



Introduction of new ancillary ligands to the iridium complexes having 2,3-diphenylquinolinato ligands for OLED

Hyun Shin Lee^a, So Youn Ahn^a, Hyun Sue Huh^b, Yunkyong Ha^{a,*}

^a Department of Information Display, Hongik University, 72-1 Mapo-gu Sangsoo-dong, Seoul 121-791, Republic of Korea

^b Department of Chemistry, Texas A&M University, College Station, TX 77843, USA

ARTICLE INFO

Article history:

Received 21 April 2009

Received in revised form 28 May 2009

Accepted 2 June 2009

Available online 7 June 2009

Keywords:

Pyrazolone-based ancillary ligands

(przl-R series)

Iridium complex

2,3-Diphenylquinolinato ligand

Red phosphorescence

OLED

ABSTRACT

We investigated the effect of an ancillary ligand (AL) on the emission color and luminous efficiencies of its complex, Ir(4-Me-2,3-dpq)₂(AL), where 4-Me-2,3-dpq represents 4-methyl-2,3-diphenylquinolinato ligand. We expected that ancillary ligand modification by introduction of the bulky substituent to the complexes might allow luminous efficiency increase by reduction of T–T annihilation. Furthermore, some ancillary ligands may contribute to fine-tuning of their complex emission colors by influencing the energy level of Ir d-orbitals upon the orbital mixing. As new ancillary ligands substituting for acac which is a typical AL in the iridium complexes, pyrazolone-based ligands, 4-R-5-methyl-2-phenyl-2,4-dihydro-pyrazol-3-one series (przl-R), were prepared, where R represents C₆H₅, C₆H₄CH₃ and C₆H₄Cl. These ligands were chelated to the iridium center to yield a new series of the iridium complexes, Ir(4-Me-2,3-dpq)₂(przl-R). The X-ray crystal structure of Ir(4-Me-2,3-dpq)₂(przl-C₆H₄Cl) was determined. The electrochemical and luminescence properties of the iridium complexes were investigated. The effect of the przl-substituents on the emission colors of the complexes was not significant. On the other hand, the luminous efficiencies of Ir(4-Me-2,3-dpq)₂(przl-C₆H₅) and Ir(4-Me-2,3-dpq)₂(przl-C₆H₄CH₃) were higher than that of Ir(4-Me-2,3-dpq)₂(acac).

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The heavy transition metal complexes usually have high phosphorescence efficiencies with large population of the emitting triplet states by strong spin–orbit coupling induced by the metal center. Among these complexes, the iridium(III) complexes were particularly known to have high quantum efficiencies and relatively short excited emissive states [1–6]. Thus, the phosphorescent iridium complexes have been used as dopants for organic light-emitting devices (OLEDs) owing to utilization of both singlet and triplet excited states for emission without their significant loss by none-emissive pathways [7,8].

There are, however, some limitations in the application of phosphorescent materials to OLEDs. Compared with the short emission life-time of the fluorescent materials, the relatively long phosphorescence life-time of the iridium complexes may cause triplet–triplet (T–T) annihilation at high currents, which can be one of the factors in lowering the efficiency [9].

According to the literature [10,11], introduction of a new bulky ancillary ligand, pyrazolonate, to red-emitting Eu(III) and Ir(III) complexes resulted in improvement of their luminous efficiency. The bulky environment of the emitting complexes might prevent quenching between the excited states, contributing to reduction

of T–T annihilation. We have focused on development of efficient orange–red and blue–green dopant combination for white OLEDs, and recently reported that the iridium complexes, Ir(4-Me-2,3-dpq)₂(acac), exhibited orange–red electroluminescence (EL) at 603 nm with luminous efficiency of 8.10 cd/A [12]. Modification of the ancillary ligand with the bulky ones in bis(2,3-diphenylquinolinato)iridium complexes might also allow luminous efficiency increase. In addition, fine-tuning of its emission color can be expected with the przl-based ligands in the iridium complex by their orbital mixing with the d-orbitals of the iridium center.

