



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl20>

Synthesis and Photophysical Studies of Heteroleptic Tris-Cyclometalated Ir(III) Complex for Red OLED

Gui Youn Park ^a, In Joon Kim ^a & Young Sik Kim ^b

^a Department of Information Display Engineering, Hongik University, Seoul, Korea

^b Department of Science and Center for Organic Materials and Information Devices, Hongik University, Seoul, Korea

Version of record first published: 22 Sep 2010

To cite this article: Gui Youn Park, In Joon Kim & Young Sik Kim (2007): Synthesis and Photophysical Studies of Heteroleptic Tris-Cyclometalated Ir(III) Complex for Red OLED, *Molecular Crystals and Liquid Crystals*, 471:1, 235-244

To link to this article: <http://dx.doi.org/10.1080/15421400701548316>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Synthesis and Photophysical Studies of Heteroleptic Tris-Cyclometalated Ir(III) Complex for Red OLED

Gui Youn Park

In Joon Kim

Department of Information Display Engineering, Hongik University,
Seoul, Korea

Young Sik Kim

Department of Science and Center for Organic Materials and
Information Devices, Hongik University, Seoul, Korea

The synthesis and photophysical study of efficient phosphorescent iridium(III) complex having two different (C[^]N) ligands are reported. In order to improve the luminescence efficiency by avoiding triplet–triplet (T–T) annihilation and study luminescent mechanism of the heteroleptic iridium complex, Ir(piq-3F)₂(dpq-4F) is designed and prepared where piq-3F and dpq-4F represent 1-(4'-fluorophenyl)isoquinoline and 2-(3'-fluorophenyl)-4-phenylquinoline, respectively. We thought that both piq-3F and dpq-4F ligands can act as a source of energy supply because of the relative HOMO energy level and the luminescence lifetime of homoleptic Ir complexes Ir(piq-3F)₃ Ir(dpq-4F)₃. However the UV-vis absorption spectra and the PL spectra of Ir(piq-3F)₂(dpq-4F) is more similar to that of Ir(piq-3F)₃. In spite of lower triplet energy level of dpq-4F, the excitation energy is not intramolecular transferred from two piq-3F ligands to one dpq-4F ligand. The luminescence occurs mainly at piq-3F ligand. It is due to the strong MLCT characteristic of piq-3F ligand. To analyze luminescent mechanism, we calculated these complexes theoretically by using computational method.

Keywords: DFT; Ir(piq-3F)₂(dpq-4F); OLED; red phosphorescence

1. INTRODUCTION

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

This work was supported by 2007 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 radiative 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 and study luminescent mechanism of the heteroleptic iridium complex, 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. In the before article, we reported Ir complexes having this luminescent mechanism. The complexes were designed on ligand exhibiting the great difference of the lifetime and the MLCT characteristic.

Herein, we report efficient phosphorescent emitters having different ligands, Ir(piq-3F)₂(dpq-4F). Previously, Ir(piq-3F)₃ and Ir(dpq-4F)₃ were known to have high phosphorescence efficiencies in electroluminescent (EL) emissions near 608 and 620 nm, respectively, because they had the metal-to-ligand charge transfer (MLCT) excited states with the similar luminescence lifetime [12,13]. The purpose of the present study is to design the 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. Synthesis and Characterization

All reagents were purchased from Aldrich except Ir(III) trichloride hydrate ($\text{IrCl}_3 \cdot \text{H}_2\text{O}$) 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: *piq-3F*

1-(4-fluorophenyl)isoquinoline ligands, *piq-F*, were obtained from the reaction of 1-chloroisoquinoline with the corresponding 4-fluorophenylboronic acids by Suzuki coupling. 1-chloroisoquinoline (0.899 g, 5.5 mmol), 4-fluorophenylboronic acid (0.699 g, 5 mmol) and tetrakis-triphenylphosphine palladium(0) (0.196 g, 0.17 mmol) were placed in

