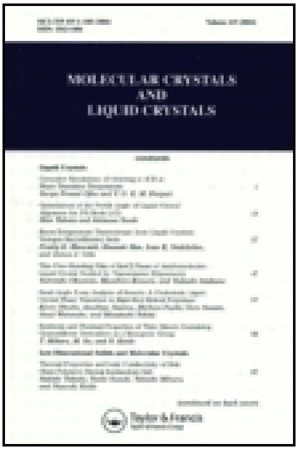

Molecular Crystals and Liquid Crystals

Heteroleptic Iridium(III) Complexes with Phenylpridine and Diphenylquinoline Derivative Ligands

Yong Hwan Park [a] , Gui Youn Park [a] & Young Sik Kim [b]

[a] Department of Information Display Engineering, Hongik University, Seoul, Korea

[b] Department of Science, Hongik University, Seoul, Korea

Version of record first published: 17 Oct 2011

To cite this article: Yong Hwan Park, Gui Youn Park & Young Sik Kim (2006): Heteroleptic Iridium(III) Complexes with Phenylpridine and Diphenylquinoline Derivative Ligands, Molecular Crystals and Liquid Crystals, 462:1, 197-207

To link to this article: http://dx.doi.org/10.1080/07370650601013179

Mol. Cryst. Liq. Cryst., Vol. 462, pp. 197–207, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/07370650601013179

Heteroleptic Iridium(III) Complexes with Phenylpridine and Diphenylquinoline Derivative Ligands

Yong Hwan Park
Gui Youn Park
Department of Information Display Engineering, Hongik University, Seoul, Korea

Young Sik Kim
Department of Science, Hongik University, Seoul, Korea

The synthesis and photophysical study of efficient phosphorescent iridium(III) complexes having two different (C^N) ligands are reported. In order to improve the luminescence efficiency by avoiding triplet-triplet (T-T) annihilation, the iridium complexes, Ir(ppy)$_2$(dpq) and Ir(ppy)$_2$(dpq-3-F), are designed and prepared where ppy, dpq and dpq-3-F represent 2-phenylpyridine, 2,4-diphenylquinoline and 2-(3-fluorophenyl)-4-phenylquinoline, respectively. Since Ir(ppy)$_3$, Ir(dpq)$_3$ and Ir(dpq-3-F)$_3$ can be placed in the metal-to-ligand charge transfer (MLCT) excited state, they absorb light effectively. Thus, ppy ligands and a dpq derivative can act as a source of energy supply. When Ir(ppy)$_2$(dpq-3-F) is placed in the lowest excited state, the excitation energy is not quenched nor deactivated but quickly transferred intramolecularly from two ppy ligands to one luminescent dpq-3-F ligand. Such transfer can occur because the triplet energy level of ppy is higher than that of dpq-3-F and light is emitted from dpq-3-F ligand in the end. Thus, Ir(ppy)$_2$(dpq-3-F) shows strong photoluminescence from dpq-3-F ligand. To analyze luminescent mechanism, we calculated these complexes theoretically by using computational method.

Keywords: Ir(ppy)$_2$(dpq); Ir(ppy)$_2$(dpq-3-F); Ir complex; OLED; red phosphorescence

1. INTRODUCTION

Since Tang and coworkers reported organic light-emitting devices (OLED) with the multi-layer structure materials [1,2] and device

---

This work was supported by 2006 Hongik University Research Fund.

Address correspondence to Young Sik Kim, Department of Science, Hongik University, Seoul, 121-791, Korea. E-mail: youngkim@hongik.ac.kr

fabrication have been extensively studied in recent years [3–5]. Luminescent materials are generally classified into two groups as fluorescent and phosphorescent ones. 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% [6]. The heavy metal complexes, particularly those containing Pt and Ir, can induce the intersystem crossing by strong spin-orbit coupling, leading to the mixing of the singlet and triplet excited states [7,8]. Spin-forbidden nature of radiative relaxation from the triplet excited state then becomes allowed, resulting in high phosphorescent efficiencies. Thus, heavy metal complexes can serve as efficient phosphors in OLEDs.

