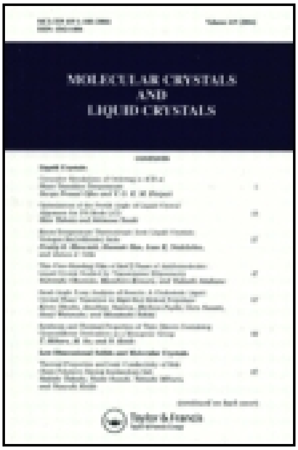

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Seung-Chan Lee [a] & Young Sik Kim [a b]

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

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

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Synthesis and Characterization of Red-emitting Iridium Complexes of 5′-Substituted 2,4-diphenylquinolines

Seung-Chan Lee[1] and Young Sik Kim[1,2]
[1]Department of Information Display, Hongik University, Seoul, Korea
[2]Department of Science, Hongik University, Seoul, Korea

To examine the substituent effect, 5′-substituted 2,4-diphenylquinoline (dpq) ligands and their iridium complexes, Ir(dpq)$_2$(acac), Ir(dpq-5F)$_2$(acac), Ir(dpq-5CH$_3$)$_2$(acac) and Ir(dpq-5OCH$_3$)$_2$(acac), were synthesized and prepared, and the photophysical properties were investigated for red electro-phosphorescent materials. The 5′-substituted phenyl ring generated 3′-positon and 5′-position isomers. However, the 5′-position of the phenyl ring is more stable than the 3′-position due to steric effects. The maximum emission wavelengths of Ir(dpq)$_2$(acac), Ir(dpq-5F)$_2$(acac), Ir(dpq-5CH$_3$)$_2$(acac) and Ir(dpq-5OCH$_3$)$_2$(acac) were found at 612, 606, 616, 606 nm, respectively. The emission spectrum of Ir(dpq-5CH$_3$)$_2$(acac) was red shifted compared to that of Ir(dpq)$_2$(acac) because the methyl group substituted on the 5′-position of the phenyl ring is an electron donating group. Ir(dpq-5F)$_2$(acac) shows highly efficient and blue-shifted luminescence because the electron withdrawing group (-F) substitute on the 5′-position of the phenyl ring lowered the HOMO level slightly. Hence MLCT coupling is increased and blue shifted luminescence by 6 nm was observed compared to Ir(dpq)$_2$(acac). Especially, Ir(dpq-5OCH$_3$)$_2$(acac) shows blue-shifted phosphorescence due to the effect of the electron withdrawing methoxyphenyl group onto the iridium atom. This destabilized the MLCT state and leads to an increased in the emission energy.

Keywords: iridium complex; luminescence; OLED; phosphorescence; red

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

1. INTRODUCTION

Electroluminescent (EL) organic materials have received much of attention due to their potential application in flat-panel displays and to the rapid progress in material design and device fabrication in recent years [1–5]. Thompson *et al.* have developed electrophosphorescent OLEDs with a high efficiency approaching 100% of the internal quantum efficiency, which utilize both singlet and triplet excitons produced at the emitting layer doped with the phosphorescent dopants [6,7]. Heavy metals such as iridium or platinum in their complex forms are known to induce intersystem crossing by strong spin-orbit coupling, leading to mixing of the singlet and triplet excited states. Thus, iridium complexes are known to have high photoluminescence (PL) efficiency and a relatively short excited state lifetime, which minimizes quenching of triplet emissive states [8,9]. Recently, $Ir(dpq)_2(acac)$, a red phosphorescent emitter, has been reported to have an emission peak at 606 nm, and the EL properties were shown to include a maximum brightness of 17457 cd/m^2 and a maximum quantum efficiency as high as 6.1% with CIE coordinates of $x = 0.61$ and $y = 0.30$ [10].

In this article, we have designed and synthesized iridium complexes, $Ir(dpq)_2(acac)$, $Ir(dpq\text{-}5F)_2(acac)$, $Ir(dpq\text{-}5CH_3)_2(acac)$ and $Ir(dpq\text{-}5OCH_3)_2(acac)$ and investigated the photophysical properties to examine the 5′-substituent effect of 2,4-diphenylquinoline (dpq) ligands.

2. EXPERIMENTAL DETAILS

2.1. Synthesis

All reagents were purchased from Aldrich Co., except Ir(III) trichloride hydrate ($IrCl3 \cdot H_2O$), which was purchased from Strem Co. 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 Co).

