors or three primary colors [8–10]. Strategies to fabricate WOLEDs include the manufacture of multilayer OLEDs by consecutive evaporation, and the manufacture of a single layer polymer blend device, where all the emitting components are mixed in one layer [11–14]. For single layer polymer blend devices, the Y. Kawamura group reported highly efficient polymer OLEDs blending the $Ir(ppy)_3$ as "sensitizer" in host and dopant materials, where the $Ir(ppy)_3$ plays the role of an intermediary between the polymer host and the emitting dopant [15]. Alternatively, we used the high efficient heteroleptic iridium complex, bis(2-phenylquinoline)(2-phenylpyridine)iridium(III) [$Ir(pq)_2(ppy)$], with ppy ligands as "sensitizers". In this paper, we proved that the efficient energy transfer from the host to the emitting ligand was based on the ppy ligand. Moreover, we demonstrated high efficient WOLEDs that emitted two colors from two doped emissive layers using an efficient red emitting phosphorescent heteroleptic iridium complex, $Ir(pq)_2(ppy)$, and a fluorescent blue emitting material, BCzVBi.

2. EXPERIMENTS

Ten devices were fabricated in this paper. Among these, two were monochromatic OLEDs to prove the highly efficient heteroleptic iridium complex, and eight were WOLEDs to optimize the device structure with an efficient heteroleptic iridium complex by adjusting the thickness of the spacer, the emitting layer and the doping concentration. The device structures for monochromatic OLEDs and WOLEDs are shown in Figures 1(a) and (b), respectively. The ten OLEDs were fabricated by high vacuum (5×10^{-7} torr.) thermal deposition of organic materials onto the surface of an 80 nm thick indium tin oxide (ITO) coated glass substrate with resistivity of $30\,\Omega/\square$. The ITO glass was chemically cleaned using acetone, methanol, distillated water and isopropyl alcohol [16]. The organic materials in the monochromatic OLEDs were deposited in the following sequence: 50 nm of the 4,4′-bis[*N*-(naphthyl)-*N*-phenylamino]biphenyl (NPB) and 30 nm of the 8% iridium complexes doped in 4,4,*N*,*N*′-dicarbazolebiphenyl (CBP) were applied as a hole transporting layer (HTL) and a red emitting layer (REML), respectively, where the iridium complexes are homoleptic $Ir(pq)_3$ and heteroleptic $Ir(pq)_2(ppy)$. Then, 30 nm of the 4,7-diphenyl-1,10-phenanthroline (BPhen) and 2 nm of the lithium quinolate (Liq) were deposited as

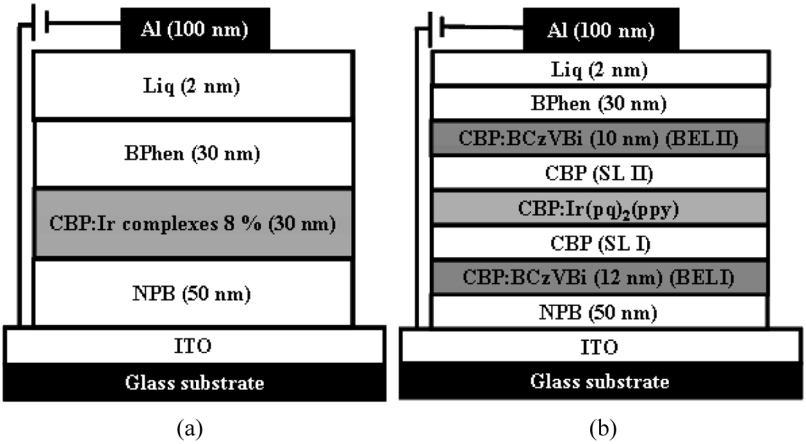

FIGURE 1 Device structures for (a) monochromatic OLEDs and (b) WOLEDs.

