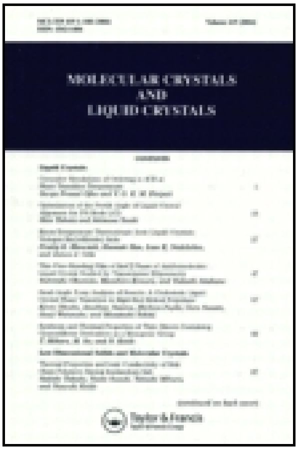

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Inter-Ligand Energy Transfer of Heteroleptic Tris-Cyclometalated Iridium Complexes and Their Applications to OLEDs

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Novel red phosphorescent heteroleptic tris-cyclometalated iridium complex, $Ir(ppy)_2(dpq\text{-}3F)$ based on 2-phenylpyridine (ppy) and 2-(3-fluorophenyl)-4-phenylquinoline (dpq-3F) ligands have been synthesized and characterized for the application in organic light-emitting diodes (OLEDs). The heteroleptic tris-cyclometalated iridium complex leads to a significant improvement in a luminous efficiency at high currents to avoid the T–T annihilation by the exciton transfer from two ppy ligands to one luminescent dpq-3F ligand decreasing the number of the luminescent ligand. This inter-ligand energy transfer (ILET) can occur because the dpq-3F-centered ^{3}MLCT state is lower than that of the ppy-centered ^{3}MLCT state and because the ILET time from the ppy-centered ^{3}MLCT state to the dpq-3F-centered ^{3}MLCT state is shorter than the radiative lifetime of $Ir(ppy)_3$. A maximum luminous efficiency of $\eta_c = 13.70\,cd/A$ and power efficiency of $\eta_p = 10.80\,lm/W$ are achieved at a current density of $J = 0.07\,mA/cm^2$. At a higher current density of $J = 100\,mA/cm^2$, $\eta_c = 9.17\,cd/A$ and $\eta_p = 2.42\,lm/W$ are obtained.

Keywords: $Ir(ppy)_2(dpq\text{-}3F)$; organic light-emitting diode; red phosphorescence

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1. INTRODUCTION

Organic Light-emitting diodes (OLEDs) have emerged as promising candidates for potential applications in the fabrication of full-color flat-panel displays with high efficiencies because they have the unique advantages of fast response, low power consumption, wide-view angle, high contrast, and large flexibility [1].

OLEDs based on phosphorescent materials were known to be able to improve electroluminescence performance significantly because both singlet and triplet excitons could be used to harvest light emission. Theoretically, the internal quantum efficiency of phosphorescent emitters can approach to about 100% [2–4]. Recently, phosphorescent materials and devices have been extensively studied to achieve a high efficiency OLEDs since Forrest and Thompson et al. reported OLEDs with phosphorescent heavy metal complexes [5–7]. 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 luminescent efficiency at high currents [8,9]. In order to improve the luminescent efficiency by avoiding T–T annihilation, the metal complex having a different species of plural ligands has been proposed [10–12]. When a metal complex having three ligands including one luminescent ligand is placed in excited state, the excited energy is transferred from two other ligands to one luminescent ligand, thus allowing a monochromatic luminescent color. Further, it is expected that the use of one luminescent ligand decreases the probability 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 highly efficient red phosphorescent OLEDs containing heteroleptic Ir complexes which show improved luminescence and current tolerant efficiency characteristics by introducing phenylpyridine (ppy) ligand for energy transfer and diphenylquinoline (dpq-3F) as a luminescent ligand. The purpose of the present study is to design the high efficient heteroleptic Ir(III) complex having different species of ligands for the highly efficient Ir(III) complex suitable for red OLED devices. In addition to the high phosphorescent efficiency, the phosphorescent mechanism of the Ir(III) complexes having different ligands is studied in comparison with those having the homoleptic Ir(III) complexes having the same species of ligands.