2.1.1. *Synthesis of Ligands (dpq, dpq-5F, dpq-5OCH$_3$ and dpq-5CH$_3$)*

These ligands were obtained from the Friedlander Reaction as illustrated in Figure 1 [11,12]. 2-aminobenzophenone, 5-methyl-2-aminobenzophenone or 5-metoxy-2-aminobenzophenone (10.0 mmol) was mixed with acetophenone (10.0 mmol) in 30 ml of glacial acetic acid according to the procedure described above. (Yield: dpq-5CH_3 2.42 g, 74%, dpq-5OCH_3 2.37 g, 69%).

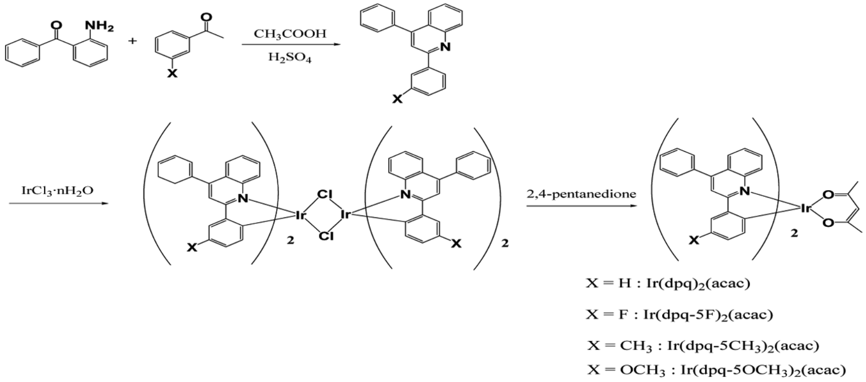

FIGURE 1 Synthesis of C^N ligands and their iridium complexes [Ir(C^N)$_2$(acac)].

2.1.2. *Synthesis of Complexes: Ir(dpq-X)$_2$(acac). (X = H, F, –CH$_3$ and –OCH$_3$)*

The cyclometalated Ir(III) μ-chloro-bridged dimer, (dpq-X)$_2$Ir (μ-Cl)$_2$Ir(dpq-X)$_2$ was synthesized by the method reported by Nonoyama with slight modification as illustrated in Figure 1 [13]. $IrCl_3 \cdot H_2O$ (0.418 g, 1.4 mmol) and H_2O (10 ml) were added to a solution of dpq-X (3.5 mmol) in 2-ethoxyethanol (30 ml). The mixture was refluxed at 120°C under argon for 30 hr and then cooled to room temperature. The solution mixture was slowly evaporated under vacuum to obtain the crude dimer, (dpq-X)$_2$Ir(μ-Cl)$_2$Ir(dpq-X)$_2$. The resultant precipitate was dissolved in dichloromethane and was chromatographed on silica gel column with dichloromethane. The dimer product was collected and dried in vacuum. (dpq-X)$_2$Ir(μ-Cl)$_2$Ir(dpq-X)$_2$ (0.50 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 hr. The solution was cooled to room temperature and the red solid was filtered. Ir(dpq-X)$_2$(acac) was obtained after chromatography on silica gel column with dichloromethane and solvent evaporation.

2.2. Optical Measurements

UV-Vis absorption spectra were measured on a Hewlett Packard 8425A spectrometer. PL spectra were measured on a Perkin Elmer LS 50B spectrometer. UV-Vis and PL spectra of iridium complexes were measured in 10^{-5} M dilute CH_2Cl_2 solution.

2.3. Theoretical Calculations

Calculations on the electronic ground states of Ir(dpq)$_2$(acac), Ir(dpq-5CH$_3$)$_2$(acac), Ir(dpq-5OCH$_3$)$_2$(acac), Ir(dpq-5 F)$_2$(acac) were carried out using Gaussian 98. The basis set of ligands was changed to 6–31 + G(d). LANL2DZ and 6–31G(d) basis sets were employed for Ir and the other atoms, respectively. To obtain the vertical excitation energies of the low-lying singlet and triplet excited states of the complexes, time-dependent density functional theory calculations using the B3LYP functional were performed at the respective ground-state geometry.