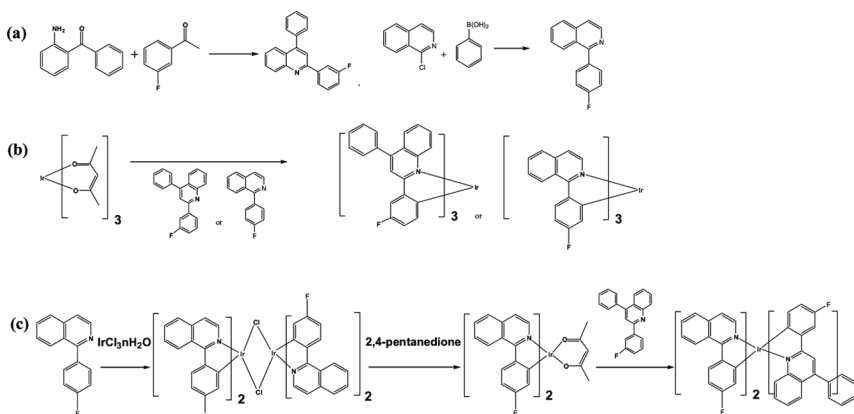


FIGURE 1 (a) Synthesis of C^N Ligands. (b) Synthesis of heteroleptic Iridium(III) complexes containing two different kinds of C^N ligands. (c) Synthesis of homoleptic Iridium(III) complexes containing one kind of C^N ligand.

20 ml of toluene, 10 ml of ethanol and 20 ml of 2 N sodium carbonate aqueous solution. The mixture was heated to reflux for 15 hr. The mixture was cooled to room temperature and extracted with 20 ml of ethyl acetate. The organic fraction were dried over anhydrous MgSO_4 , filtered and pumped dry. The residue was chromatographed on a silica gel column with ethyl acetate/hexane (1:3). The product were collected and dried in vacuum to yield white powder in 64% yield.

2.1.2. Synthesis of Ligand: dpq-3F

dpq-3F ligand was obtained from the Friedlander reaction [14,15]. The concentrated sulfuric acid of 1.0 ml was added to a solution of 1.972 g (10.0 mmol) of 2-aminobenzophenone and 1.381 g (10.0 mmol) of 3'-fluoroacetophenone (for dpq-4F) 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 icy concentrated ammonium hydroxide solution of 15 ml of 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).

2.1.3. Synthesis of Heteroleptic Ir(III) Complex: Ir(piq-3F)₂(dpq-4F)

Cyclometalated Ir(III) μ -chloro-bridged dimers of the general formula, $(\text{piq-3F})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{piq-3F})_2$, were synthesized by the method reported by Nonoyama with slight modification [16]. $\text{IrCl}_3 \cdot \text{H}_2\text{O}$ (1.490 g, 5 mmol) and H_2O (10 ml) were added to a solution of piq-3F (12.5 mmol) in 2-ethoxyethanol (30 ml). The mixture was refluxed at 120°C under the argon atmosphere for 12 h and then cooled to room temperature. The solution mixture was evaporated under the vacuum slowly to obtain the crude product $(\text{piq-3F})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{piq-3F})_2$. 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. $(\text{piq-3F})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{piq-3F})_2$ (0.51 mmol) and 2,4-pentanedione ($d = 0.975$, 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. $\text{Ir}(\text{piq-3F})_2(\text{acac})$ was obtained after the chromatographing on silica gel column with dichloromethane to yield a bright yellow powder. $\text{Ir}(\text{piq-3F})_2(\text{acac})$ (1 mmol) and dpq-3F ligand (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 .

2.1.4. Synthesis of Homoleptic Ir(III) Complex: $\text{Ir}(\text{piq-3F})_3$, $\text{Ir}(\text{dpq-4F})_3$

These complexes were prepared from $\text{Ir}(\text{acac})_3$ and the corresponding ligand by a reported procedure [9]. $\text{Ir}(\text{acac})_3$ (245 mg, 0.5 mmol) and piq-3F (or dpq-4F) (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 8425 A spectrometer. The PL spectra were obtained on Perkin Elmer LS 50B spectrometer. UV-Vis and PL spectra of $\text{Ir}(\text{piq-3F})_3$, $\text{Ir}(\text{dpq-4F})_3$ and $\text{Ir}(\text{piq-3F})_2(\text{dpq-4F})$ were measured with a 10^{-5} M dilute solution in CH_2Cl_2 .

