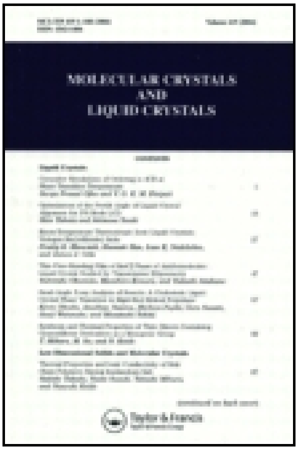

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Red Electrophosphorescent Devices Based on Heteroleptic Tris-cyclometalated Iridium Complexes with Fluorinated 2,4-diphenylquinoline Ligands

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New heteroleptic tris-cyclometalated iridium complex having two different (C^N) ligands, [Ir(dpq)$_2$(dpq-3F)] (dpq = 2,4-diphenylquinoline, dpq-3F = 2-(3′-fluorophenyl)-4-phenylquinoline), have been synthesized and characterized for an efficient red organic light-emitting diodes (OLEDs). The iridium phosphors emit bright red light with its maximum at 608 nm. The heteroleptic tris-cyclometalated iridium complex [Ir(dpq)$_2$(dpq-3F)] is shown to be a more efficient electrophosphor than the homoleptic tris-cyclometalated iridium complex [Ir(dpq-3F)$_3$] to avoid the T-T annihilation by decreasing the number of the luminescent ligand. A maximum luminous efficiency was 10.9 cd/A at a current density of $J = 0.6\,mA/cm^2$. At a higher current density of $J = 100\,mA/cm^2$, the luminous efficiency maintained 54% of its maximum value as 5.9 cd/A.

Keywords: heteroleptic ligands; organic light-emitting diodes; red phosphorescent material; triplet-triplet annihilation

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1. INTRODUCTION

Recently, phosphorescent materials and devices have been extensively studied to achieve a high efficiency in organic light-emitting diodes (OLEDs) since Forrest and Thompson *et al.* reported OLEDs with phosphorescent heavy metal complexes [1–3]. The heavy metal, such as iridium or platinum, in the complexes is known to induce the intersystem crossing by strong spin-orbit coupling, leading to mixing of the singlet and triplet excited states [4–5]. Radiative relaxation of spin-forbidden nature from the triplet excited state is then allowed, resulting in high phosphorescence efficiencies. Thus, iridium complexes and platinum complexes have extensively been introduced to the emitting layer as dopants. Unfortunately, most of phosphors have a long lifetime, which leads to dominant triplet-triplet (T-T) annihilation at increasing currents. The occurrence of T-T annihilation decreases the performance of a phosphorescent material, particularly its maximum brightness and luminous efficiency at high currents [6–7]. Lamansky *et al.* [8] reported that a series of bis-cyclometalated iridium complexes with β-diketonato ancillary ligands such as $Ir(ppy)_2(acac)$ gave a wide range of emission colors with high phosphorescence yields comparable to those of tris-cyclometalated homoleptic iridium complexes. However, Tsuboyama *et al.* [9] show that the complexes with the acetylacetonate ligand tend to thermally decompose at relatively low temperature. These results indicate that iridium complexes having three (C^N) ligands are thermally more stable than the acetylacetonate complexes. Thus, in order to improve the luminous efficiency by avoiding T-T annihilation, the iridium complexes [$Ir(dpq)_2(dpq\text{-}3F)$] having two different species of (C^N) ligands has been proposed [10–12]. The iridium complex has been designed to minimize the number of luminescent ligand to cause luminescence from a particular ligand. More specifically, when the iridium complex [$Ir(dpq)_2(dpq\text{-}3F)$] is placed in excited state, the excited energy is located in dpq-3F ligand, thus allowing a monochromatic luminescent color and increased color purity. Further, it is expected that the use of one luminescent ligand decreases the probability of occurrence of energy transition between spatially adjacent molecules of the metal complex, leading to a decrease in quenching or energy deactivation.

In this article, we report efficient red phosphorescent OLEDs containing heteroleptic tris-cyclometalated iridium complexes [$Ir(dpq)_2(dpq\text{-}3F)$] which show improved luminescence and current tolerant efficiency characteristics by introducing different species of plural ligands, dpq and dpq-3F.

2. EXPERIMENTAL

Figure 1 shows the chemical structures of synthesized red iridium complexes: Ir(dpq)$_2$(dpq-3F) and Ir(dpq-3F)$_3$, where dpq and dpq-3F represent 2,4-diphenylquinoline and 2-(3′-fluorophenyl)-4-phenylquinoline, respectively. The device configuration used in this study is shown below. Other organic materials used as carrier transport, carrier injection and host materials were supplied by Gracel Display Incorporation in Korea.