Unfortunately, most of phosphorescent emitters have a long lifetime, which leads to the dominant triplet-triplet (T-T) annihilation at high current. The occurrence of T-T annihilation decreases the performance of a phosphorescent material, particularly its maximum brightness and luminescence efficiency at high currents [9,10].

In order to improve the luminescence efficiency by avoiding T-T annihilation, the metal complex having a different species of plural ligands has been proposed [11]. The metal complex has been designed to transfer the energy of exciton smoothly between ligands placed in its excited states. More specifically, when a metal complex having one luminescent ligand among three ligands is placed in the lowest excited state, the excited energy is transferred from the other two ligands to one luminescent ligand. Furthermore, it is expected that the use of one luminescent ligand decreases the probability of energy transition between spatially adjacent molecules, leading to the decrease of quenching or energy deactivation.

Herein, we report two efficient phosphorescent emitters having different ligands, $Ir(ppy)_2(dpq)$ and $Ir(ppy)_2(dpq\text{-}3\text{-}F)$ where ppy, dpq and dpq-3-F represent 2-phenylpyridine, 2,4-diphenylquinoline and 2-(3-fluorophenyl)-4-phenylquinoline, respectively. Previously, $Ir(ppy)_2(acac)$ and $Ir(dpq)_2(acac)$ were known to have high phosphorescence efficiencies in electroluminescent (EL) emissions near 516 and 614 nm, respectively, because they had the metal-to-ligand charge transfer (MLCT) excited state [12,13]. The purpose of the present study is to design the high efficient Ir(III) complex with the 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 ligand species.

2. EXPERIMENTAL

2.1. Synthesis and Characterization

All reagents were purchased from Aldrich except Ir(III) trichloride hydrate ($IrCl_3 \cdot H_2O$) which was purchased from Strem and used without further purification. All reactions were carried out under a nitrogen or argon atmosphere. Solvents were dried by standard procedures. All column chromatography was performed with the use of silica gel (230-Mesh, Merck). The synthesis method is shown in Figure 1.

2.1.1. Synthesis of Ligand: dpq, dpq-3-F

Dpq and dpq-3-F ligands were obtained from the Friedlander Reaction [14,15]. Concentrated sulfuric acid 1.0 ml was added to a solution of 1.972 g (10.0 mmol) of 2-aminobenzophenone and 1.169 g (10.0 mmol)

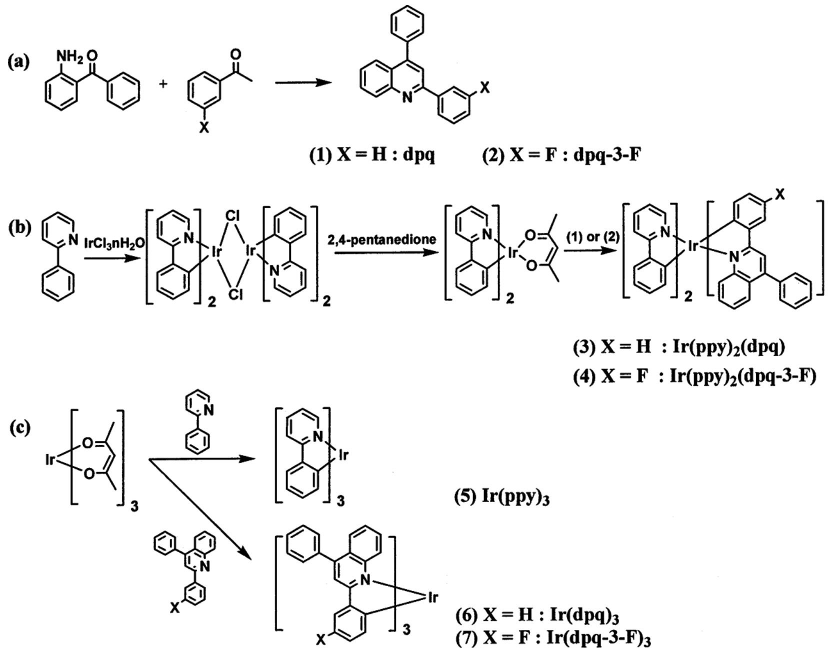

FIGURE 1 (a) Synthesis of C^N ligands, (b) synthesis of heteroleptic iridium complexes containing two different kinds of C^N ligands, and (c) synthesis of homoleptic iridium complexes containing one kind of C^N ligand.