3. RESULTS AND DISCUSSION

Stable structures were calculated in Gaussian 98 and 03, as shown in Figure 2. And the relative energies of the iridium complex are shown in Table 1. The 5′-substituted phenyl ring generated 3′-positon and 5′-position isomers. However, the F−, CH$_3$–, and OCH$_3$– substituted ligands give the 5′-position isomers lower energy in them. As

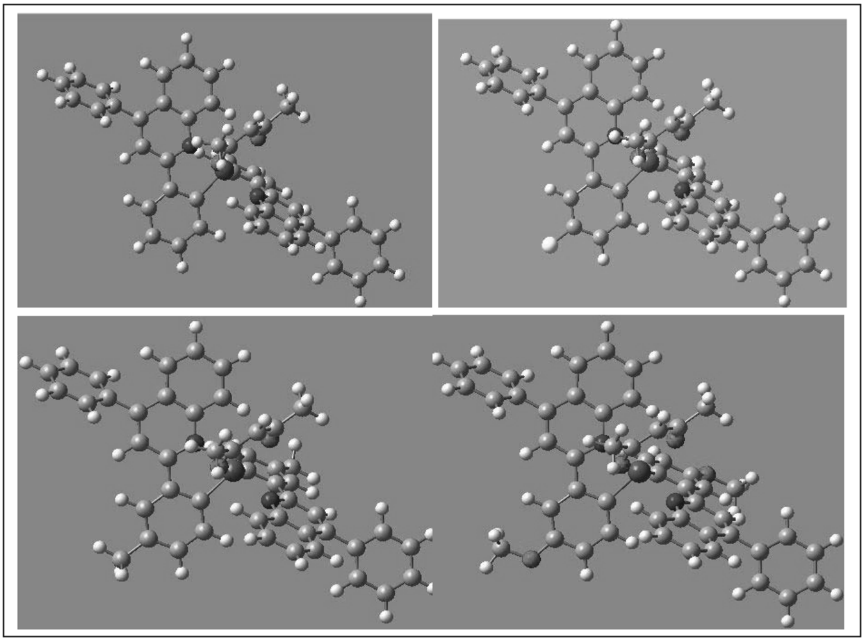

FIGURE 2 Calculated most stable geometry structure of Ir(dpq)$_2$(acac), Ir(dpq-5 F)$_2$(acac), Ir(dpq-5CH$_3$)$_2$(acac), and Ir(dpq-5OCH$_3$)$_2$(acac).

TABLE 1 Calculated Relative Energies, HOMO and LUMO Energies, Band Gaps, Measured T_1 Energies and Relative Quantum Yields of Ir(dpq)$_2$(acac) and Ir(dpq-5 F)$_2$(acac), Ir(dpq-5CH$_3$)$_2$(acac), and Ir(dpq-5OCH$_3$)$_2$(acac)

Complex	E_{rel} (KJ/mol)^a	HOMO (eV)^b	LUMO (eV)^b	Band gap (eV)^b	PL (exp) (eV)^c	Φpl (rel)^d
Ir(dpq)$_2$(acac)		−4.754	−1.783	2.971	2.029	0.14
Ir(dpq-3 F)$_2$(acac)	5.25	−4.957	−1.883	3.047	–	–
Ir(dqp-5 F)$_2$(acac)	0.0	−4.975	−1.856	3.118	2.049	0.36
Ir(dpq-3CH$_3$)$_2$(acac)	26.25	−4.716	−1.823	2.893	–	–
Ir(dpq-5CH$_3$)$_2$(acac)	0.0	−4.642	−1.750	2.892	2.017	0.13
Ir(dpq-3OCH$_3$)$_2$(acac)	10.50	−4.442	−1.440	2.982	–	–
Ir(dpq-5OCH$_3$)$_2$(acac)	0.0	−4.445	−1.464	2.989	2.049	0.07

[a] Relative energies are the difference between the total energies of the 3-position and 5-position isomers, with the lower energy set to zero.

[b] Calculated by Gausian 98/6–31 + G(d). LANL2DZ and 6–31G(d) basis sets.

[c] Measured in 10^{-5}M dilute CH$_2$Cl$_2$ solution.

[d] Relative photoluminescence quantum yield are compare Ir(ppy)3 (Φ = 0.40) with another Ir complexes.

presented in Table 1, the 3′-position isomer give 5.25, 26.25, and 10.5 KJ/mol higher energy due to steric effects. To protect the Ir complexes from isomerization and impurities, we use a method of recrystallization and repeated column chromatography. GC/MS data of the Ir(dpq)$_2$acac and Ir(dpq-5OCH$_3$)$_2$(acac) are shown in Figure 3. In Figure 3, the highest mass spectrums are 753.32 and 813.40 molecular weight respectively. (Calculated molecular weight is 852.02 and 912.06). Due to the GC/MS measurement method, acac structure is easily taken off from the iridium complex. (Calculated acac molecular weight is 99.11). All products compare the calculated function of the UV-Vis absorption peak to the measured UV-Vis absorption spectra. The UV-Vis absorption spectra of the Ir(dpq)$_2$(acac), Ir(dpq-5CH$_3$)$_2$(acac), Ir(dpq-5OCH$_3$)$_2$(acac), Ir(dpq-5 F)$_2$(acac) solution are shown in Figure 4. The MLCT absorption peaks of Ir(dpq)$_2$(acac) and Ir(dpq-5CH$_3$)$_2$(acac) are observed at 470, 512, and 550 nm. Overall profiles of the absorption spectrum and the peak position of the MLCT absorption of Ir(dpq-5CH$_3$)$_2$(acac) are very similar to those of Ir(dpq)$_2$(acac). However, the MLCT absorption peaks for Ir(dpq-5 F)$_2$(acac) appeared at 465, 489, and 548 nm, and for Ir(dpq-5OCH$_3$)$_2$(acac) were shown at 460, 502, and 550 nm. In addition, the intensity of absorption spectrum of Ir(ppy)$_2$(dpq-5 F) is greater than that of Ir(dpq)$_2$(acac). The strong MLCT transition occurs because of the strong coupling between the 5d-orbital of the iridium atom and the HOMO of the dpq-5 F ligand.