To investigate UV/vis absorption and photoluminescence of the phosphors, the phosphor solution in CHCl$_3$ was prepared, and the characteristics were investigated with H.P 8452A and P.S LS50B.

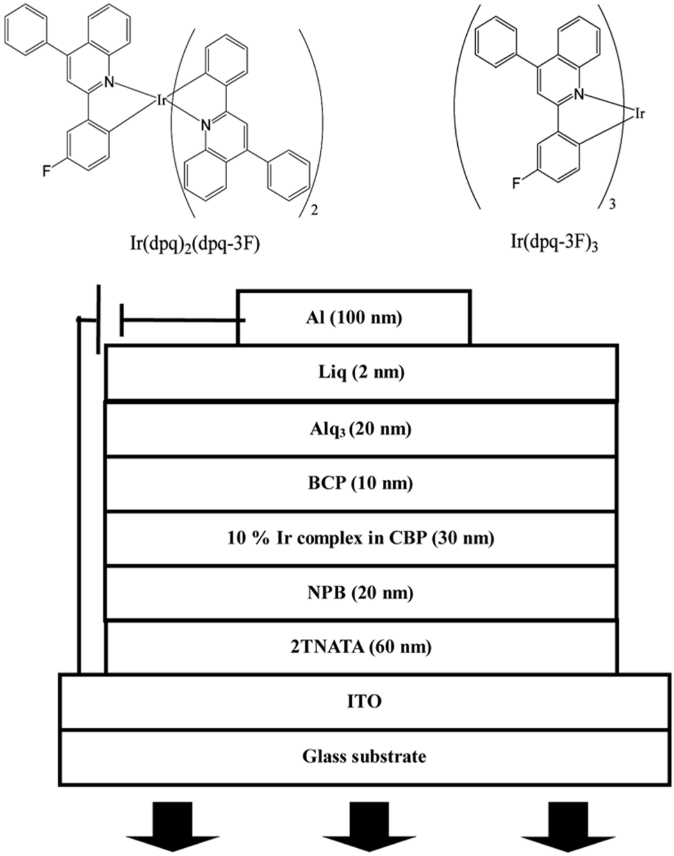

FIGURE 1 Molecular structures of iridium complexes and the device configuration.

OLEDs were fabricated by high vacuum (5×10^{-7} Torr) thermal deposition of organic materials onto the surface of an indium tin oxide (ITO, 30 $\Omega/\square$, 80 nm) coated glass substrate. The ITO glass was chemically cleaned using acetone, methanol, distillated water and isopropyl alcohol. The organic materials were deposited in the following sequence: 60 nm of 4,4′,4″-tris[2-naphthylphenylamino]triphenylamine (2-TNATA) and 20 nm of 4,4′-bis[*N*-(naphthyl)-*N*-phenyl-amino]-biphenyl (NPB) were applied as a hole injection layer (HIL) and a hole transporting layer (HTL), respectively, followed by a 30 nm thick emissive layer (EML) of iridium complexes doped in 4,4,*N*,*N*′-dicarbazolebiphenyl (CBP). The phosphors' doping rate was 10%. 10 nm thick bathocuproine (BCP), 20 nm thick tris-(8-hydroxyquinoline) aluminum (Alq_3) and 2 nm thick Lithium quinolate (Liq) were deposited as an exciton blocking layer, as an electron transporting layer (ETL) and as an electron injection layer (EIL), respectively. The typical organic deposition rate was 0.2 nm/sec. Finally, 100 nm of Al was deposited as a cathode. The active area of the OLEDs was 0.09 cm^2. After the fabrication, the current density–voltage (J–V) characteristics of the OLEDs were measured with a source measure unit (Kiethley 236) and the luminance and CIE chromaticity coordinates of the fabricated devices were measured using a chromameter (MINOLTA CS-100A). All measurements were performed in ambient conditions under DC voltage bias.

3. RESULTS AND DISCUSSION

Figure 2 depicts the photoluminescence (PL) spectra of homoleptic and heteroleptic iridium complexes in CH_2Cl_2. The PL spectra of Ir(dpq-3F)$_3$ and Ir(dpq)$_2$(dpq-3F) showed the maximum emission at 604 nm and 603 nm, respectively, while Ir(dpq)$_3$ showed the maximum emission at 591 nm. The overall profile of PL spectra and the peak position of the heteroleptic Ir(dpq)$_2$(dpq-3F) are very similar to those of Ir(dpq-3F)$_3$. It provides the evidence that the luminescence of the heteroleptic Ir(dpq)$_2$(dpq-3F) occurs mainly at the dpq-3F ligand. This is because the highest occupied molecular orbital (HOMO) energy level of Ir(dpq)$_2$(dpq-3F) is lower than that of Ir(dpq-3F)$_3$ due to an electron-withdrawing characteristics of F-substituent. Thus the strong metal-to ligand charge transfer (MLCT) transition is allowed by the mixing between the π character of the ligand and the 5d character of the centric heavy metal ion [12].