2.3. Theoretical Calculation

Calculations on the electronic ground states of piq-3F , dpq-4F ligands and $\text{Ir}(\text{piq-3F})_2(\text{dpq-4F})$ were carried out using the B3LYP density functional theory (DFT) and compared with those of $\text{Ir}(\text{piq-3F})_3$ and $\text{Ir}(\text{dpq-4F})_3$. LANL2DZ [17] and 6-31G(d) [18] basis sets were employed for Ir and the other atoms, respectively. Through the calculation of the ground state geometry, the electronic structure is examined in terms of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs). 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. We noted that our results were performed to the molecules only in 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 state since the spin-orbit coupling effect is not included in current TD-DFT results.

3. RESULTS AND DISCUSSION

In order to improve the luminescence efficiency by avoiding T–T annihilation and to study the luminescent mechanism of the heteroleptic iridium complex, Ir(piq-3F)₂(dpq-4F) is 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(piq-3F)₂(dpq-4F) and the second one involves the iridium complexes having only one kind of C[^]N ligand (homoleptic complexes) such as Ir(piq-3F)₃ and Ir(dpq-4F)₃. 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 piq-3F ligands and one of dpq-4F. The syntheses of ligands, heteroleptic complexes and homoleptic complexes are shown in Figure 1.

The HOMO and LUMO energy levels of the ground state of homoleptic Ir(III) complexes of piq-3F and dpq-4F ligands were shown in Figure 2. Comparing HOMO and LUMO energy levels of piq-3F and dpq-4F complexes, we confirmed that HOMO and LUMO energy level of dpq-4F complex are located between those of piq-4F. So, in the case of Ir(piq-3F)₂(dpq-4F), we expected that the excited energy is absorbed in piq-3F because of strong MLCT characteristic, that the excitation energy is transferred from piq-3F to dpq-4F, because the dpq-4F has lower LUMO energy level than that of the piq-3F. But experimental result does not agree perfectly with expectation.

The UV-vis absorption spectra of heteroleptic and homoleptic Ir(III) complexes, Ir(piq-3F)₃, Ir(dpq-4F)₃ and Ir(piq-3F)₂(dpq-4F) in 10^{−5} M CH₂Cl₂ at room temperature were shown in Figure 3. Both ¹MLCT and ³MLCT peaks are observed for these complexes. The absorption peaks of Ir(piq-3F)₃ is located at 400, 460, 480 and 520 nm. The absorption bands below 420 nm can be assigned to the spin-allowed ¹π – π* transition and the band around 460 nm to a spin-allowed ¹MLCT band and the band around 480 and 520 nm can be assigned to a spin-forbidden ³MLCT band. MLCT absorption is allowed by the strong mixing

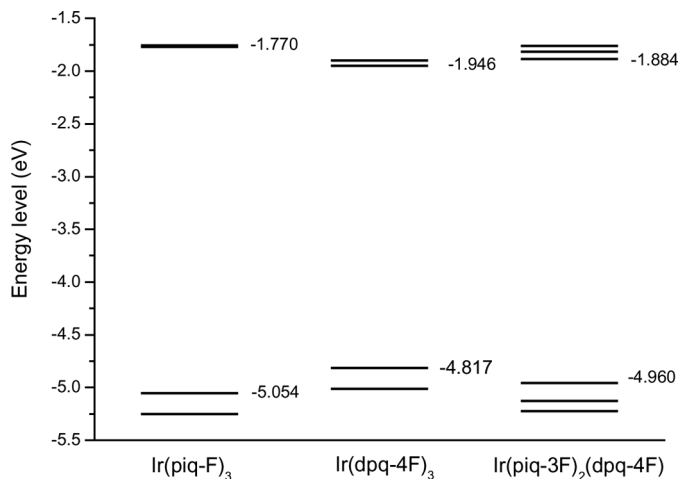


FIGURE 2 HOMO and LUMO energy levels of Ir(piq-3F)₃ and Ir(dpq-4F)₃ complexes.

between the π character of the ligand and the 5d character of the centric metal in HOMOs. The MLCT absorption peaks of Ir(dpq-4F)₃ are observed at 410, 460, 480 and 550 nm. The overall profile of

