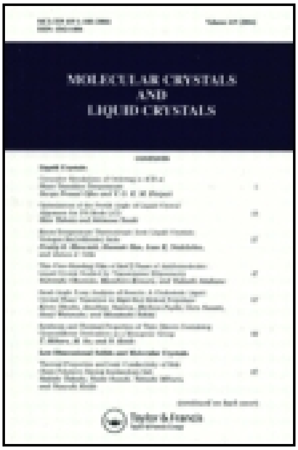

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New Red Electrophosphorescent Organic Light-Emitting Devices Based on Ir(III) Complex of 2,3,4-Triphenylquinoline

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New Red Electrophosphorescent Organic Light-Emitting Devices Based on Ir(III) Complex of 2,3,4-Triphenylquinoline

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Novel red-emitting electrophosphorescent devices were fabricated by doping an Ir complex, Ir(tpq)$_2$(acac), based on 2,3,4-triphenylquinoline (tpq) ligand. The EL spectrum of the device showed emission maximum peak at 611 nm and CIE coordinates of that were (0.664, 0.332) at 12 V, respectively, due to long conjugation length of Ir(tpq)$_2$(acac). The luminance of the device with Ir(tpq)$_2$(acac) was 4160 cd/m^2 at 14 V. The maximum luminous efficiencies and power efficiency of the device with Ir(tpq)$_2$(acac) were 3.14 cd/A (8.01 mA/cm^2) and 1.82 lm/W (0.24 mA/cm^2). More characteristics and charge transport mechanism will be discussed.

Keywords: Ir(tpq)$_2$(acac); long conjugated length; red-emitting electrophosphorescent devices

PACS numbers: 81.16.Be; 81.40.Tv

1. INTRODUCTION

Since the first great discovery that organic material emits visible light in multilayered structure when a bias voltage was applied on the structure by Tang and coworkers [1,2], organic light emitting diode (OLED) and emitting materials [3,4] have been developed fast. One of the key points of OLED development for full-color display is to find

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out materials emitting pure colors of red, green and blue (RGB). Luminescent materials for OLED devices are generally classified into two groups; fluorescence and phosphorescence. The OLED based on phosphorescent materials can significantly improve electroluminescence performance because the heavy metal, such as iridium or platinum, in the complexes induce the intersystem crossing by strong spin-orbit coupling, leading to mixing of the singlet and triplet excited states [5,6]. While, the design and synthesis of efficient red phosphorescent materials are basically more difficult because their luminescence quantum yields tend to decrease as the emission wavelength increase in accordance with low energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Thus, the design and synthesis of new organic ligands for Ir complexes is highly desirable in order to improve the efficiency and the color purity [7–16]. Cyclometalated $Ir(ppy)_3$, where ppy represents 2-phenylpyridine, has been extensively applied as a green emitting material for OLEDs. The strong emission is believed to start from the triple excited states possessing both π-π^* and metal-to-ligand-charge-transfer (MLCT) characteristics. Thus, it is anticipated that tuning the emission to the red color can be qualitatively achieved by lowering the energy level of either π-π^* or MLCT states of Ir derivatives. There are several strategies to obtain the good red electrophosphorescent material. The first method is to elongate the conjugation length properly. If conjugation length is increased, the tuned material shows more reddish color because energy gap decreases. The second method is to replace one of CH groups at the pyridyl ring of phenylpyridine ligand by a nitrogen atom. Because the nitrogen atom in the pyridyl ring acts as an electronegative atom, the energy level of LUMO is lowered without any change of the HOMO energy level. As a result, the energy gap decreases and the emission become more reddish. Finally, the last method is to add withdrawing and donation functional group to the pyridyl ring and the phenyl ring, respectively. Insertion of an extra electron withdrawing group such as F at pyridyl ring decreases the LUMO energy level and an extra electron donating group such as CH_3 at phenyl ring increases the HOMO energy level. Therefore, the energy gap decreases and the emission of the tuned material is shifted to red region.