The electroluminescence (EL) characteristics of devices with iridium complexes at the applied voltage of 12 V are shown in Figure 3. We note that there is no voltage dependence of the EL spectra 6 V to

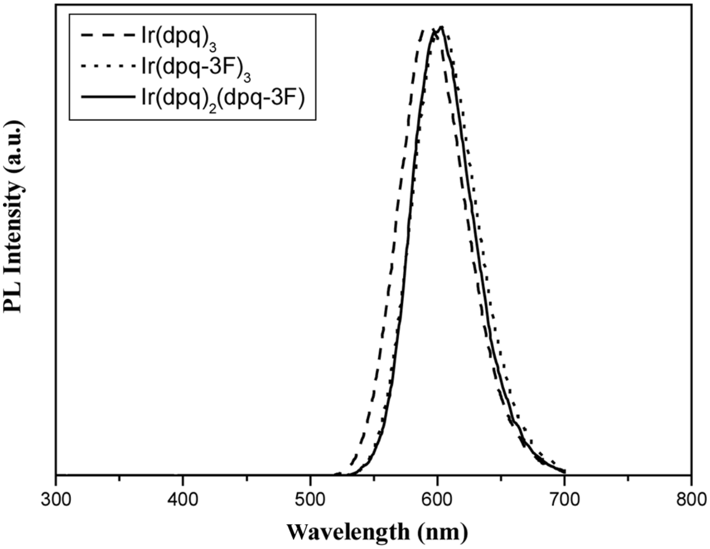

FIGURE 2 PL spectra of iridium complexes.

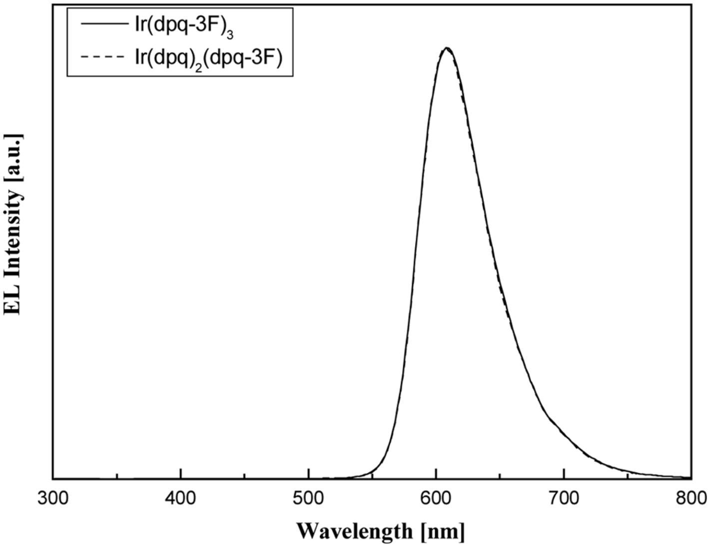

FIGURE 3 EL spectra of iridium complexes at an applied voltage of 12 V.

TABLE 1 Electrophosphorescent Data for Iridium Complexes

Complex	EL [nm]	Max. LE [cd/A]	Max. PE [lm/W]	CIE (x, y)
$Ir(dpq\text{-}3F)_3$	608	8.17	7.33	(0.634, 0.365)
$Ir(dpq)_2(dpq\text{-}3F)$	608	10.9	8.40	(0.633, 0.365)

14 V, and the maximum EL peak is independent of the guest concentration. The devices exhibit a strong red EL peak at around 608 nm with low turn-on voltages for light emission at 1 cd/m^2 of 3.0–3.5 V and Commission International de L'Eclairage (CIE) color coordinates of (0.633, 0.365). Key performance characteristics of the devices are listed in Table 1. The EL spectrum resembles its corresponding PL spectrum, which indicates that both EL and PL arise from the same excited states or the same type of exciton. It also provides the evidence that the luminescence of the heteroleptic $Ir(dpq)_2(dpq\text{-}3F)$ occurs mainly at the dpq-3F ligand.