2. EXPERIMENTAL

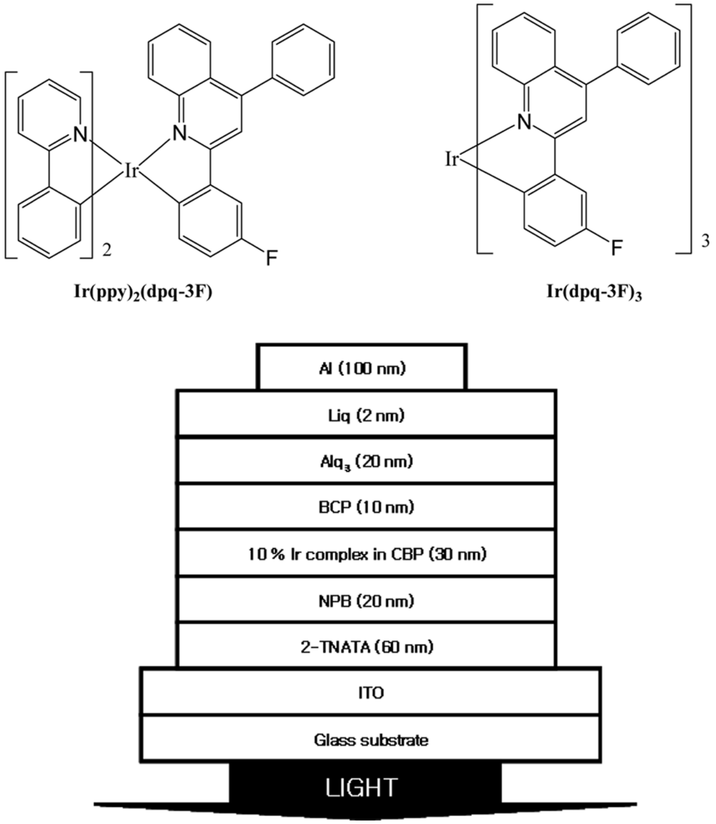
2.1. UV-Absorption and Photoluminescence (PL) Measurement

UV-Vis absorption spectra were measured on Hewlett Packard 8425 A spectrometer. The PL spectra were obtained on Perkin Elmer LS 50B spectrometer. UV-Vis and PL spectra of Ir(dpq-3F)$_3$ and Ir(ppy)$_2$(dpq-3F) were measured with a 10^{-5} M dilute solution in CH_2Cl_2.

2.2. Fabrication of Devices

OLEDs using Ir(dpq-3F)$_3$ and Ir(ppy)$_2$(dpq-3F) as red dopants in emitting layers were fabricated. Other organic materials used as carrier transport, carrier injection and host materials were supplied by Gracel Display Incorporation in Korea.

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 Ω/□, 80 nm) coated glass substrate. The ITO glass was cleaned with acetone, methanol, distillated water and isopropyl alcohol [13]. 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 the Ir complexes doped in 4,4,*N*,*N*′-dicarbazolebiphenyl (CBP). The doping rate of the phosphor, an Ir complex, 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 0.1 nm/sec. Finally, 100 nm of Al was deposited as a cathode. Molecular structure of Ir complexes and configuration of OLEDs with Ir complexes as red dopant were shown in Figure 1. Molecular structure of other materials for HIL, HTL, host and ETL are found in the literature [14]. 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). 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.



Ir(ppy)$_2$(dpq-3F)

Ir(dpq-3F)$_3$

FIGURE 1 Molecular structure of Ir complexes and configuration of OLEDs with Ir complexes as red dopant.

3. RESULTS AND DISCUSSION

In order to improve the luminescence efficiency by decreasing T–T annihilation, new phosphorescent heteroleptic iridium complexes having a different species of plural ligands are designed for the application in OLEDs. The iridium complexes prepared herein can be classified into two groups. The heteroleptic complex is Ir(ppy)$_2$(dpq-3F), and the homoleptic complexes are Ir(ppy)$_3$and Ir(dpq-3F)$_3$. The molecular structure is showed in Figure 1.

In homoleptic complex cases, luminescence efficiency may decrease because of the saturated quenching effect caused by the energy transfer between the same species of ligands. Therefore, we have prepared and characterized heteroleptic Ir(III) complex having two ppy ligands and one of dpq-3F as a luminescent ligand. This heteroleptic complex exhibits more red-shifting emission peak than Ir(ppy)$_3$ and have higher luminescence efficiency than that of homoleptic Ir(III) complex, Ir(dpq-3F)$_3$.