of acetophenone (for dpq) or 1.126 g (10.0 mmol) of 3′-fluoroacetophenone (for dpq-3-F) in 30 ml of glacial acetic acid. The solution was heated to reflux for 4 h. The reaction mixture was then cooled and dripped slowly with stirring into an ice cold solution of 15 ml of concentrated ammonium hydroxide in 40 ml of water. The resultant yellow precipitate was filtered, washed with water, and dissolved in dichloromethane. The organic fraction was separated and dried over anhydrous $MgSO_4$, and pumped to dry. The solid was chromatographed on a silica gel column with dichloromethane (CH_2Cl_2).

2.1.2. Synthesis of Heteroleptic Ir(III) Complex : $Ir(ppy)_2(dpq)$, $Ir(ppy)_2(dpq\text{-}3\text{-}F)$

Cyclometalated Ir(III) μ-chloro-bridged dimers of the general formula, $(ppy)_2Ir(\mu\text{-}Cl)_2Ir(ppy)_2$, were synthesized by the method reported by Nonoyama with slight modification [16]. $IrCl_3{\cdot}H_2O$ (1.490 g, 5 mmol) and H_2O (10 ml) were added to a solution of ppy (1.78 ml, 12.5 mmol) in 2-ethoxyethanol (30 ml). The mixture was refluxed at 120°C under argon for 12 h and then cooled to room temperature. The solution mixture was evaporated under vacuum slowly to obtain the crude product $(ppy)_2Ir(\mu\text{-}Cl)_2Ir(ppy)_2$. The resultant precipitate was dissolved in dichloromethane and was filtered chromatographically on silica gel column with dichloromethane. The product portion was collected and dried in vacuum. $(ppy)_2Ir(\mu\text{-}Cl)_2Ir(ppy)_2$ (0.959 g, 0.51 mmol) and 2,4-pentanedione (0.17 ml, $d = 0.975$, 1.73 mmol) were mixed with Na_2CO_3 (250 mg) in 2-ethoxyethanol (30 ml). The mixture was refluxed for 2 h. The solution was cooled to room temperature and the yellow solid was filtered. $Ir(ppy)_2(acac)$ was obtained after the chromatographing on silica gel column with dichloromethane to yield a bright yellow powder. $Ir(ppy)_2(acac)$ (600.14 mg, 1 mmol) and L ligand ($L =$ dpq or dpq-3-F) (2 mmol) were dissolved in 20 ml of glycerol and refluxed for 10 h. After cooling, 20 ml of 1 N HCl solution was added and the resulting precipitate was filtered off. The residue was purified by silica gel chromatography using CH_2Cl_2.

2.1.3. Synthesis of Homoleptic Ir(III) Complex: $Ir(ppy)_3$, $Ir(dpq)_3$, $Ir(dpq\text{-}3\text{-}F)_3$

These complexes were prepared from $Ir(acac)_3$ and the corresponding ligand by a reported procedure [9]. $Ir(acac)_3$ (245 mg, 0.5 mmol) and ppy (or dpq, dpq-3-F) (2 mmol) were dissolved in 20 ml of glycerol and refluxed for 12 h. After cooling, 20 ml of 1 N HCl solution was added and the resulting precipitate was filtered off. The residue was purified by silica gel chromatography using CH_2Cl_2.