Thus, 4-R-5-methyl-2-phenyl-2,4-dihydro-pyrazol-3-one (przl-R) series were prepared as new ancillary ligand substitutes for acac in the iridium complexes, and their iridium complexes, Ir(4-Me-2,3-dpq)₂(przl-R), were synthesized, where R represents C₆H₅, C₆H₄CH₃ and C₆H₄Cl at 4-position of the pyrazolone. The crystal structure of Ir(4-Me-2,3-dpq)₂(przl-C₆H₄Cl) was determined and this is the first structure of the iridium complexes which contain 4-Me-2,3-dpq as a main ligand. We investigated the photoabsorption properties of the complexes with their UV–Vis spectra and studied the electrochemical characteristics with their cyclic voltammetric diagrams. We compared the photoluminescence (PL) and electroluminescence (EL) properties of Ir(4-Me-2,3-dpq)₂(przl) with those of the previously reported Ir(4-Me-2,3-dpq)₂(acac) to find how the przl ancillary ligands have an influence on the luminous efficiency and emission wavelength of the iridium complexes.

* Corresponding author. Tel.: +82 2 320 1490; fax: +82 2 3142 0335.

E-mail address: ykha@hongik.ac.kr (Y. Ha).

2. Experimental

2.1. Synthesis and characterization

Iridium trichloride hydrate ($\text{IrCl}_3 \cdot \text{H}_2\text{O}$) was purchased from Strem Co. All other reagents were purchased from Aldrich Co. and used without further purification. All reactions were carried out under an argon atmosphere. Solvents were dried by standard procedures. All column chromatography was performed on silica gel (230-mesh, Merck Co.) column. ^1H NMR spectra were recorded with a Varian Mercury 300 MHz spectrometer at Sungkyunkwan University. FAB-MS and elemental analysis were performed with JMS-AX505WA and EA1110, respectively, at Seoul National University in Korea.

2.1.1. Synthesis of ligands and iridium complexes

Prazolone ligands (przl-R series). 1-Phenyl-3-methyl-5-prazolone (1.75 g, 10.0 mmol) in 40 ml of 1,4-dioxane were placed in a 100 ml flask, and calcium hydroxide (1.78 g) and barium hydroxide (1.03 g) were added. The corresponding acyl chloride (benzoyl chloride, 4-methylbenzoyl chloride or 4-chlorobenzoyl chloride (11.6 mmol)) was dripped slowly to the solution mixture under stirring. After the reflux for 24 h, the reaction mixture was poured into a 70 ml solution of ice-cold hydrochloric acid [$\text{HCl}:\text{H}_2\text{O} = 3:7$ (v/v)], and the resulting yellow precipitate was filtered and recrystallized from acetone and water. Yield: 60%.

4-Me-2,3-dpq. 4-Me-2,3-dpq Ligand [12] were obtained according to Friedlander reaction [13] with the corresponding precursors, 2-aminoacetophenone (1.35 g, 1.21 ml, 10.0 mmol) and deoxybenzoin (1.96 g, 10.0 mmol). Yield: 75%.

$\text{Ir}(4\text{-Me-2,3-dpq})_2(\text{acac})$. $\text{Ir}(4\text{-Me-2,3-dpq})_2(\text{acac})$ was prepared according to the procedure previously reported [12]. Yield: 62%. Anal. Calc. for $\text{C}_{49}\text{H}_{39}\text{IrN}_2\text{O}_2$: C, 66.72; H, 4.69; N, 3.18. Found: C, 65.54; H, 4.77; N, 2.90%.

$\text{Ir}(4\text{-Me-2,3-dpq})_2(\text{przl-R})$. First, the cyclometallated Ir(III) μ -chloro-bridged dimer, $(4\text{-Me-2,3-dpq})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(4\text{-Me-2,3-dpq})_2$ (3.10 g, 1.90 mmol), was prepared according to Nonoyama method [14]. Second, the resulting dimer and a przl-R (6.50 mmol) were mixed with Na_2CO_3 (500 mg) in 2-ethoxyethanol (30 ml). The mixture was refluxed for 2 h and the resulting red solid was filtered after cooling. $\text{Ir}(4\text{-Me-2,3-dpq})_2(\text{przl-R})$ was purified by chromatography on silica gel column with CH_2Cl_2 and by recrystallization from CH_2Cl_2 /hexane.

$\text{Ir}(4\text{-Me-2,3-dpq})_2(\text{przl-C}_6\text{H}_5)$. A red powder (yield: 65%). MS (FAB): m/z 1058 (M^+) (4.69%); 781 (100%); 482 (7.77%); 296 (4.05%). ^1H NMR(ppm): δ 8.46–6.40 (aromatic H's 36H); 1.21 (CH_3 's of przl, 3H); 2.53, 2.51 (CH_3 's of 4-Me-2,3-dpq, 3H each).