In this paper, $Ir(tpq)_2(acac)$, where tpq represents 2,3,4-triphenylquinoline, is designed and analyzed as a new red emitting material by following the strategy of conjugation length increase described above. $Ir(tpq)_2(acac)$ emits from a predominantly ^{3}MLCT excited state and its PL spectra showed a peak at 607 nm. Thus, the iridium complex is a good candidate for an efficient electrophosphorescent material.

2. EXPERIMENTAL DETAILS

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 $Ir(tpq)_2(acac)$ were measured with a 10^{-5} M dilute solution in CH_2Cl_2.

2.2. Fabrication of Device

OLED using $Ir(tpq)_2(acac)$ as red dopants in emitting layers was fabricated. The $Ir(tpq)_2(acac)$ phosphor dopant was synthesized in our laboratory [17]. Other organic materials used as carrier transport, carrier injection and host materials were supplied by Gracel Display Incorporation in Korea. OLED was 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 cleaned with acetone, methanol, distillated water and isopropyl alcohol [18]. 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. Configuration of device was shown in Figure 1. 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.

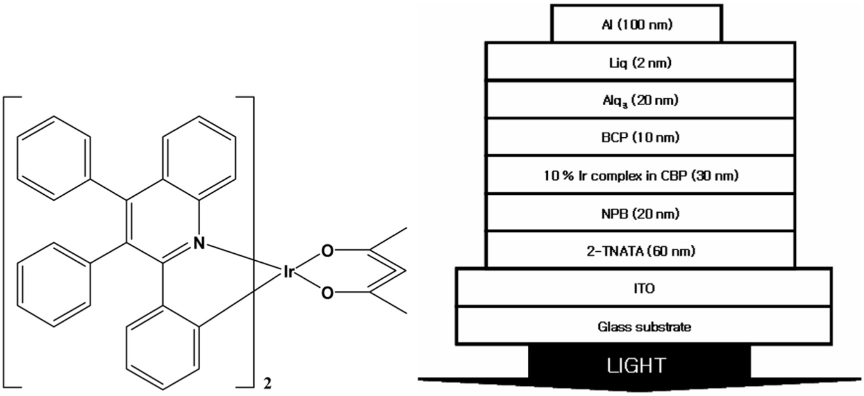

FIGURE 1 Molecular structure of Ir(tpq)$_2$(acac) and device structure using the Ir(tpq)$_2$(acac) as red dopant.

2.3. Theoretical Calculation

We have theoretically calculated the energy level of several ligands. Density functional theory (DFT) of B3LYP with 6-31G(d) basis set was used for the geometry optimization and the energy level calculation of the ground state of the ligands. To obtain the vertical excitation energies of the low-lying singlet and triplet excited states of the ligands, time-dependent DFT (TD-DFT) calculations using the B3LYP functional was performed at the respective ground-state geometry, where the basis set of ligands was changed to 6-31+G(d).

3. RESULTS AND DISCUSSION

In order to improve the color purity by increasing the conjugation length, new red phosphorescent iridium complex, Ir(tpq)$_2$(acac), were designed for the application in OLEDs. The molecular structures were shown in Figure 1.

Figure 2 depicted the UV-vis. and photoluminescence (PL) spectrum of Ir complex in CH_2Cl_2. The strong absorption bands in the UV region with distinct vibronic features were assigned to the spin-allowed $^1\pi$-π^* transition of the cyclometalated tpq ligands. Weak and broad absorption bands were shown in the wavelength region longer than 480 nm. The weak absorption shoulder peaks at 489 and 575 nm for Ir(tpq)$_2$(acac) were likely to be ascribed to the ^{1}MLCT and ^{3}MLCT transitions, respectively. Moreover, the PL spectrum of Ir(tpq)$_2$(acac) showed the emission band at 607 nm.