a electron transporting layer (ETL) and electron injection layer (EIL), respectively. Conversely, the organic materials in WOLEDs were deposited in the following sequence: 50 nm of the NPB and 12 nm of the 4,4′-bis(9-ethyl-3-carbazovinylene)-1,1′-biphenyl (BCzVBi) doped in CBP were applied as a HTL and blue emitting layer I (BEML I), respectively, followed by a spacer layer I (SL I) [17]. Then, $Ir(pq)_2(ppy)$ doped in CBP as a REML, followed by a SL II and BEML II. Next, 30 nm of the BPhen and 2 nm of the Liq were deposited as a ETL and EIL, respectively. The typical organic deposition rate was 0.1 nm/s. Finally, Al was evaporated with growth rates of 0.1 nm/s until the thickness reached 10 nm to ensure good interface characteristics between the organic materials and metal, and then deposited with the growth rates of 1 nm/s until the thickness reached 100 nm. Eight of the devices were fabricated in this study to optimize the CIE coordinates and efficiency of the WOLEDs. The active area of the OLEDs was 0.09 cm^2. After fabrication, the current density–voltage (J-V) characteristics of the OLED were measured with a source measure unit (Keithley 236) and the luminescence and CIE chromaticity coordinates of the fabricated devices were measured using a chromameter (MINOLTA CS-100A). In addition, the electroluminescence (EL) spectrum was measured with a CCD type of spectra meter, the IVL 2000 from JBS International Corporation. All measurements were performed in ambient conditions under DC voltage bias.

3. RESULTS AND DISCUSSION

We prepared the heteroleptic and homoleptic tris-cyclometalated iridium complexes, Ir(pq)$_2$(ppy) and Ir(pq)$_3$, as red emitting dopants for WOLEDs. The molecular structures of the two iridium complexes are shown in Figure 2. In this paper, we firstly fabricated monochromatic red emitting devices 1 and 2 with homoleptic Ir(pq)$_3$ and heteroleptic Ir(pq)$_2$(ppy), respectively, to select the optimal iridium complex for WOLEDs, as shown in Figure 1(a). Devices 1 and 2 showed a maximum luminescence efficiency of 11.50 cd/A and 13.80 cd/A, respectively. The luminescence efficiency of device 2 was higher than that of device 1, while the electroluminescence (EL) spectra of devices 1 and 2 shown nearly the same emission characteristics due to the pq ligand, as shown in the inset of Figure 2. This means that the emission of Ir(pq)$_2$(ppy) only occurred on the pq ligand and thus, that the ppy ligand plays the role of cascade for the energy transfer from the host (CBP) to the pq ligand of the dopant [Ir(pq)$_2$(ppy)] in heteroleptic

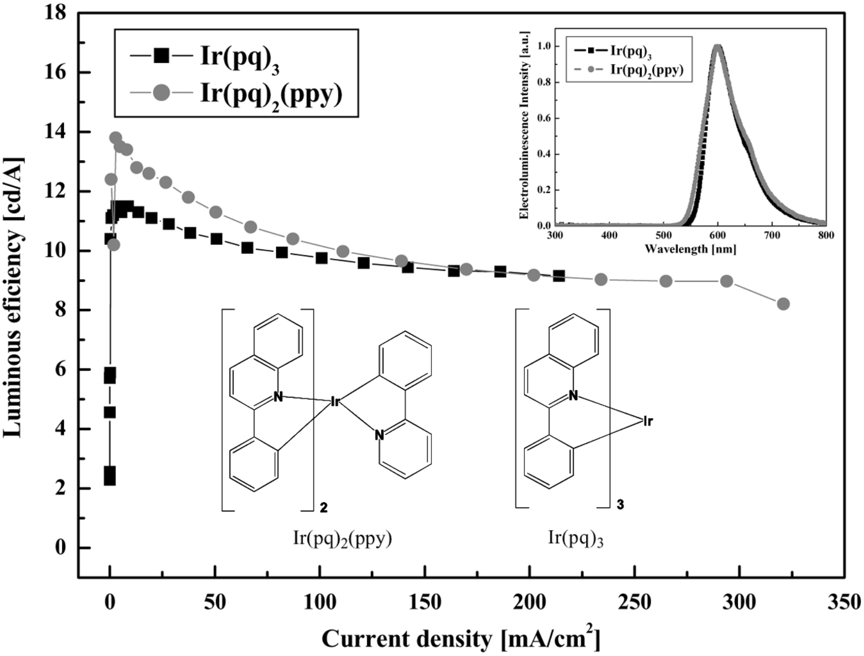

FIGURE 2 Luminous efficiency of monochromatic devices with Ir(pq)$_3$ (device 1) and Ir(pq)$_2$(ppy) (device 2). Inset: EL spectra of devices 1 and 2 at applied voltage of 12 V and molecular structures of Ir(pq)$_3$ and Ir(pq)$_2$(ppy).