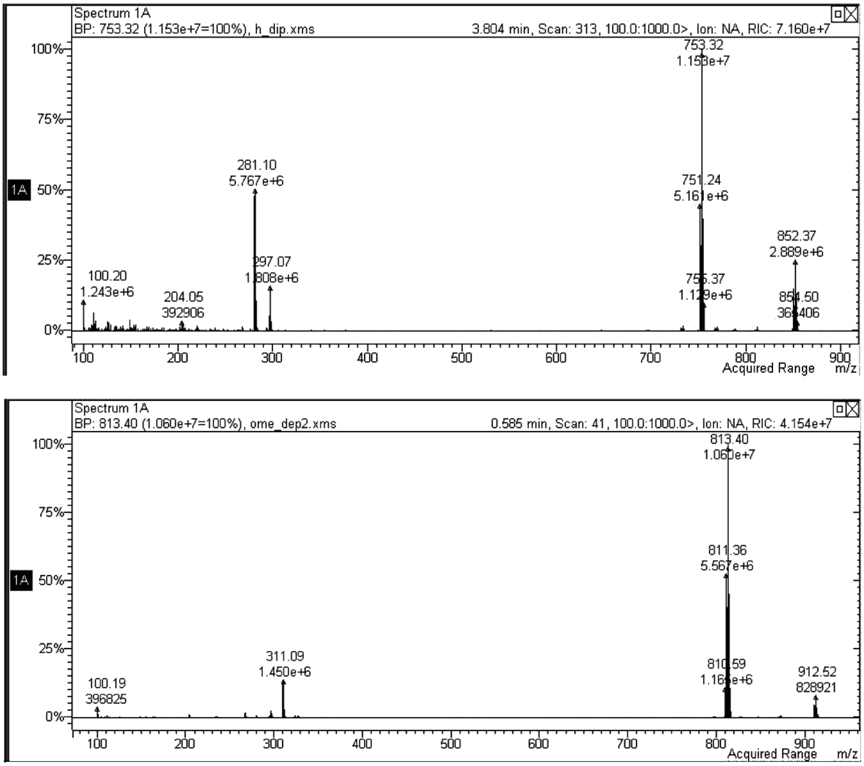

FIGURE 3 GC/MS data of the Ir(dpq)$_2$acac and Ir(dpq-5OCH$_3$)$_2$(acac).

The emission spectra of the complexes, calculated relative energies, HOMO and LUMO energies, band gaps, measured T$_1$ energies and relative quantum yields are shown in Figure 5 and Table 1. The maximum emission wavelength of Ir(dpq-5 F)$_2$(acac), Ir(dpq-5CH$_3$)$_2$(acac), and Ir(dpq-5OCH$_3$)$_2$(acac) in CH$_2$Cl$_2$ was recorded at 606, 616, and 606 nm, and measured T$_1$ energies of Ir(dpq-5 F)$_2$(acac), Ir(dpq-5CH$_3$)$_2$(acac), and Ir(dpq-5OCH$_3$)$_2$(acac) were 2.029, 2.049, 2.017, and 2.049 electron volt, respectively. For comparison, the PL spectrum of Ir(dpq)$_2$(acac) shows an emission peak at 612 nm in CH$_2$Cl$_2$. It was found that the PL spectrum of Ir(dpq-5CH$_3$)$_2$(acac) was red shifted compared to that of Ir(dpq)$_2$(acac) because the methyl group substituted on the 5′-position of the phenyl ring is an electron donating group. So the methyl group strongly affected the HOMO more than the LUMO. The emission spectrum of Ir(dpq-5 F)$_2$(acac) shows efficient blue-shifted luminescence spectra because the electron withdrawing group (-F) on the 5′-position of the phenyl ring lowered