The UV-vis absorption spectra of Ir(ppy)$_3$, Ir(dpq-3F)$_3$ and Ir(ppy)$_2$(dpq-3F) in CH_2Cl_2 are shown in Figure 2. The characteristic of the MLCT absorption spectra for Ir(ppy)$_2$(dpq-3F) resembles that of Ir(dpq-3F)$_3$ and their intensities are close to these of Ir(ppy)$_3$. The MLCT absorption peaks of Ir(dpq-3F)$_3$ occur at 460, 512 and 560 nm, respectively. However, the MLCT absorption peaks of the heteroleptic Ir(ppy)$_2$(dpq-3F) are observed at 410, 460, 480 512 and 560 nm where the MLCT peaks of both Ir(ppy)$_3$ and Ir(dpq-3F)$_3$ are located. In addition, the shape of absorption spectra of Ir(ppy)$_2$(dpq-3F) are mixed with Ir(ppy)$_3$ and Ir(dpq-3F)$_3$. It provides the evidence that MLCT absorption of the Ir(ppy)$_2$(dpq-3F) occurs at the ppy as well as dpq-3F ligands. Because HOMO energy level of dpq-3F ligand is similar with that of ppy ligand, MLCT absorption at both ppy and dpq-3F ligands is allowed.

The PL spectra of the homoleptic and heteroleptic complexes on CH_2Cl_2 are shown in Figure 3. The PL spectra of Ir(dpq-3F)$_3$ and Ir(ppy)$_2$(dpq-3F) show a similar characteristics of emission band at 597 nm and 600 nm, respectively. This is because the triplet energy level of Ir(ppy)$_3$ is higher than that of Ir(dpq-3F)$_3$ and because the

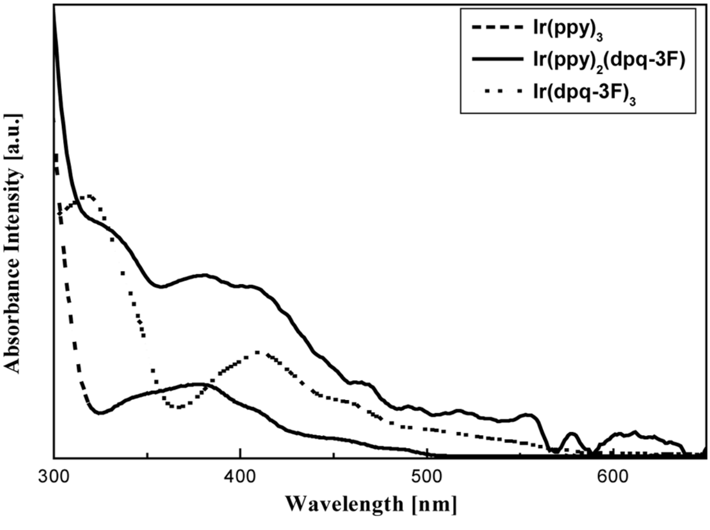


FIGURE 2 UV-vis absorption spectra of Ir(ppy)$_3$, Ir(dpq-3F)$_3$ and Ir(ppy)$_2$(dpq-3F).

energy transfer time from ppy to dpq-3F within ns time scale is shorter than the radiative lifetime of Ir(ppy)$_3$. Thus, Ir(ppy)$_2$(dpq-3F) is placed in the excited state, the excitation energy is quickly inter-ligand energy transferred from two ppy ligands to one luminescent dpq-3F ligand. It allow a monochromatic luminescent color and to improve the luminescent by the decrease of quenching or energy deactivation.

Figure 4 showed the electroluminescence (EL) characteristics of devices with the Ir complexes at the applied voltage of 12 V. The EL spectra of Ir(dpq-3F)$_3$ and Ir(ppy)$_2$(dpq-3F) have a maximum at a wavelength of $\lambda_{\max} = 608\,\text{nm}$ and 604 nm, respectively. The main peak of the devices coincided with the PL peaks of the emitting dopants, which indicated that EL was originated from the emission of the dopant. In the case of heteroleptic Ir complexes, Ir(ppy)$_2$(dpq-3F), the only difference between their PL and EL spectra was the presence of the weak shoulder peak at around 510 nm which was considered as the emission of Ir(ppy)$_3$. That is, hot alcoholic solvent, we predicted, scrambling of ligands and the formation of multiple products, which are difficult to separate. However, the main EL peaks of the devices didn't change with the various applied voltage from 4 V to 14 V.