iridium complex, $Ir(pq)_2(ppy)$. The role of the cascade was reported as a "sensitizer" by Y. Kawamura etc, where $Ir(ppy)_3$ as a sensitizer intermediates between the polymer host and the emitting dopant [15]. Moreover, it was reported in our prior paper that OLEDs with heteroleptic iridium complexes have higher efficiencies than OLEDs with homoleptic iridium complexes [18]. The ppy ligand as "sensitizer" to enable efficient energy transfer from the host (CBP) to the emission ligand (pq) was successfully employed to produce highly efficient OLEDs. Therefore, the heteroleptic iridium complex, $Ir(pq)_2(ppy)$, is suited to serve as a red dopant for highly efficient WOLEDs.

In order to optimize the white emitting color and efficiency of device 2 with heteroleptic $Ir(pq)_2(ppy)$, the eight WOLEDs (devices 3∼10) were fabricated with various structures as shown in Figure 1(b) and Table 1. The optimization process of the WOLED structure was accomplished in four steps. First, in order to improve the efficiency of the devices, the doping concentration of red dopant, $Ir(pq)_2(ppy)$, was optimized. Second, the thickness of the CBP spacers was also adjusted for higher efficiency. The third and fourth steps involved optimizing the doping concentration of blue dopant, BCzVBi, and the thickness of the REML to ensure the color purity of the WOLED.

The first step began with analysis of the electrical and optical characteristics of devices 3∼6 for which the doping concentration of $Ir(pq)_2(ppy)$ ranged from 4% to 16%. The maximum luminescence and power efficiency were increased up to 16.20 cd/A and 9.51 lm/W, respectively, in the 12% $Ir(pq)_2(ppy)$ doped device 5 as shown in Figure 3. This is because the increased concentration of the dopant increases the number of excitons. However, when the $Ir(pq)_2(ppy)$ with the 16% concentration was doped in CBP, the efficiency decreased slightly or remained unchanged, because of triplet-triplet annihilation

TABLE 1 WOLED Structures with Various Doping Concentration and Thickness

Device	Bule emission layer [BEL I]	Spacer layer [SL II]	Red emission layer	Spacer layer [SL II]
3	5% (12 nm)	4 nm	4% (8 nm)	6 nm
4	5% (12 nm)	4 nm	8% (8 nm)	6 nm
5	5% (12 nm)	4 nm	12% (8 nm)	6 nm
6	5% (12 nm)	4 nm	16% (8 nm)	6 nm
7	5% (12 nm)	7 nm	12% (8 nm)	7 nm
8	8% (12 nm)	7 nm	12% (8 nm)	7 nm
9	8% (12 nm)	7 nm	12% (4 nm)	7 nm
10	8% (12 nm)	7 nm	12% (2 nm)	7 nm

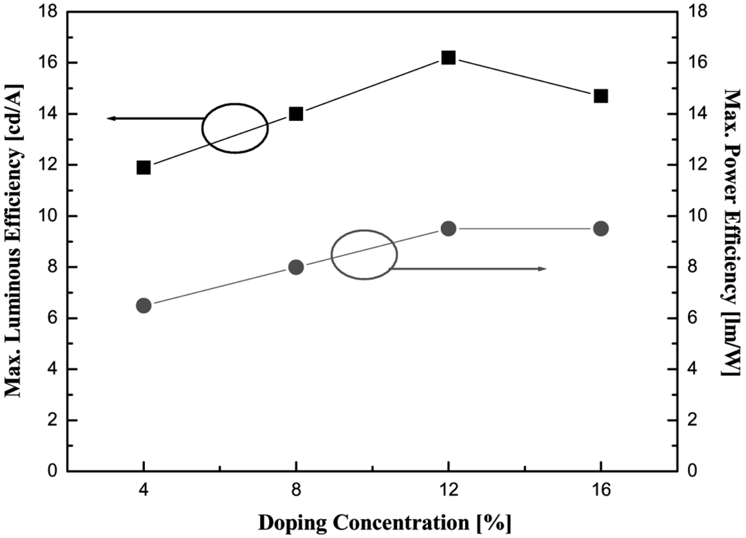

FIGURE 3 Maximum luminous efficiency and power efficiency of devices 3~6 as doping concentration of red dopant, Ir(pq)$_2$(ppy).