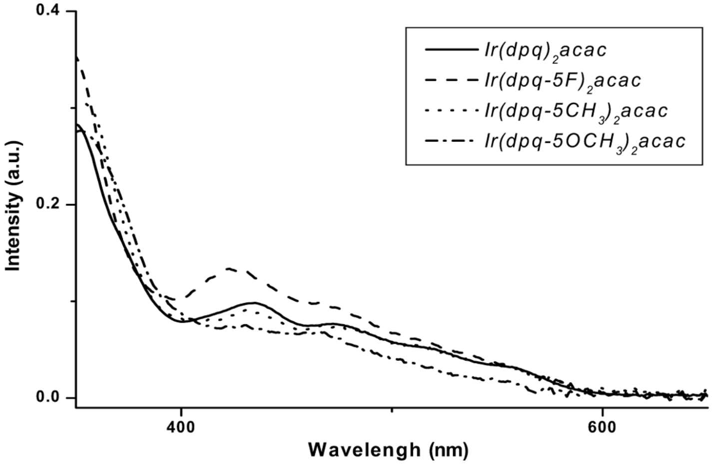

FIGURE 4 UV-Vis absorption spectra of Ir(dpq)$_2$(acac), Ir(dpq-5 F)$_2$(acac), Ir(dpq-5CH$_3$)$_2$(acac), and Ir(dpq-5OCH$_3$)$_2$(acac).

the HOMO level slightly, increasing the MLCT coupling and blue-shifted luminescence by 6 nm compared to that of Ir(dpq)$_2$(acac). And, Although the methyl and methoxy group on the 5′-position of the phenyl ring of Ir(dpq-5CH$_3$)$_2$(acac) and Ir(dpq-5OCH$_3$)$_2$(acac) shows blue-shifted phosphorescence wavelength. It is because that

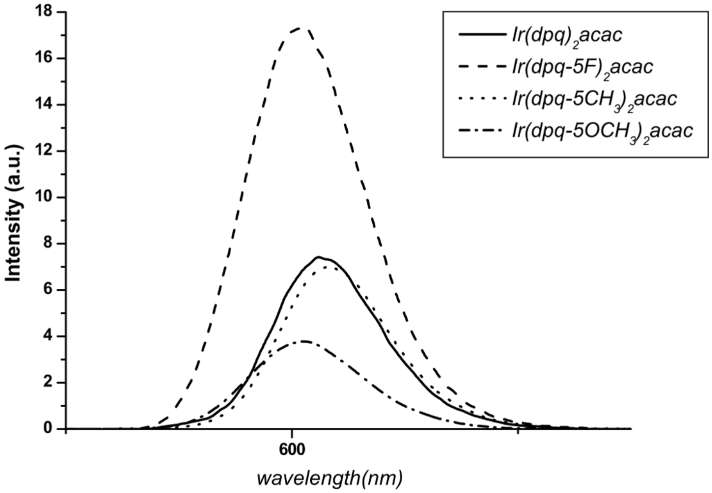

FIGURE 5 PL spectra of Ir(dpq)$_2$(acac), Ir(dpq-5 F)$_2$(acac), Ir(dpq-5CH$_3$)$_2$(acac), and Ir(dpq-5OCH$_3$)$_2$(acac).

although the methoxy and methyl group increased the HOMO energy level, it strongly increased the LUMO more than the HOMO. Especially, Ir(dpq-5OCH_3)$_2$(acac) shows blue-shifted phosphorescence wavelength even though the methoxy group (–OCH_3) substituted on the 5′-position of the phenyl ring is an electron donating group. It is because the methoxy group on the 5′-position raises both the LUMO and HOMO level. Moreover, the methoxyphenyl group onto the iridium atom destabilized the MLCT state and leads to an increase in the emission energy. Thus, the emission wavelength is blue-shifted.

4. CONCLUSIONS

We have studied a 5’substitutent effect of Ir(dpq)$_2$(acac) for the materials in red emissive OLEDs. We found that substitution on phenyl ring has influence on the emission wavelength and efficiency. The maximum emission wavelength of Ir(dpq-5 F)$_2$(acac), Ir(dpq-5CH_3)$_2$ (acac), and Ir(dpq-5OCH_3)$_2$(acac) in CH_2Cl_2 was recorded at 606, 616, and 606 nm, respectively. While the substitution of EWG (−5 F) caused blue-shift of emission wavelength from 612 nm to 606 nm and improved the efficiency withdrawing group (-F) on the 5′-position of the phenyl ring lowered the HOMO level slightly increased PL efficiency by decreasing the HOMO energy level.

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