The device with the heteroleptic Ir complex showed a significant improvement in a luminance compared to those with the homoleptic Ir complex. As shown in Figure 5, the device with Ir(ppy)$_2$(dpq-3F) exhibited the higher luminance characteristics as a function of the current density than those with Ir(dpq-3F)$_3$. At the applied voltage

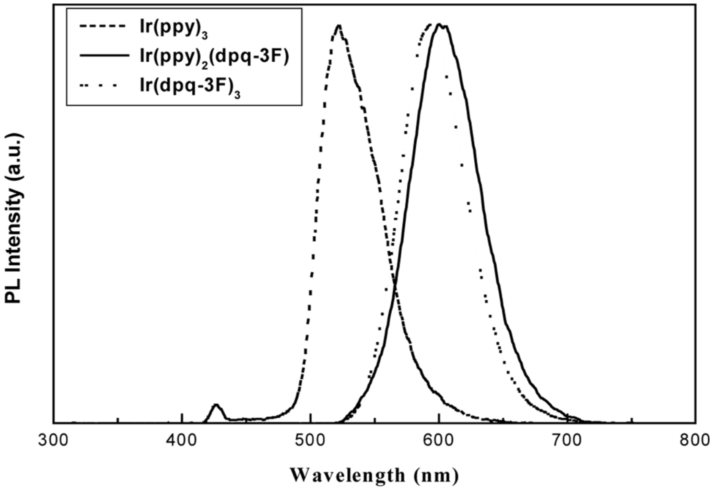


FIGURE 3 PL spectra of Ir(ppy)$_3$, Ir(dpq-3F)$_3$ and Ir(ppy)$_2$(dpq-3F).

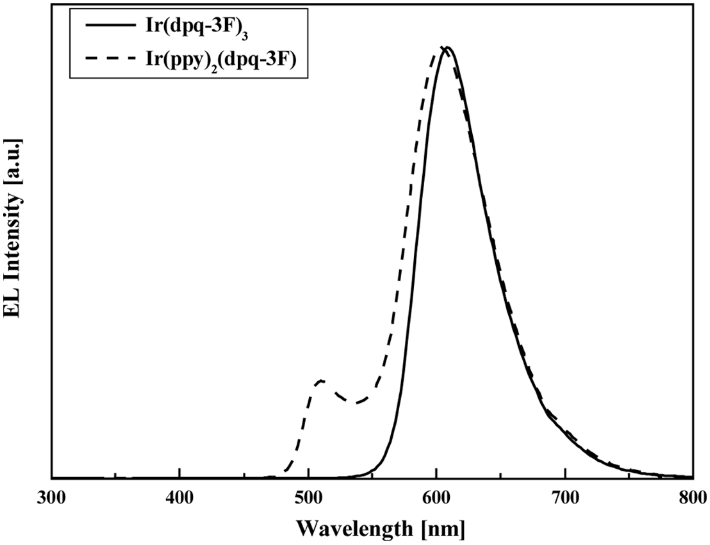


FIGURE 4 Emission spectra of OLEDs using Ir complexes as red dopants at 12 V.

of 14 V, the luminance maxima of the devices are 18800 cd/m^2 ($J = 231$ mA/cm^2) for Ir(ppy)$_2$(dpq-3F), 11400 cd/m^2 ($J = 244$ mA/cm^2) for Ir(dpq-3F)$_3$. Figures 6 and 7 showed the luminous efficiency

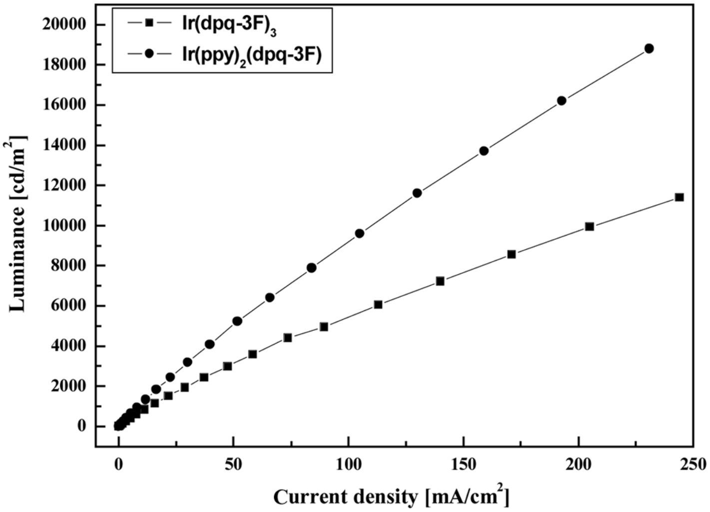


FIGURE 5 Luminance curves as increasing the current density of OLEDs.