$\text{Ir}(4\text{-Me-2,3-dpq})_2(\text{przl-C}_6\text{H}_4\text{CH}_3)$. A red powder (yield: 60%). MS (FAB): m/z 1072 (M^+) (9.70%); 781 (100%); 482 (6.28%); 296 (3.32%). ^1H NMR(ppm): δ 8.49–6.43 (aromatic H's 35H); 1.28, 1.21 (CH_3 's of przl, 3H each); 2.54, 2.53 (CH_3 's of 4-Me-2,3-dpq, 3H each). Anal. Calc. for $\text{C}_{62}\text{H}_{47}\text{IrN}_4\text{O}_2$: C, 69.45; H, 4.42; N, 5.23. Found: C, 68.72; H, 4.37; N, 5.07%.

$\text{Ir}(4\text{-Me-2,3-dpq})_2(\text{przl-C}_6\text{H}_4\text{Cl})$. A red powder (yield: 55%). MS (FAB): m/z 1092 (M^+) (12.42%); 781 (66.82%); 307 (23.75%); 289 (11.96%); 154 (100%); 136 (65.06%). ^1H NMR(ppm): δ 8.45–6.41 (aromatic H's 35H); 1.25 (CH_3 's of przl); 2.53, 2.51 (CH_3 's of 4-Me, 3H each). Anal. Calc. for $\text{C}_{61}\text{H}_{44}\text{ClIrN}_4\text{O}_2$: C, 67.05; H, 4.06; N, 5.13. Found: C, 67.23; H, 4.10; N, 5.03%.

2.1.2. X-ray crystal structure determination

The suitable single crystal of $\text{Ir}(4\text{-Me-2,3-dpq})_2(\text{przl-C}_6\text{H}_4\text{Cl})$ was recrystallized from CH_2Cl_2 -hexane. The X-ray data was collected with a Bruker Smart APEX2 diffractometer equipped with a Mo X-ray tube. Intensity data were empirically corrected for

absorption with SADABS [15]. The calculations were carried out with SHELXTL programs [16]. The structures were solved by direct methods. The non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were generated in idealized positions and refined using the riding model. Details on crystal data, intensity collection, and refinement details are given in Ref. [17].

2.2. Optical and electrochemical measurements

UV-Vis absorption spectra were measured with a Hewlett Packard 8425A spectrometer. PL spectra were measured on a Perkin Elmer LS 50B spectrometer. The UV-Vis and PL spectra of iridium complexes in the solution state were measured in 10^{-5} M CH_2Cl_2 solution. Cyclic voltammograms were obtained at scan rate of 100 mV/s, and tetrabutylammonium hexafluorophosphate was added as an electrolyte in CH_2Cl_2 and DMF solution.

2.3. Device fabrication and measurements

The OLEDs containing the iridium complexes as a red dopant in emitting layers were fabricated. The ITO glass was cleaned with acetone, methanol, distilled water and isopropyl alcohol. The organic materials used as carrier transport, carrier injection and host materials were supplied by Gracel Display Incorporation in Korea. The OLED was fabricated by high vacuum (5×10^{-7} torr) thermal deposition of the organic materials onto the surface of an indium tin oxide (ITO, $30 \Omega/\square$, 80 nm) coated glass substrate. 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*-phenylamino]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 iridium complex phosphor doped in 4,4',*N,N'*-dicarbazolebiphenyl (CBP). The doping ratio of the phosphor was 10%. Bathocuproine (BCP, 10 nm), tris-(8-hydroxyquinolino)aluminum (Alq_3 , 20 nm) and lithium quinolate (LiQ, 2 nm) 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/s. Finally, 100 nm of Al was deposited as a cathode. 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 (Keithley 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.

3. Results and discussion

Pyrazolone series as ancillary ligands in the Ir complexes have not only suitable triplet energy levels matching 5d orbital of Ir, but also good carrier transporting properties. The energy level matching may lead to better metal-to-ligand charge transfer (MLCT), resulting in high luminous efficiency of the complex and improvement of carrier transport can lead to better performance of the device. Our earlier results [18] indicated that ancillary ligand replacement of acac with przl in the iridium complexes containing diphenylquinoxaline (dpqx) ligands as main ligands could improve the emission efficiency and result in fine-tuning of the emission wavelength. However, the iridium complexes containing dpqx as a main ligand suffer from poor efficiency in spite of good chromacity. On the other hand, we found that the device containing $\text{Ir}(4\text{-Me-2,3-dpq})_2(\text{acac})$ showed better efficiency than that of $\text{Ir}(\text{dpqx})_2(\text{acac})$. Therefore, the iridium complexes coordinated with 4-Me-dpq and przl-R li-