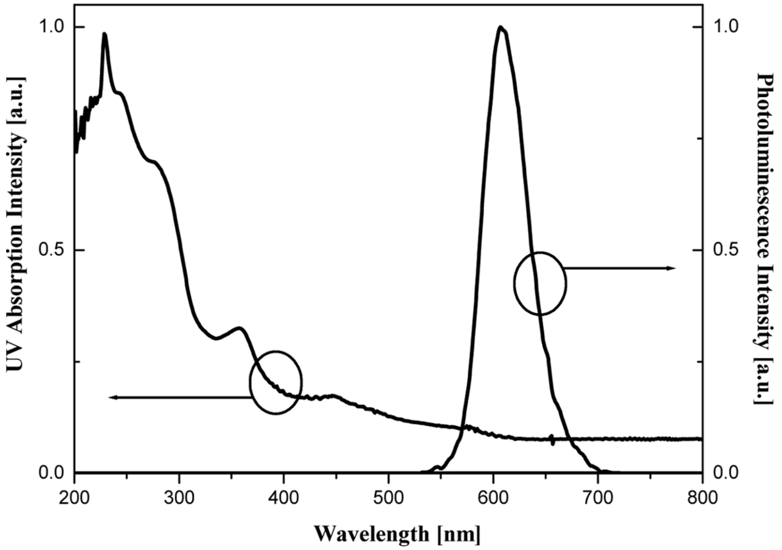

FIGURE 2 UV-vis. and PL spectra of Ir(tpq)$_2$(acac) in CH_2Cl_2.

Electrical characteristics of device with Ir(tpq)$_2$(acac) were shown in Figures 3 and 4. As shown in Figure 3, the maximum luminance of the device was 4160 cd/m^2 ($J = 184$ mA/cm^2) for Ir(tpq)$_2$(acac), when device was applied from 0 V to 14 V. Figure 4 and figure inserted in Figure 4 showed the luminous efficiencies and power efficiencies of the device, respectively, as a function of the applied current density. The maximum luminous and power efficiencies of the device were 3.14 cd/A ($J = 8.01$ mA/cm^2) and 1.82 lm/W ($J = 0.24$ mA/cm^2) for Ir(tpq)$_2$(acac). In the generality of cases, the performance of OLEDs is considered to be severely affected by T-T (triplet-triplet) annihilation as the applied current increases. Thus, the luminous efficiency of OLEDs is decreased crucially with the increased current [19]. However, the efficiency of device with Ir(tpq)$_2$(acac) was maintained to 71.97% at 184 mA/cm^2. It is because that the bulky structure of Ir(tpq)$_2$(acac) leading to steric hindrance effect. Therefore, the device with Ir(tpq)$_2$(acac) maintained the high efficiency in spite of increase of current density because T-T annihilation was suppressed.

Figure 5 showed the energy level of several ligands. The HOMO levels of phenylquinoline (ppy), diphenylquinoline (dpq), triphenylquinoline (tpq) and dpq-3-F ligands were −6.119 eV, −5.915 eV, – 5.873 eV and −6.172 eV, respectively. In case of devices using the Ir complex as dopant, the efficiency is depended on the MLCT characteristics of

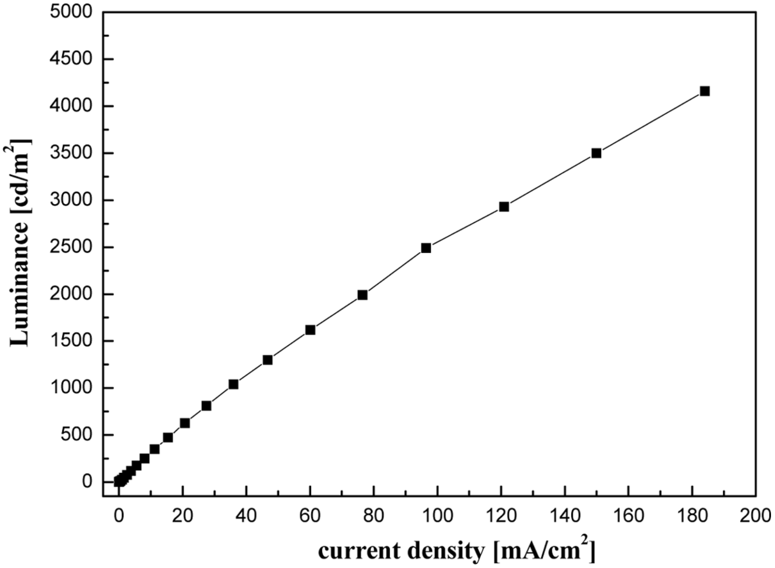

FIGURE 3 Luminance curves as increasing the current density of OLEDs.