The devices with tris-cyclometalated iridium complexes of heteroleptic ligands showed improved performance compared to those with homoleptic tris-cyclometalated iridium complexes. As shown in Figure 4, the devices with $Ir(dpq)_2(dpq\text{-}3F)$ showed the higher luminance characteristics as a function of the current density than the devices with $Ir(dpq\text{-}3F)_3$. At the applied voltage of 12 V, the luminance

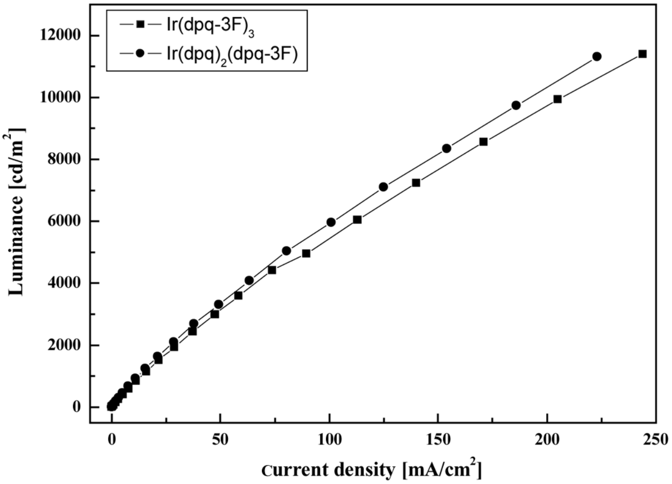

FIGURE 4 Luminance characteristics of iridium complexes at various current densities.

maxima of the devices are 11400 cd/m^2 (J = 244 mA/cm^2) for Ir(dpq-3F)$_3$ and 11300 cd/m^2 (J = 223 mA/cm^2) for Ir(dpq)$_2$(dpq-3F). Figure 5 shows the luminous efficiencies of the devices as a function of the applied current densities. As similar to the luminance characteristics, the maximum efficiencies of the devices with heteroleptic dopants are higher than those of the devices with homoleptic dopants. The maximum luminous efficiencies of the devices were 10.9 cd/A at the current density of 0.6 mA/cm^2 and 8.17 cd/A at 0.14 mA/cm^2 for Ir(dpq)$_2$(dpq-3F) and Ir(dpq-3F)$_3$, respectively. The efficiency of Ir(dpq)$_2$(dpq-3F) at the current density of 100 mA/cm^2 was maintained to 54% (5.9 cd/A) of its maximum value.

The performance of OLEDs is considered to be severely affected by T-T annihilation as the applied current increases. Thus, the luminous efficiency decreases crucially with the increased current [13]. From the luminance and efficiency characteristics of the devices as shown in Figures 4 and 5, it is apparent that the devices containing homoleptic tris-cyclometalated iridium complexes are more affected by T-T annihilation than the devices containing heteroleptic tris-cyclometalated iridium dopants. It indicates that the heteroleptic ligands prevent the T-T annihilation via efficient exciton transfer from ppy ligands to the luminescent ligand, piq or piq-F.

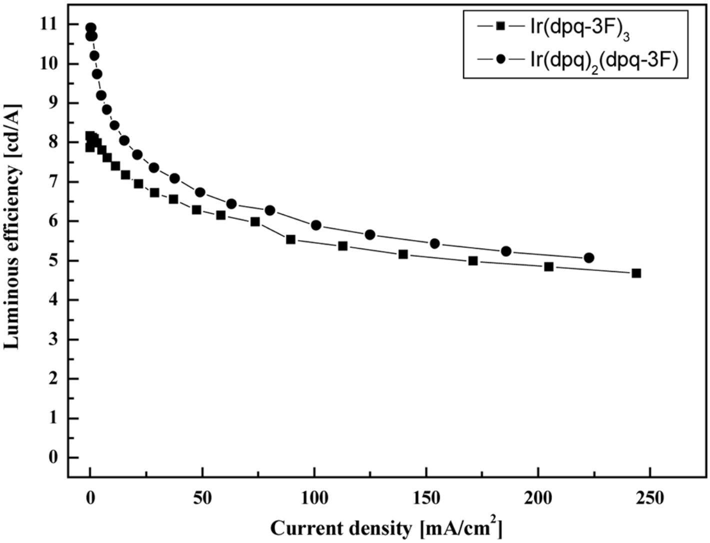

FIGURE 5 Luminous efficiencies of iridium complexes at various current densities.

4. CONCLUSIONS

We have fabricated an efficient red phosphorescent organic light-emitting diodes employing new heteroleptic tris-cyclometalated iridium complex [Ir(dpq)$_2$(dpq-3F)], and studied their electrical and optical characteristics compared to the devices with the homoleptic tris-cyclometalated iridium complex [Ir(dpq-3F)$_3$]. Significant improvements of new heteroleptic tris-cyclometalated iridium complex [Ir(dpq)$_2$(dpq-3F)] in the current efficiency at high currents were achieved due to minimizing T-T annihilation and saturation of the ligand excited states.

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