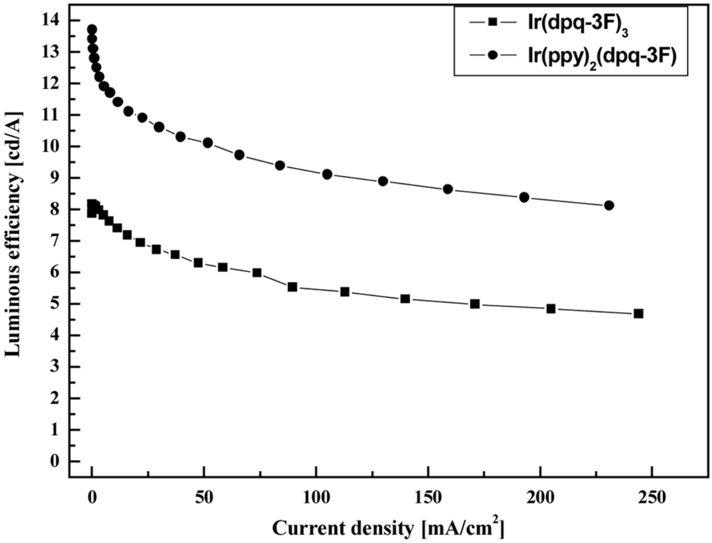


FIGURE 6 Luminous efficiency curves as increasing the current density of OLEDs.

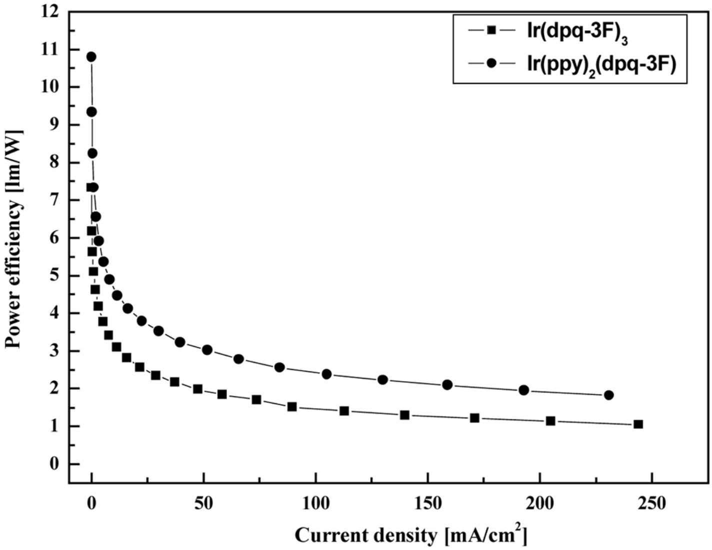


FIGURE 7 Power efficiency curves as increasing the current density of OLEDs.

TABLE 1 Electroluminescence Characteristics of the Homoleptic and Heteroleptic Ir Complexes

Red dopant	Max. Luminance $[cd/m^2]$ At 14 V	Max. η_c(cd/A) [Max η_p(l m/W)]	η_c(cd/A) [η_p(l m/W)] at $J = 10\,mA/cm^2$	η_c(cd/A) [η_p(l m/W)] at $J = 100\,mA/cm^2$	λ_{max}
$Ir(dpq\text{-}3F)_3$	11400	8.17 [7.33]	7.40 [3.11]	5.45 [1.47]	608 nm
$Ir(ppy)_2(dpq\text{-}3F)$	18800	13.70 [10.80]	11.7 [4.90]	9.17 [2.42]	604 nm

(η_c) and power efficiency (η_p) of the devices, respectively, as a function of the applied current densities. Similar to the luminance characteristics, the maximum η_c and η_p of the device with heteroleptic dopant $Ir(ppy)_2(dpq\text{-}3F)$ are superior to those of the devices with homoleptic dopant $Ir(dpq\text{-}3F)_3$. The maximum $\eta_c(\eta_p)$ of the devices were 13.70 cd/A A (10.80 lm/W) at the current density of $0.07\,mA/cm^2$ and 8.17 cd/A (7.33 lm/W) at $0.03\,mA/cm^2$ for $Ir(ppy)_2(dpq\text{-}3F)$ and $Ir(dpq\text{-}3F)_3$, respectively. At a higher current density of $J = 100\,mA/cm^2$, η_c and η_p of $Ir(ppy)_2(dpq\text{-}3F)$ were 9.17 cd/A and 2.42 lm/W, respectively, which is significantly higher than those of $Ir(dpq\text{-}3F)_3$ with 5.45 cd/A and 1.46 lm/W. Table 1 summarizes the electroluminescence characteristics of the homoleptic and heteroleptic Ir complexes.