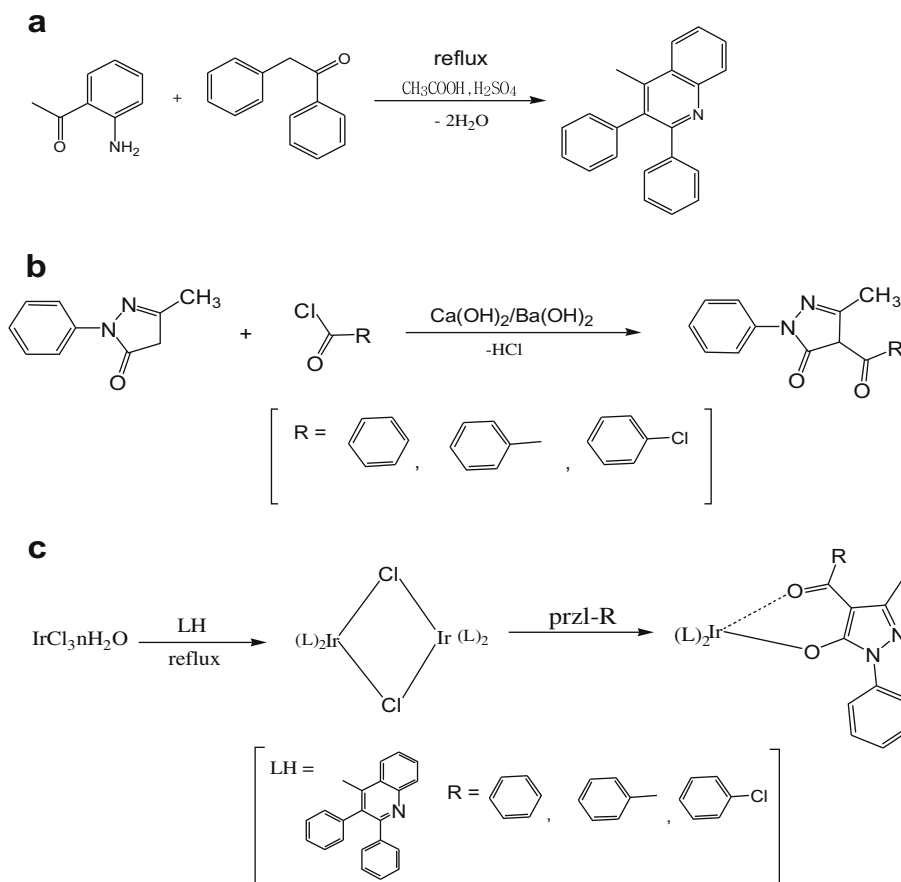


Fig. 1. Synthetic scheme of the ligands and the iridium complexes.

gands were synthesized and investigated as red phosphors in OLEDs in this study.

The main ligand, 4-Me-2,3-dpq, which determines the emission color of the complexes was synthesized according to Friedlander reaction, as illustrated in Fig. 1a. A series of przl ancillary ligands, 4-R-5-methyl-2-phenyl-2,4-dihydro-pyrazol-3-one ($R = C_6H_5$, p - $C_6H_4CH_3$ and p - C_6H_4Cl) were prepared as shown in Fig. 1b. The R groups were chosen to study the electronic effects of the R at a przl ligand on the luminescence properties of their complexes. The synthesis of iridium complexes $Ir(4\text{-Me-}2,3\text{-dpq})_2(\text{przl-R})$ involved two steps, formation of the iridium dimer and the following coordination of przl-R, as summarized in Fig. 1c. As a reference, $Ir(4\text{-Me-}2,3\text{-dpq})_2(\text{acac})$ was also prepared, according to the procedure reported previously [12]. The iridium complexes prepared herein were characterized by 1H NMR, FAB-MS and elemental analysis.