2.2. UV-Absorption and Photoluminescence (PL) Measurement

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

2.3. Theoretical Calculation

Calculations on the electronic ground states of ppy, dpq, dpq-3-F ligands, Ir(ppy)$_2$(dpq) and Ir(ppy)$_2$(dpq-3-F) were carried out using the B3LYP density functional theory (DFT) and compared with those of Ir(ppy)$_3$ and Ir(dpq)$_3$. LANL2DZ [17] and 6-31G(d) [18] basis sets were employed for Ir and the other atoms, respectively. For the calculated ground state geometries, the electronic structure is examined in terms of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs). And the electronic populations on the central atom were calculated to show the significant admixture of ligand π character with the amount of metal 5d character in the occupied molecular orbitals related to those MLCT transitions. To obtain the vertical excitation energies of the low-lying singlet and triplet excited states of the complexes, time-dependent density functional theory (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). Typically, the lowest 10 triplet and 10 singlet roots of the nonhermitian eigenvalue equations were obtained to get the vertical excitation energies and compared with the absorption spectra to examine each peak. The ground-state B3LYP and excited-state TD-DFT calculations were carried out using Gaussian 98 [19]. We noted that our results pertain only to the ground state geometry. If there are significant geometry changes in the excited state, the luminescence properties of complex could change significantly from the presented results. In addition, the TD-DFT results do not provide information on the oscillator strength of the triplet excited states since the spin-orbit coupling effects are not included in current TD-DFT results.

3. RESULTS AND DISCUSSION

In order to improve the luminescence efficiency by avoiding T-T annihilation, new phosphorescent 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 first group includes the iridium complexes having two different C^N ligand structures (heteroleptic complexes) such as Ir(ppy)$_2$(dpq) and Ir(ppy)$_2$(dpq-3-F) and the second one involves the iridium complexes having only one kind of C^N ligand (homoleptic complexes) such as Ir(ppy)$_3$, Ir(dpq)$_3$ and Ir(dpq-3-F)$_3$. The HOMO and LUMO energy levels of the ground state of ppy, dpq and dpq-3-F ligands were shown in Figure 2. Comparing HOMO and LUMO of dpq and dpq-3-F with those of ppy, we confirmed that the energy gaps between HOMO and LUMO of dpq and dpq-3-F come between that of ppy. 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) complexes having two ppy ligands and one dpq or dpq-3-F as a luminescent ligand. These complexes exhibit more red-shifting emission peak than Ir(ppy)$_3$ and have higher luminescence efficiency than that of homoleptic Ir(III) complexes, Ir(dpq)$_3$ and Ir(dpq-3-F)$_3$. The syntheses of ligands, heteroleptic complexes and homoleptic complexes are shown in Figure 1.

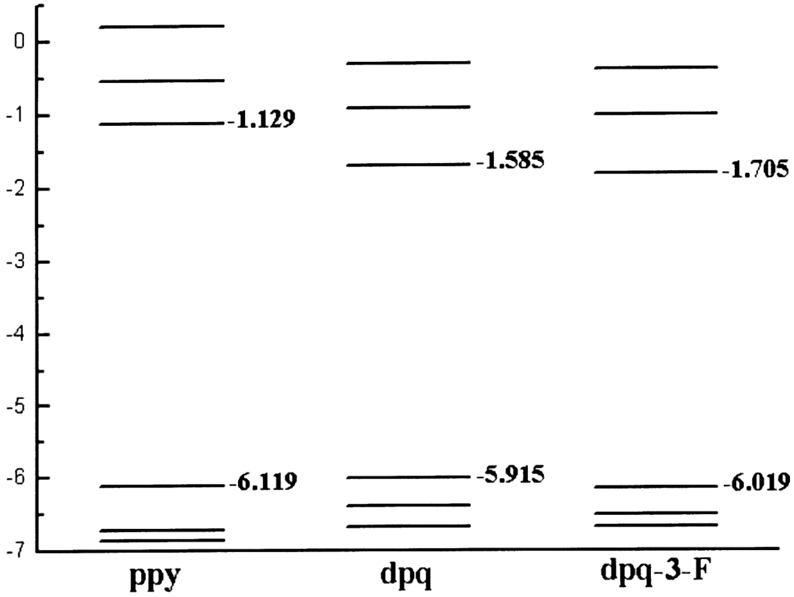

FIGURE 2 HOMO and LUMO energy levels of ppy, dpq and dpq-3-F ligand.