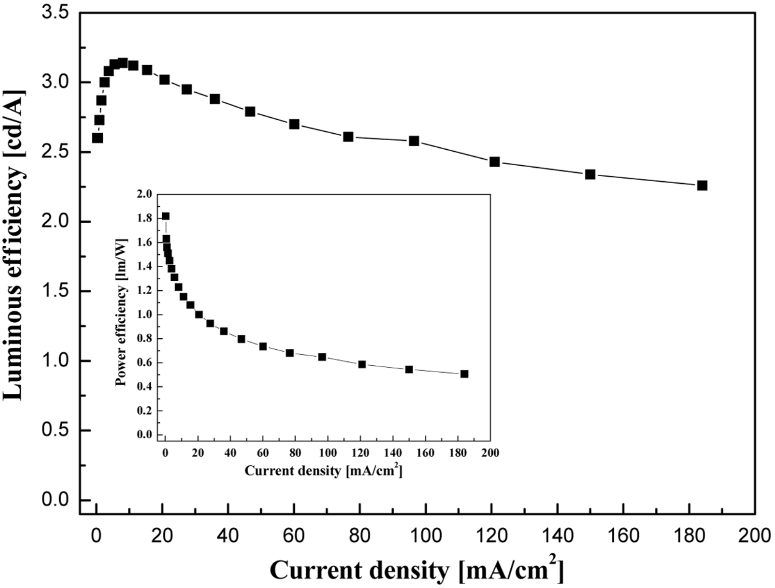

FIGURE 4 Luminous efficiency (inset:power efficiency) curves as increasing the current density of OLEDs.

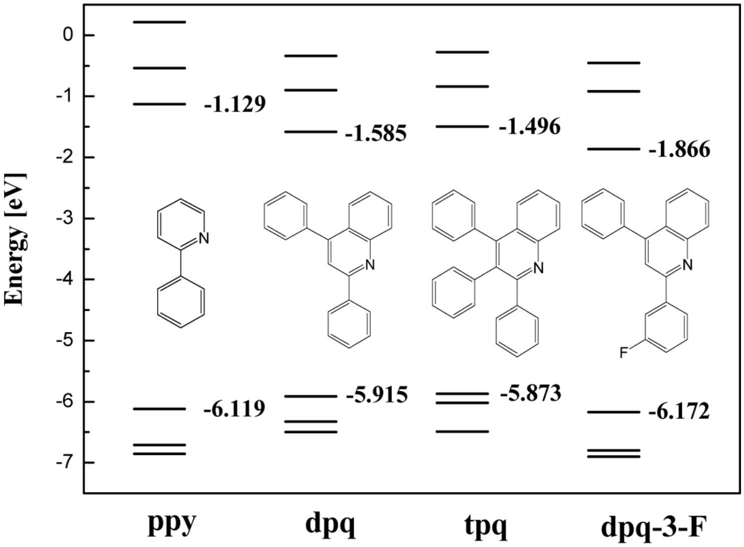

FIGURE 5 HOMO and LUMO energy levels of ppy, dpq, tpq and dpq-3-F ligands.