We have obtained single crystal to elucidate the structure of the iridium complexes containing 4-Me-2,3-dpq. Among them, the suitable single crystal of $Ir(4\text{-Me-}2,3\text{-dpq})_2(\text{przl-}C_6H_4Cl)$ was recrystallized from layer diffusion of CH_2Cl_2 –hexane and structurally characterized by X-ray diffraction. There are two crystallographically distinct molecules in an asymmetric unit, which are geometric isomers. The structures of these two molecules are given in Figs. 2a and 2b. Each displays two chelating 4-Me-2,3-dpq and one przl- C_6H_4Cl ligands, with the difference of przl chelate disposition to the iridium center. The iridium center is 6-coordinated with a distorted octahedral $[IrN_2C_2O_2]$ core, retaining the *cis*-C,C- and *trans*-N,N-chelate disposition. The Ir–N, Ir–O, and Ir–C bond lengths are in the range of 2.060(5)–2.077(4), 2.175(4)–2.186(4), and 1.969(6)–2.009(5) Å, respectively. The Ir–O bonds in the complex are especially longer than the mean value of 2.088 Å reported in the Cambridge Crystallographic Database [19]. Such a distorted

structure with very similar Ir–N, Ir–C, and Ir–O bond lengths has been reported with $Ir(\text{NAPQ})_2(\text{acac})$ showing the Ir–O bond lengths of 2.175 Å where NAPQ represents 2-(naphtha-1-yl)-4-phenylquin-

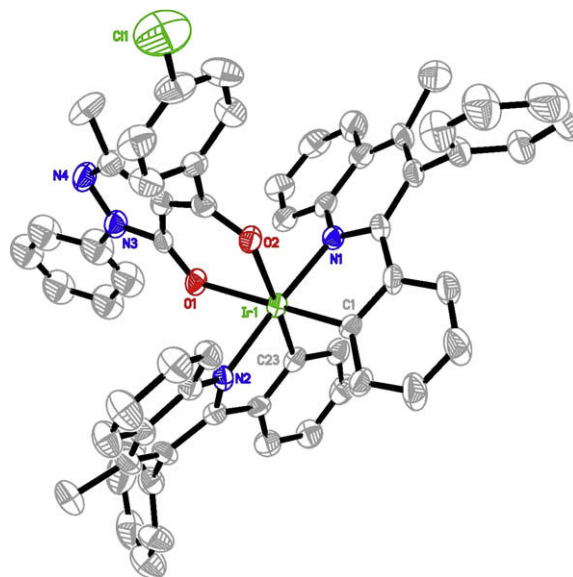


Fig. 2a. ORTEP drawing of one molecule $Ir(4\text{-Me-}2,3\text{-dpq})_2(\text{przl-}C_6H_4Cl)$ in an asymmetric unit showing the atom-labeling scheme and 30% probability thermal ellipsoids. Selected bond distances (Å) and bond angles ($^\circ$): Ir1–N1 2.070(4), Ir1–N2 2.077(4), Ir1–O1 2.182(4), Ir1–O2 2.186(4), Ir1–C1 1.971(5), Ir1–C23 1.969(6); N1–Ir1–C1 78.9(2), N1–Ir1–O1 81.7(2), N2–Ir1–C23 79.5(2), N2–Ir1–O2 100.1(2), N1–Ir1–N2 176.9(2), O1–Ir1–C1 176.0(4), O2–Ir1–C23 176.3(2).

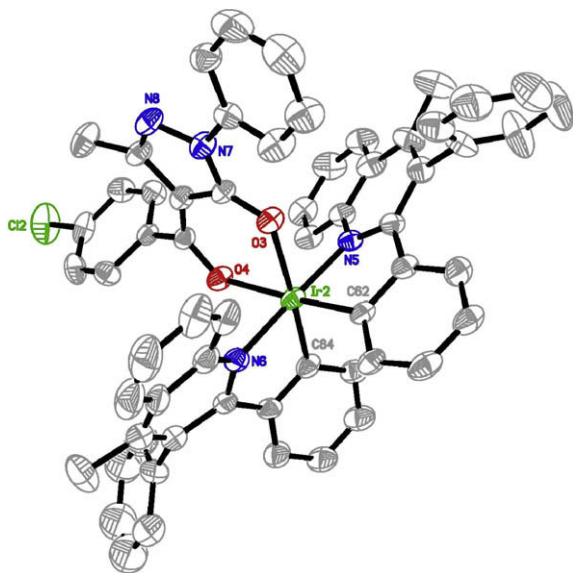


Fig. 2b. ORTEP drawing of the other molecule $\text{Ir}(4\text{-Me-2,3-dpq})_2(\text{przl-C}_6\text{H}_4\text{Cl})$. Selected bond distances (Å) and bond angles ($^\circ$): Ir2–N5 2.063(5), Ir2–N6 2.060(5), Ir2–O3 2.182(4), Ir2–O4 2.175(4), Ir2–C62 1.979(6), Ir2–C84 2.009(5); N5–Ir2–C62 79.2(2), N5–Ir2–O3 80.2(2), N6–Ir2–C84 79.1(2), N6–Ir2–O4 82.6(2), N5–Ir2–N6 177.8(2), O3–Ir2–C84 176.3(4), O4–Ir2–C62 176.2(2).