The UV-vis absorption spectra of heteroleptic and homoleptic complexes were compared and shown in Figure 3. The absorption wavelengths were red-shifted as ppy ligand was replaced with dpq or dpq-3-F ligand. Both ^{1}MLCT and ^{3}MLCT peaks are observed for these complexes, *vide infra*. The high degree of spin-orbit coupling is evident, reflecting the in comparing the oscillator strengths for the two MLCT peaks. Figure 3(a) shows the absorption spectra of the

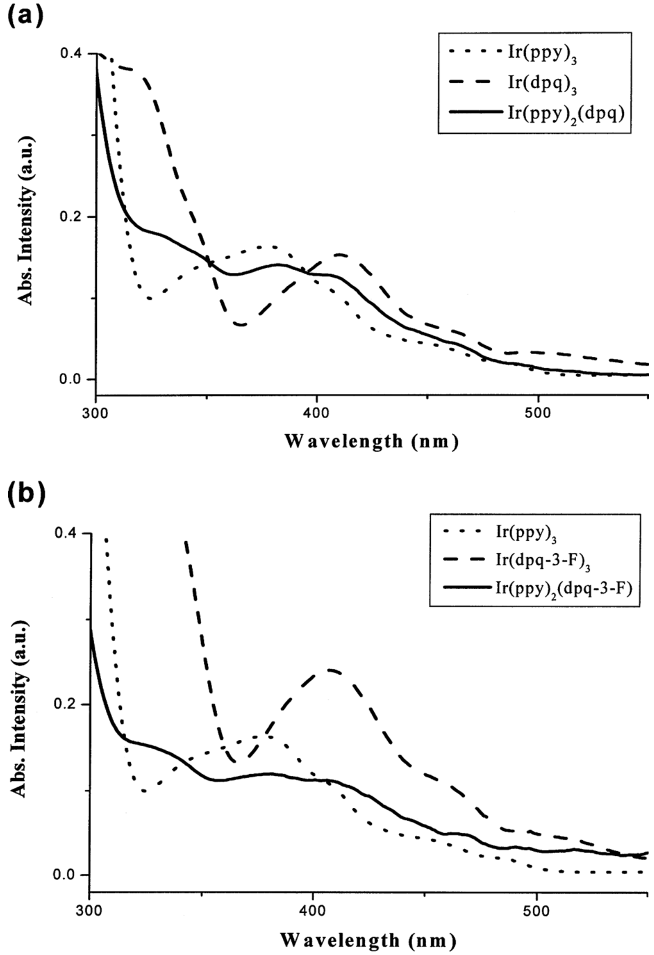

FIGURE 3 UV-vis absorption spectra of the homoleptic and heteroleptic iridium(III) complexes in 10^{-5} M CH_2Cl_2 at room temperature: (a) Ir(ppy)$_3$, Ir(dpq)$_3$ and Ir(ppy)$_2$(dpq), (b) Ir(ppy)$_3$, Ir(dpq-3-F)$_3$ and Ir(ppy)$_2$(dpq-3-F).

Ir(ppy)$_3$, Ir(dpq)$_3$ and Ir(ppy)$_2$(dpq) in 10^{-5} M CH_2Cl_2 at room temperature. The absorption peaks for Ir(ppy)$_3$ fall at 410, 460 and 490 nm, respectively, with less than a factor of two difference in their extinction coefficients. Strong spin-orbit coupling by the iridium center gives the formally spin-forbidden ^{3}MLCT intensity comparable to the allowed ^{1}MLCT one. The MLCT absorption peaks of Ir(ppy)$_2$(dpq) are observed at 410, 460, 480 and 530 nm where MLCT peaks of Ir(ppy)$_3$ as well as of Ir(dpq)$_3$ are located. The characteristic of the MLCT absorption spectra for Ir(ppy)$_2$(dpq) and for Ir(dpq)$_3$ are also very similar. It provides that MLCT absorption of the Ir(ppy)$_2$(dpq) occurs at the ppy as well as dpq ligands.

The absorption spectra of Ir(ppy)$_3$, Ir(dpq-3-F)$_3$ and Ir(ppy)$_2$(dpq-3-F) in CH_2Cl_2 are shown in Figure 3(b). The characteristic of the MLCT absorption spectra for Ir(ppy)$_2$(dpq-3-F) resembles that of Ir(dpq-3-F)$_3$ and their intensities are close to these of Ir(ppy)$_3$. The MLCT absorption peaks of Ir(dpq-3-F)$_3$ occur at 460 and 530 nm, respectively. However, the MLCT absorption peaks of Ir(ppy)$_2$(dpq-3-F) are observed at 410, 460, 480, and 530 nm where the MLCT peaks of both Ir(ppy)$_3$ and Ir(dpq-3-F)$_3$ are located. In addition, the characteristics of the MLCT absorption spectra for Ir(ppy)$_2$(dpq-3-F) and Ir(dpq-3-F)$_3$ are very similar. It indicates the evidence that MLCT absorption of the Ir(ppy)$_2$(dpq-3-F) occurs at ppy ligand as well as at dpq-3-F ligand.