due to too high a doping concentration. The CIE coordinates of devices 3~6 were gradually reddish as the doping concentration of Ir(pq)$_2$(ppy) increased from 4% to 16%, and this is shown in Table 2. As a results, we confirmed that the improved efficiency of device 5 was due to the heteroleptic Ir complex, Ir(pq)$_2$(ppy).

For the other steps, we fabricated devices 7~10 with an optimized Ir(pq)$_2$(ppy) doping concentration of 12%, as shown in Table 1. The luminescence efficiency and luminance of devices 7~10 are shown in Figure 4 and the inset figure in Figure 4, respectively. In the second

TABLE 2 Electrical and Optical Characteristics of the Device 1~8

Device	Luminance at 14 V [mA/cm^2]	Max. luminous efficiency [cd/A]	Max. power efficiency [lm/W]	CIE coordinates at 12 V (x, y)
3	19500	11.90	6.49	(0.436, 0.338)
4	26900	14.00	7.99	(0.486, 0.371)
5	22800	16.20	9.51	(0.496, 0.372)
6	18800	14.70.	9.51	(0.503, 0.360)
7	27000	18.50	10.90	(0.519, 0.377)
8	25400	20.80	13.10	(0.503, 0.370)
9	25400	18.90	11.90	(0.468, 0.366)
10	23100	16.90	5.28	(0.407, 0.337)

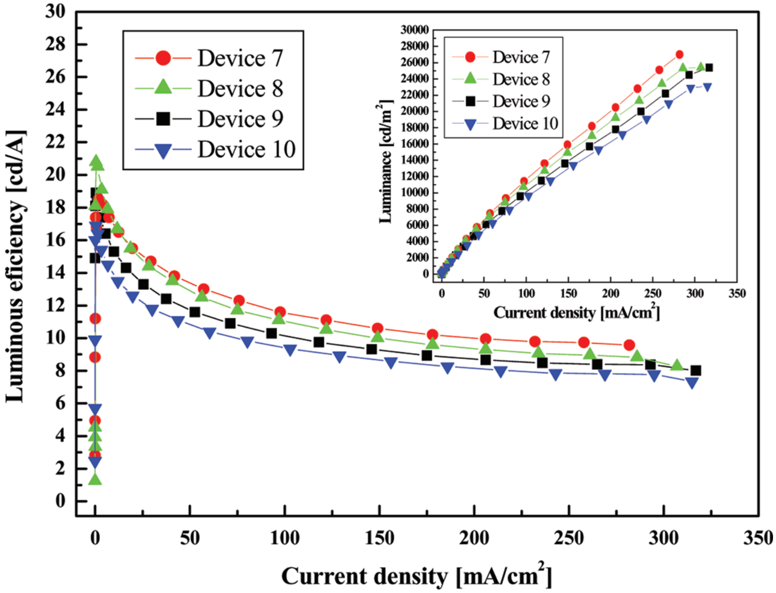

FIGURE 4 Luminous efficiency (inset: luminance) of devices 7∼10 by changing the spacer thickness, doping concentration of blue dopant and thickness of red emissive layer.

step, device 7 was fabricated to improve its efficiency. Device 7, with increased spacers I and II, with a thickness of 7 nm, shows a higher maximum luminescence and a power efficiency of 18.50 cd/A and 10.90 lm/w, respectively, both higher than that of device 5. This is because the diffusion of singlet excitons from the fluorescent dopant to the phosphor dopant is negligible due to their intrinsically short diffusion lengths (∼4 nm) [17]. The 7 nm thick spacer layers I and II, located between the BCzVBi doped layer and the Ir(pq)$_2$(ppy) doped layer, minimized the exchange energy loss by blocking the singlet excitons. However, first and second method improved only the efficiency characteristics of the devices; the emissions retained the same level of reddish color. Thus, the method to obtain a pure white emission color was focused on the third and last steps.