oline [20]. These observations support the large steric hindrance caused by the bulky przl ligand as well as the main ligands.

The UV–Vis absorption spectra of the complexes in CH_2Cl_2 are shown in Fig. 3. The strong absorption bands between 200 and 400 nm in the ultraviolet region are assigned to the spin-allowed $^1\pi\text{-}\pi^*$ transition of the cyclometalated 4-Me-2,3-dpq ligand in the complexes. The weak bands between 400 and 460 nm in the visible region are assigned to the spin-allowed metal-to-ligand charge transfer band ($^1\text{MLCT}$), and the weaker absorption bands at the longer wavelengths can be attributed to the spin-forbidden $^3\text{MLCT}$ and spin-orbit coupling enhanced $^3\pi\text{-}\pi^*$ transition. The formally spin-forbidden $^3\text{MLCT}$ gains the intensity by mixing with the higher-lying $^1\text{MLCT}$ transition through the strong spin-orbit coupling on the iridium center [21]. The absorption patterns of the complexes prepared in this study are similar, suggesting that change of the ancillary ligand does not make significant contribution to the absorption process of the complex.

We investigated the electrochemical properties of the complexes, using cyclic voltammetry (CV). The HOMO and the LUMO energies of $\text{Ir}(4\text{-Me-2,3-dpq})_2(\text{AL})$ where AL represents acac, przl- C_6H_5 , przl- $\text{C}_6\text{H}_4\text{CH}_3$ or $\text{C}_6\text{H}_4\text{Cl}$ were estimated. The oxidation which indicates the HOMO of the complexes was reversible. The oxidation potential of $\text{Ir}(4\text{-Me-2,3-dpq})_2(\text{przl-C}_6\text{H}_4\text{Cl})$ was 5.20 eV, the highest among the complexes studied herein, but the overall HOMO differences among the complexes were less than 0.1 eV only. The reduction potentials (LUMO) of the complexes did not

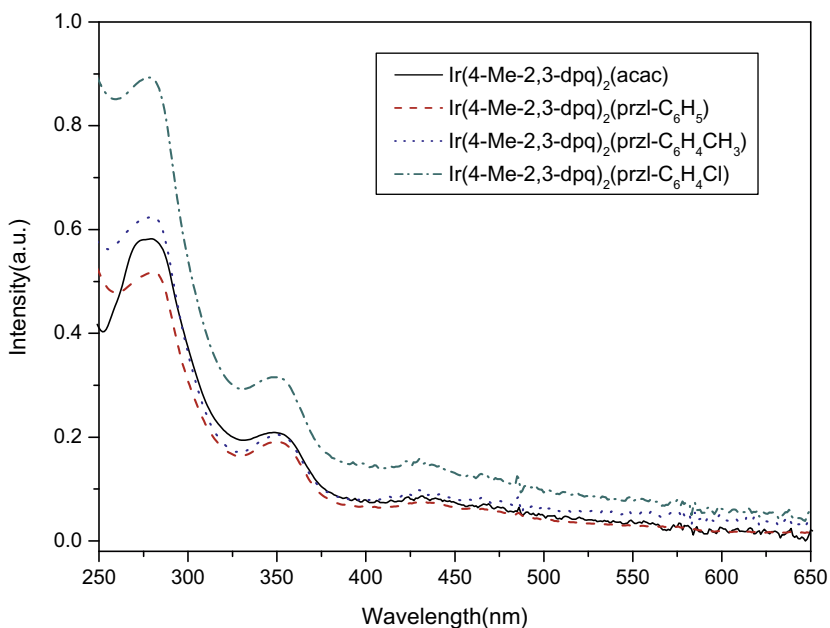


Fig. 3. UV–Vis absorption spectra of the iridium complexes.

Table 1
Physical parameters for the complexes.