The results of the device with heteroleptic Ir complex as red dopant showed more superior electrical characteristics than that with homoleptic Ir complex. On the basis of these experimental results, the most probable mechanism of electrophosphorescence of the OLED using the heteroleptic iridium complex is shown in Figure 8. Electron-hole

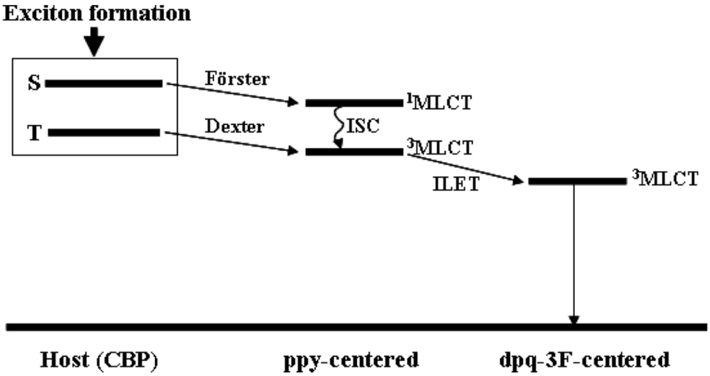


FIGURE 8 Mechanism of electrophosphorescence of OLED by the inter–ligand energy transfer.

recombination creates singlet (S) and triplet (T) excitons in the host material (CBP). Singlet and triplet excitons are transferred into the ppy-centered ^{1}MLCT state by a Forster process and the ppy-centered ^{3}MLCT state by Dexter process, respectively. The ppy-centered ^{1}MLCT state is subject to intersystem crossing (ISC) due to the strong spin-orbit coupling and transfer to the ppy-centered ^{3}MLCT state. Inter-ligand energy transfer (ILET) from the ppy-centered ^{3}MLCT state to the dpq-3F-centered ^{3}MLCT state followed by the luminescence from the dpq-3F-centered ^{3}MLCT state. This ILET-mediated luminescence is supported by following reasons. The dpq-3F-centered ^{3}MLCT state is lower than that of the ppy-centered ^{3}MLCT state and the ILET time (within ns time scale) from the ppy-centered ^{3}MLCT state to the dpq-3F-centered ^{3}MLCT state is shorter than the radiative lifetime of Ir(ppy)$_3$. As a result, light emits with the red emission from the dpq-3F-centered ^{3}MLCT state. It allow a monochromatic luminescent color and to improve the luminous efficiency by the decrease of quenching or energy deactivation. A high luminous efficiency can be realized by decreasing the number of the luminescent ligand.

The performance of OLEDs is considered to be severely affected by T–T annihilation as the applied current increases. Thus, the luminous efficiency of OLEDs decreases crucially with the increased current [15]. From the luminance and efficiency in Figure 6 and 7 it was apparent that the devices containing the homoleptic Ir complexes were more affected by T–T annihilation than the devices containing the heteroleptic Ir dopants.

4. CONCLUSIONS

We have fabricated highly efficient red phosphorescent organic light-emitting diodes employing the new heteroleptic Ir complexes, Ir(ppy)$_2$(dpq-3F), and studied their electrical and optical characteristics compared to the devices with the homoleptic Ir complexes, Ir(dpq-3F)$_3$. Significant improvements of the device containing the new heteroleptic Iridium complex, Ir(ppy)$_2$(dpq-3F), were achieved in the luminance, luminous efficiency and power efficiency. It was suggested that the exciton transfer from two ppy ligands to one luminescent dpq-3F ligand could suppress T–T annihilation and saturation of the ligand excited states by decreasing the number of the luminescent ligand, leading to better performance of the device at high currents.

If it was possible to reduce the impurity peak of Ir(ppy)$_3$ at 510 nm, the electrical characteristics and color purity could be much more improved. In order to suppress the impurity peak of Ir(ppy)$_3$, it is necessary to purify the mixture of Ir complexes by recrystallized in several times and/or by using the sublimation method.

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