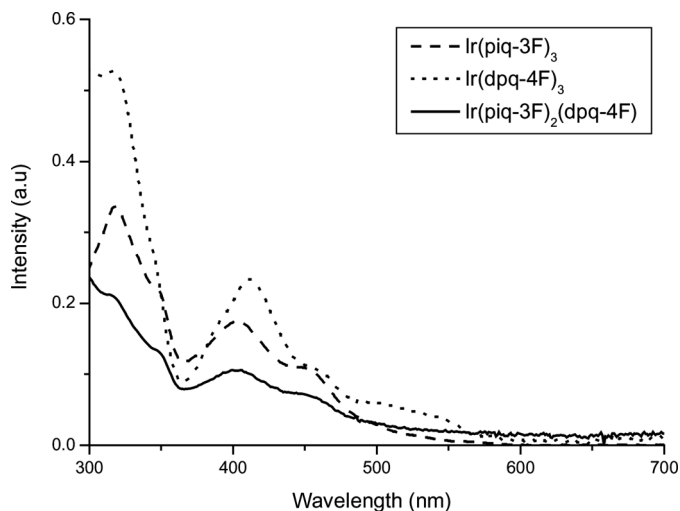


FIGURE 3 UV-vis absorption spectra of Ir(piq-3F)₃, Ir(dpq-4F)₃ and Ir(piq-3F)₂(dpq-4F) in 10⁻⁵ M CH₂Cl₂.

absorption spectrum and the peak position of the MLCT absorption of the heteroleptic $\text{Ir}(\text{piq-3F})_2(\text{dpq-4F})$ are very similar to those of $\text{Ir}(\text{piq-3F})_3$. It provides the evidence that MLCT absorption of the heteroleptic $\text{Ir}(\text{piq-3F})_2(\text{dpq-4F})$ occurs mainly at the piq-3F ligand. Because MLCT characteristic of $\text{Ir}(\text{piq-3F})_3$ is stronger than that of $\text{Ir}(\text{dpq-4F})_3$, MLCT absorption is allowed mainly by the piq-3F ligand.

The PL spectra of the homoleptic and heteroleptic complexes on CH_2Cl_2 are shown in Figure 4. The PL spectra of $\text{Ir}(\text{piq-3F})_2(\text{dpq-4F})$ and $\text{Ir}(\text{piq-3F})_3$ show an emission band at 594 nm, while $\text{Ir}(\text{dpq-4F})_3$ show the maximum emission peak at 604 nm. We expected that the heteroleptic complex $\text{Ir}(\text{piq-3F})_2(\text{dpq-4F})$ has red-shifted emission peak than that of $\text{Ir}(\text{piq-3F})_3$ by emitting from the mixed state of piq-3F and dpq-4F ligands. However, the PL spectra of $\text{Ir}(\text{piq-3F})_2(\text{dpq-4F})$ is similar to that of $\text{Ir}(\text{piq-3F})_3$. Therefore, the luminescence occurs mainly at piq-3F ligand. The dpq-4F ligand acts not as an emitting ligand but as an ancillary ligand to increase the luminescence efficiency by avoiding T-T annihilation.

In order to examine which ligand mainly contributes to the MLCT transition process of $\text{Ir}(\text{piq-3F})_2(\text{dpq-4F})$, the d-orbital characteristics of HOMOs and LUMOs were investigated after geometry optimization of the molecular structure of this complex using the density functional theory (DFT). In Figure 5, contour plots of the three highest HOMOs and three lowest LUMOs of $\text{Ir}(\text{piq-3F})_2(\text{dpq-4F})$ are shown. These

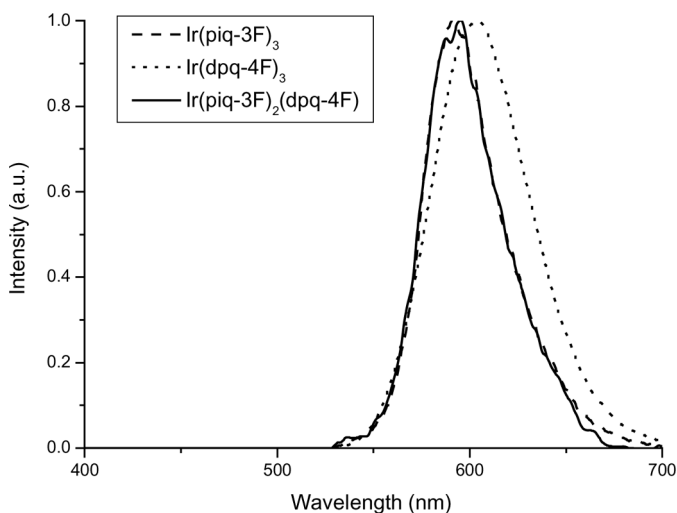


FIGURE 4 PL spectra of $\text{Ir}(\text{piq-3F})_3$, $\text{Ir}(\text{dpq-4F})_3$ and $\text{Ir}(\text{piq-3F})_2(\text{dpq-4F})$.