Ir complex. The Ir complex with phenylpyridine (ppy) ligand is known in high efficient MLCT characteristic because the lowest triplet excited state is not ^{3}LC excited state but ^{3}MLCT state due to the HOMO level of ppy very close to t_{2g} level of Ir atom. When conjugation length is increased, it enhances the contribution of ^{3}LC in the lowest triplet excited state because the energy of ^{3}LC state is lowered than the ^{3}MLCT state, which leads to low efficiency. This problem can be solved by lowering the HOMO level of ligand through substitution of the electron withdrawing group such as fluorine at pyridyl. It can be confirmed in Figure 5 that HOMO levels of dpq and tpq ligand were highly far from that of ppy ligand having the good MLCT characteristics as reference, while that of dpq-3-F was very similar to that of ppy ligand. Therefore, $Ir(tpq)_2(acac)$ with low maximum luminous efficiency of 3.14 cd/A can be improved by substituting the electron withdrawing group at pyridyl.

Figure 6 and the inset in Figure 6 showed the electroluminescence (EL) spectrum and CIE coordinates. The CIE coordinates of the device with $Ir(tpq)_2(acac)$ was (0.664, 0.332) at 12 V. We note that there is no current density dependence of the CIE coordinates from the about 1 mA/cm^2 to 180 mA/cm^2. The device with $Ir(tpq)_2(acac)$, substituted two phenyl to quinoline side of phenyl-quinoline (pq) ligand, showed the more reddish emission as comparing with $Ir(dpq)_2(acac)$ [20] which

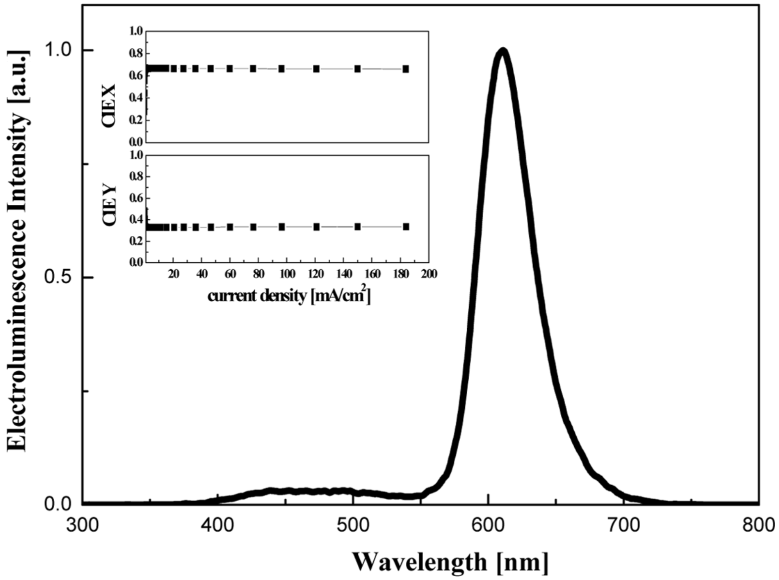

FIGURE 6 EL spectrum of OLED using the Ir(tpq)$_2$(acac) at 12 V. (Inset:CIE coordinates curves as increasing the current density).

attached one phenyl to quinoline side of pq ligand. It provided the evidences that band gap between HOMO and LUMO was decreased with increase of conjugation length by substitution of two phenyl. However, functions of phenyl substitution have not only influence on decrease of band gap between HOMO and LUMO, but also increase of LOMO energy level because phenyl is donating group. Unless the effect of HOMO energy level increase was participated, we can obtain the more reddish emission. The EL spectrum of device with Ir(tpq)$_2$(acac) showed the emission peak at 611 nm.

4. SUMMARY AND CONCLUSIONS

In summary, we reported optical and electrical properties of the phosphorescent Ir(tpq)$_2$(acac) in order to find a new red emitting material for the application in OLEDs. The electroluminescence (EL) of device with Ir(tpq)$_2$(acac) showed the largest emission efficiency with maximum at 611 nm. Significant improvements of the device containing the new red Ir complex, Ir(tpq)$_2$(acac), were achieved in the color purity and efficiency maintenance at high currents. It was suggested that the increased conjugation length of Ir(tpq)$_2$(acac) leads to the red shift of the emission and the suppression of the T-T annihilation.

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