In spite of the similar absorption characteristic of two heteroleptic complexes, the emission mechanism of Ir(ppy)$_2$(dpq) is different from that of Ir(ppy)$_2$(dpq-3-F). This emission mechanism difference originates from the energy level difference in HOMOs and LUMOs. The emission spectra of the homoleptic and heteroleptic complexes in 10^{-5} M CH_2Cl_2 at room temperature are shown in Figure 4. The maximum and the second emission peaks of Ir(ppy)$_2$(dpq) were the same as those of Ir(ppy)$_3$ and Ir(dpq)$_3$ at 514 and 591 nm, respectively. In addition, the emission spectrum of Ir(ppy)$_2$(dpq-3-F) shows the similar trend with that of Ir(ppy)$_2$(dpq). The greenish emission peak of Ir(ppy)$_2$(dpq-3-F) was the same as that of Ir(ppy)$_3$ at 514 nm, while reddish one was observed at 601 nm. The fluorine of dpq-3-F ligand acts as a withdrawing functional group, leading to the lower energy levels of the ligand. In the case of dpq ligand, the decreasing tendency of the LUMOs is rather drastic than that of the HOMOs as shown in Figure 2. As a result, the emission peak of Ir(ppy)$_2$(dpq-3-F) is more reddish than that of Ir(ppy)$_2$(dpq). However, intensities of the maximum and the second higher peaks show the contrast compared to those were on the contrary to that of Ir(ppy)$_2$(dpq). HOMO and LUMO energy levels of the ground state of Ir complexes containing