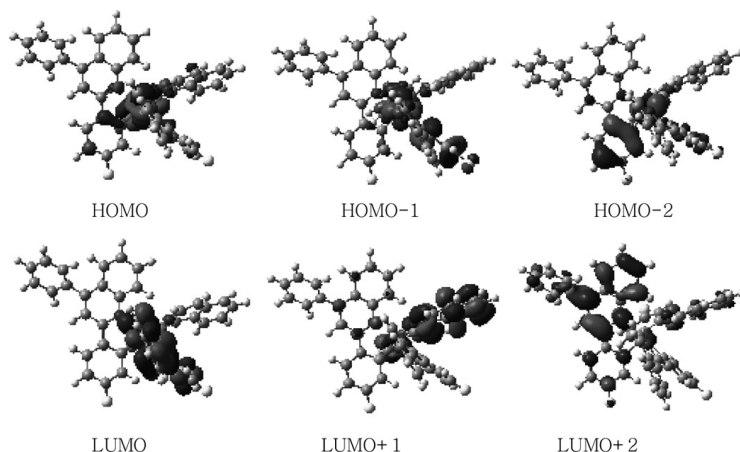


FIGURE 5 Contour plots of HOMOs and LUMOs of $\text{Ir}(\text{piq-3F})_2(\text{dpq-4F})$ where dpq-4F ligand is located at the left side.

orbitals are important because dominant excitations and emissions mainly occur due to the electronic transition among those orbitals. Three HOMOs and LUMOs show to have orbitals that are localized mainly in piq-3F ligands, where the calculated electron population in centric Ir atom is 49.34%. It concluded that three HOMOs and three LUMOs have different characters with respect to each other, as the former has mainly the strong metallic character of the 5d orbital of the centric Ir atom while the latter has the character of the piq-3F ligand. It shows that the electronic transition between those orbitals would be the MLCT. MLCT has been known to occur when the $\text{Ir}(\text{III})$ complex illuminates intensified phosphorescent light. $\text{Ir}(\text{piq-3F})_2(\text{dpq-4F})$ has a large electron population of 49.34%, which is rather similar to that of $\text{Ir}(\text{ppy})_3$ (51%) as known strong MLCT material. Therefore, it is expected that $\text{Ir}(\text{piq-3F})_2(\text{dpq-4F})$ may have a high phosphorescence emitting characteristics.

In the luminescent mechanism of $\text{Ir}(\text{piq-3F})_2(\text{dpq-4F})$, the excited energy absorption and the luminescence occur mainly at the piq-3F ligand because of strong MLCT characteristic of piq-3F ligand. Also, because the radiative lifetime of $\text{Ir}(\text{piq-3F})_3$ is shorter than that of $\text{Ir}(\text{dpq-4F})_3$. As a result, light emits with the red emission from piq-3F ligand. Thus it allows a monochromatic luminescent color. The luminescence intensity of $\text{Ir}(\text{piq-3F})_2(\text{dpq-4F})$ is stronger than that of $\text{Ir}(\text{piq-3F})_3$ and $\text{Ir}(\text{dpq-4F})_3$ because it is improved the luminescent by the decrease of quenching or energy deactivation.

4. CONCLUSIONS

In summary, we report the detailed syntheses and photophysical properties of the phosphorescent iridium(III) complex having a different species of plural (C[^]N) ligands in order to improve the luminescence efficiency by avoiding T–T annihilation and study luminescent mechanism of the heteroleptic iridium complex. We have synthesized the iridium complex such as Ir(piq-3F)₂(dpq-4F) and studied their photophysical properties for the application in OLEDs. As a result, in the case of Ir(piq-3F)₂(dpq-4F), the excited energy is absorbed mainly from piq-3F ligands and the excitation energy is not intramolecular transferred to dpq-4F ligand but emits in piq-3F, because of stronger MLCT characteristic and shorter lifetime of piq-3F. Therefore the absorption and luminescence is concerned on piq-3F. The dpq-3F ligand increases the luminescence efficiency by avoiding T–T annihilation.

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). *Synth. 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., Diao, 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.