Complex	λ_{abs} (nm^{a})	λ_{em} (nm^{a})	E_{ox} (V^{b})	E_{red} (V^{b})	HOMO (eV^{c})	LUMO (eV^{c})	ΔE (eV^{d})
$\text{Ir}(4\text{-Me-2,3-dpq})_2(\text{acac})$	279, 431, 466	604	0.30	1.82	5.10	2.98	2.12
$\text{Ir}(4\text{-Me-2,3-dpq})_2(\text{przl-C}_6\text{H}_5)$	281, 350, 431, 465	601	0.37	1.79	5.17	3.01	2.16
$\text{Ir}(4\text{-Me-2,3-dpq})_2(\text{przl-C}_6\text{H}_4\text{CH}_3)$	280, 351, 430, 465	599	0.37	1.89	5.17	2.91	2.26
$\text{Ir}(4\text{-Me-2,3-dpq})_2(\text{przl-C}_6\text{H}_4\text{Cl})$	278, 348, 430, 465	601	0.40	1.77	5.20	3.03	2.17

^a Measured in CH_2Cl_2 solution.

^b Scan rate: 100 mV/s, electrolyte: tetrabutylammonium hexafluorophosphate. The potentials are quoted against the internal ferrocene standard.

^c Deduced from the equation $\text{HOMO} = 4.8 + E_{\text{ox}}$, $\text{LUMO} = 4.8 - E_{\text{red}}$.

^d Calculated from the equation $\Delta E = \text{HOMO} - \text{LUMO}$ [21].

show the reversible wave. Ir(4-Me-2,3-dpq)₂(przl-C₆H₄CH₃) and Ir(4-Me-2,3-dpq)₂(przl-C₆H₄Cl) had the lowest LUMO at 2.91 eV and the highest LUMO at 3.03 eV, respectively. Again, the differences were not conspicuous change across the complexes. Thus, it was concluded that there was no evident electronic effect of the ancillary ligand substituents on the electrochemical properties of the complexes in this study. The detailed CV data were summarized in Table 1 [22]. Resulting ΔE_s ($E_{\text{ox}} - E_{\text{red}}$) of the complexes were calculated to show subtle changes in the range of 2.12–2.26 eV. Though these band gaps somewhat correlate with their PL wavelengths, *vide infra*, it does not seem to have meaning within the experimental errors of their CVs and PLs.

The PL spectra of the iridium complexes in 10⁻⁵ M CH₂Cl₂ solution are shown in Fig. 4. The emission maxima for Ir(4-Me-2,3-dpq)₂(acac), Ir(4-Me-2,3-dpq)₂(przl-C₆H₅), Ir(4-Me-2,3-dpq)₂(przl-C₆H₄CH₃) and Ir(4-Me-2,3-dpq)₂(przl-C₆H₄Cl) appeared at 604, 601, 599 and 601 nm, respectively. The wavelengths of PL peaks were not shifted significantly upon change of the ancillary ligand in the complexes. Such similar PL data are consistent with both the absorption spectral results. Therefore, the ancillary ligands, either acac or przl-R series, do not seem to change the band gaps of their complexes significantly. It thereby indicates that the main ligand, 4-Me-2,3-dpq, is the important factor in determining the emission color of its complexes.