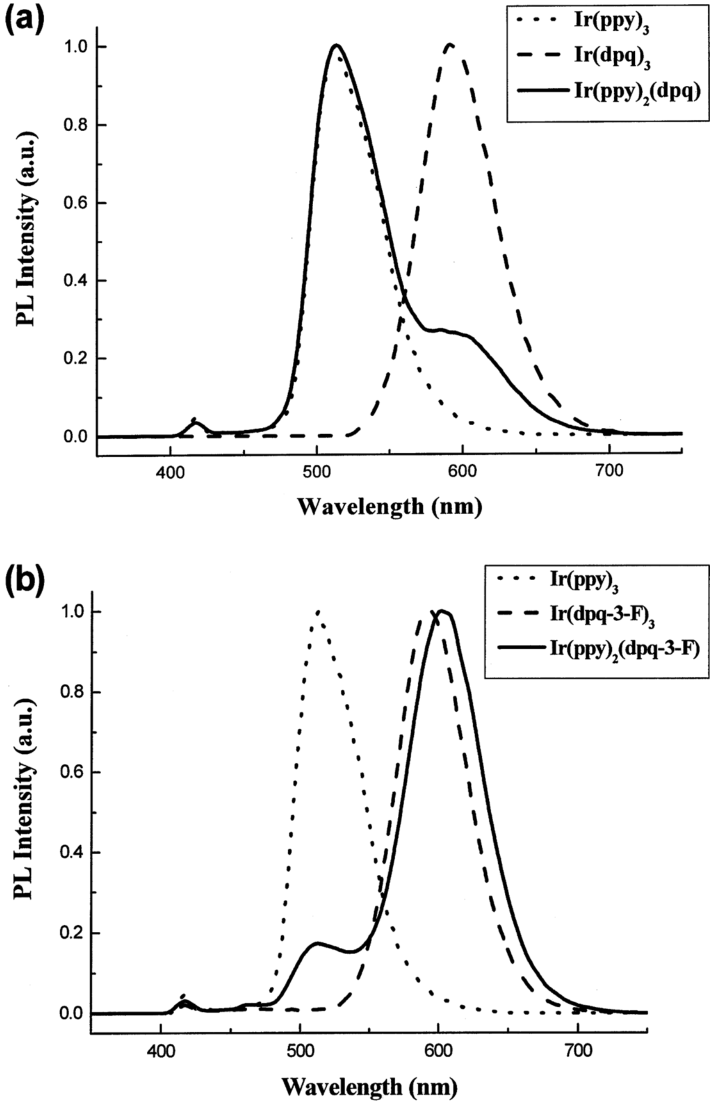

FIGURE 4 Phosphorescence spectra of the homoleptic and heteroleptic iridium(III) complexes in 10^{-5} M CH_2Cl_2 at room temperature: (a) $Ir(ppy)_3$, $Ir(dpq)_3$ and $Ir(ppy)_2(dpq)$, (b) $Ir(ppy)_3$, $Ir(dpq\text{-}3\text{-}F)_3$ and $Ir(ppy)_2(dpq\text{-}3\text{-}F)$.

both ppy and dpq were −5.56 eV, −2.63 eV, −5.10 eV and −2.60 eV respectively, as shown in Table 1. As shown in Figure 5, by comparing HOMOs and LUMOs of $Ir(dpq)_3$ with those of $Ir(ppy)_3$, we confirm that

TABLE 1 Photophysical Characteristic of $Ir(ppy)_2(acac)$ and $Ir(dpq)_2(acac)$

	Absorbance λ (log ε)	Emission λ_{max}(nm)	Q.Y.	HOMO (eV)	LUMO (eV)
$Ir(ppy)_2(acac)$[1]	260(4.5), 345(3.8), 412(3.4), 460(3.3), 497(3.4)	516	0.34	−5.10	−2.60
$Ir(dpq)_2(acac)$[2]	275(4.6), 342(4.1), 432(3.5), 474(3.4), 553(3.1)	614	0.14	−5.56	−2.63

[1] Ref. [13].
[2] Ref. [12].

the HOMO levels of the homoleptic complex containing dpq are located between HOMO and LUMO levels of the homoleptic complex containing ppy. However, because the LUMO levels of the complex containing dpq exist higher than those of the complex containing ppy, the absorption energy of ppy groups can not transfer to dpq groups. Therefore, in the case of the emission mechanism of $Ir(ppy)_2(dpq)$, emission can show more strongly in the green region than in the red region. On the contrary, the HOMO and LUMO levels of the complex containing dpq-3-F are located between those of ppy due to the effect by fluorine. As a result, the absorption energy of ppy groups can transfer to the dpq group. Therefore, in the case of the emission mechanism of $Ir(ppy)_2(dpq\text{-}3\text{-}F)$, the emission, in fact, show strongly in the red region than in the green region.

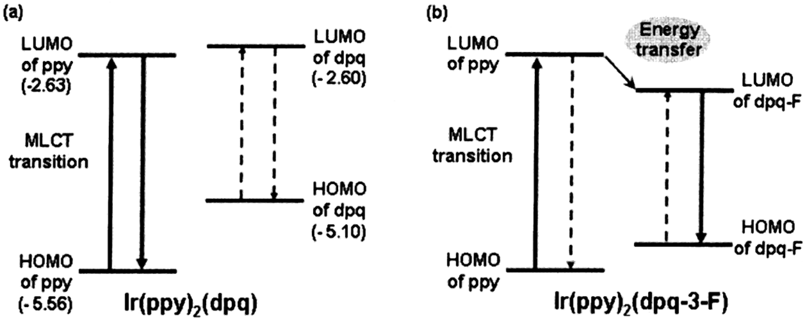

FIGURE 5 (a) Absorption and emission mechanism of $Ir(ppy)_2(dpq)$ and (b) absorption and emission mechanism of $Ir(ppy)_2(dpq\text{-}3\text{-}F)$.