On the third step, device 8, with its BCzVBi doping concentration increased to 8%, was fabricated to increase the blue emission intensity of the devices. Device 8 had a higher maximum luminescence and power efficiency of 20.80 cd/A and 13.10 lm/W, respectively, than that of the 5% BCzVBi doped device 7, due to the increased number of excitons on the blue emissive layer. However, the luminescence efficiency of device 8 was less than that of device 7 over all current density regions except for the maximum luminescence efficiency observed at low current density, as shown in Figure 4. Moreover, the emission color of device 7 was still reddish, with coordinates of (0.503, 0.370), at the applied voltage of 12 V. This is because the singlet energy transfer from the host (CBP) to the dopant (BCzVBi) is caused by Förster energy transfer. Förster energy transfer occurs at the long distance (~10 nm) between the host and dopant molecules, thus, a high concentration of fluorescent dopant leads to lower efficiency [19].

Lastly, devices 9 and 10 were fabricated to investigate the effect of the thickness of the REML compared with device 8. Although the efficiencies of devices 9 and 10 show lower maximum luminous and power efficiency than that of device 8 due to the decreased exciton formation site on the REML, the color purity of devices 9 and 10 was improved, with CIE coordinates of (0.468, 0.366) and (0.407, 0.337) at applied voltage of 12 V, respectively. These changes of color purity can be also confirmed in EL spectra, as shown in Figure 5. Therefore, we could obtained the optimal WOLED with maximum luminescence efficiency and CIE coordinates of 16.90 cd/A and (0.407, 0.337) for device 10. The electrical characteristics and CIE coordinates of all WOLEDs (device 3~10) used in this paper are summarized in Table 2.

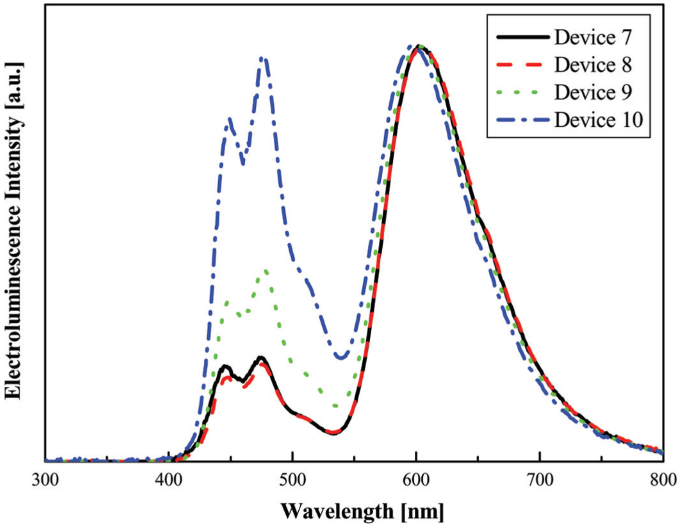

FIGURE 5 EL spectra of devices 7~10 at applied voltage of 12 V.

4. CONCLUSIONS

In conclusion, the heteroleptic iridium complex, Ir(pq)$_2$(ppy), used as red emitting dopant for white organic light-emitting diodes (WOLEDs) had higher maximum luminescence efficiency (13.80 cd/A) than that of the homoleptic tris-cyclometalated iridium complex, Ir(pq)$_3$, due to efficient cascade exciton transfer. The "sensitizer", ppy ligand, which allowed for efficient energy transfer from the host (CBP) to the emission ligand (pq), was successfully employed for highly efficient OLEDs and the Ir(pq)$_2$(ppy) used in WOLEDs. The WOLEDs were optimized by adjusting the concentration of the dopants, spacer thickness and emission layer thickness. The optimized WOLED (device 10) had a maximum luminescence efficiency of 16.90 cd/A and CIE coordinates of (0.407, 0.337) at applied voltage of 12 V.

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