4. CONCLUSIONS

In summary, we report the detailed syntheses and photophysical properties of the phosphorescent iridium(III) complexes having a different species of plural (C^N) ligands in order to improve the luminescence efficiency by avoiding T-T annihilation. We have thus synthesized the iridium complexes such as Ir(ppy)$_2$(dpq) and Ir(ppy)$_2$(dpq-3-F) and studied their photophysical properties for the application in OLEDs. As a result, high LUMO levels of the dpq group make energy transfer from ppy group forbidden. In the case of Ir(ppy)$_2$(dpq-3-F), energy levels of HOMO and LUMO exist between those of the complex containing ppy. Thus, Ir(ppy)$_2$(dpq-3-F) emits red light, receiving absorption energy of ppy group. Therefore, Ir(ppy)$_2$(dpq-3-F) allows a high efficiency luminescence and a red emission color originated from dpq-3-F ligand.

REFERENCES

[1] Tang, C. W. & VanSLyke, S. A. (1987). *Appl. Phys. Lett.*, *51*, 913.
[2] Baldo, M. A., Thompson, M. E., & Forrest, S. R. (2000). *Nature*, *403*, 750.
[3] Lamansky, S., Djurovich, P., Murphy, D., Abdel-Razzaq, F., Lee, H. E., Adachi, C., Burrow, P. E., Forrest, S. R., & Thompson, M. E. (2001). *J. Am. Chem. Soc.*, *123*, 4304.
[4] Park, N. G., Kwak, M. Y., Kim, B. O., Kwon, O. K., Kim, Y. K., You, B. R., Kim, T. W., & Kim, Y. S. (2002). *Jpn. J. Appl. Phys.*, *41*, 1523.
[5] Park, N. G., Lee, J. E., Park, Y. H., & Kim, Y. S. (2004). *Syth. Met.*, *145*, 279.
[6] Lamansky, S., Djurovich, P., Murphy, D., Abdel-Razzaq, F., Kwong, R., Tsyba, I., Bortz, M., Mui, B., Bau, R., & Thompson, M. E. (2001). *Inorg. Chem.*, *40*, 1704.
[7] Baldo, M. A., Thompson, M. E., & Forrest, S. R. (1999). *Pure Appl. Chem.*, *71*, 2095.
[8] Brooks, J., Babaya, T., Lamansky, S., Djurovich, P. I., Tsyba, I., Bau R., & Thompson, M. E. (2002). *Inorg. Chem.*, *41*, 3055.
[9] Kohler, A., Wilson, J. S., & Friend, R. H. (2002). *Adv. Mater.*, *14*, 701.
[10] Tamayo, A. B., Alleyne, B. D., Djurovich, P. I., Lamansky, S., Tsyba, I., Ho, N. N., Bau, R., & Thompson, M. E. (2003). *J. Am. Chem. Soc.*, *125*, 7377.
[11] Rho, H. H., Lee, Y. H., Park, Y. H., Park, G. Y., Ha, Y. K., & Kim, Y. S. (2006). *Jpn. J. Appl. Phys.*, *45*, 568.
[12] Tsuboyama, A., Iwawaki, H., Furugori, M., Mukaide, T., Kamatani, J., Igawa, S., Moriyama, T., Miura, S., Takiguchi, T., Okada, S., Hoshino, M., & Ueno, K. (2003). *J. Am. Chem. Soc.*, *125*, 12971.
[13] Wu, F. I., Su, H. J., Shu, C. F., Luo, L., Diau, W. G., Cheng, C. H., Duan, J. P., & Lee, G. H. (2005). *J. Mater. Chem.*, *15*, 1035.
[14] Imai, Y., Johnson, E. F., Katto, T., Kurihara, M., & Sittle, J. K. (1975). *J. Polym. Sci. Polym. Chem. Ed.*, *13*, 2233.
[15] Zhang, X., Fan, X., Wang, J., & Li, Y. (2004). *J. Chin. Chem. Soc.*, *51*, 1339.
[16] Nomoyama, M. (1975). *J. Organomet. Chem.*, *86*, 263.
[17] Hay, P. J. & Wadt, W. R. (1985). *J. Chem. Phys.*, *82*, 270.
[18] Hehre, W. J., Ditchfield, R., & Pople, J. A. (1972). *J. Chem. Phys.*, *56*, 2257.
[19] Frisch, M. J. *et al.* (1988). Gaussian 98, Revision A.9, Gaussian, Inc., Pittsburgh, PA.