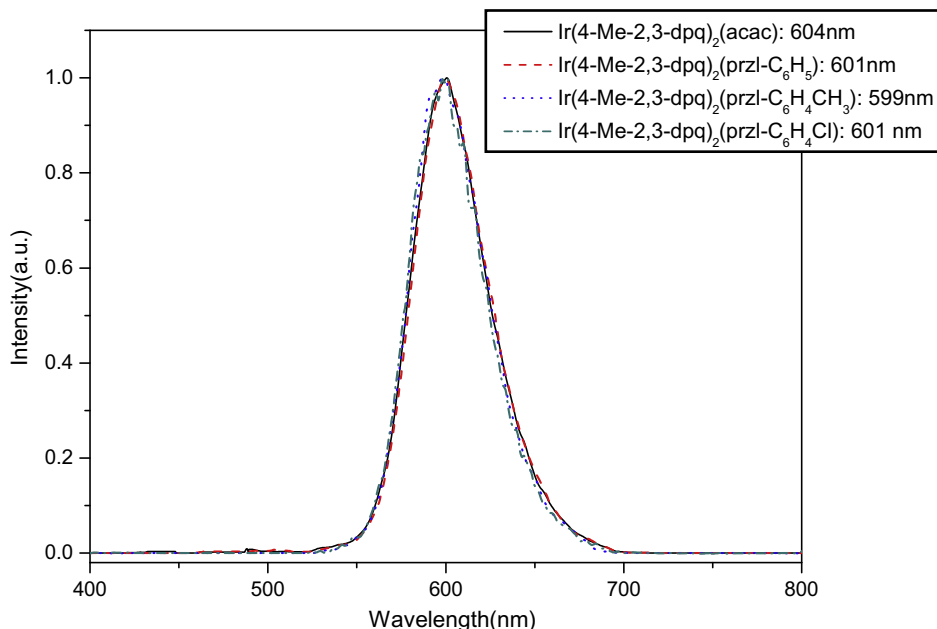


Fig. 4. PL spectra of the iridium complexes.

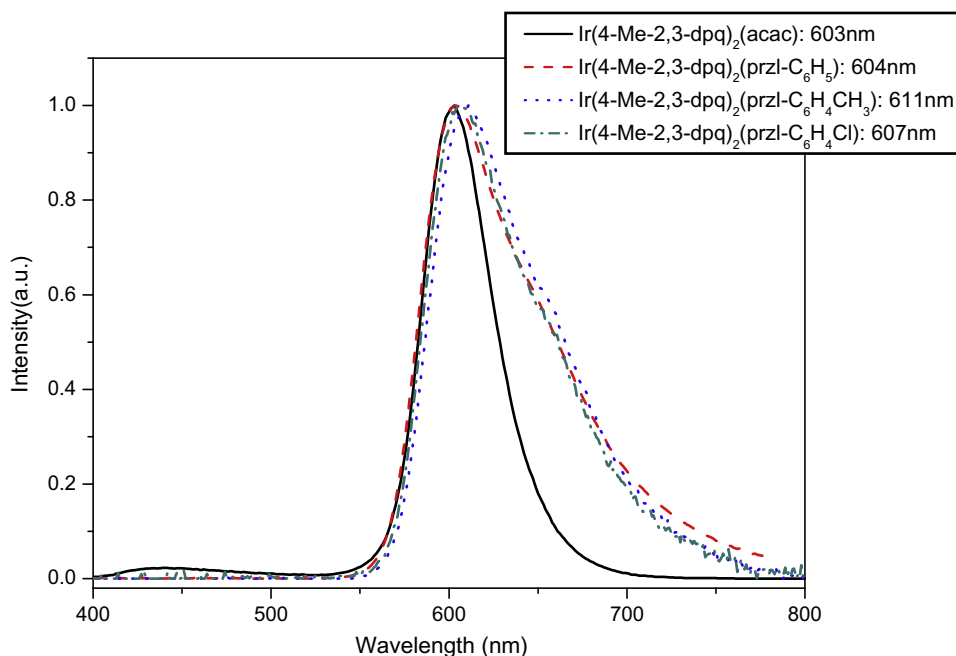


Fig. 5. EL spectra of the iridium complexes.

Table 2
Characteristics of OLED devices of the iridium complexes.

Ir complex	EL λ_{max} (nm)	Luminance (cd/m ²)	Luminance efficiency (cd/A)	CIE
Ir(4-Me-2,3-dpq) ₂ (acac)	603	12 800	8.10	(0.644, 0.352)
Ir(4-Me-2,3-dpq) ₂ (przl-C ₆ H ₅)	604	11 920	11.38	(0.629, 0.370)
Ir(4-Me-2,3-dpq) ₂ (przl-C ₆ H ₄ CH ₃)	611	6550	10.10	(0.635, 0.380)
Ir(4-Me-2,3-dpq) ₂ (przl-C ₆ H ₄ Cl)	607	2980	5.38	(0.629, 0.367)

The electroluminescence properties of the iridium complexes were also investigated. The configuration of the EL device with Ir(4-Me-2,3-dpq)₂(przl-R) was ITO/2-TNATA/NPB/CBP: 10% dopant/BCP/Alq₃/Liq/Al. The EL of the complexes containing przl ligands exhibited the red emission around 604–611 nm, similar to their PL bands (Fig. 5). Similarity of PL and EL supports that the red EL is originated from the iridium complex dopant in the emitting layer of the device. The detailed EL properties of the przl complexes were found to be different from those of Ir(4-Me-2,3-dpq)₂(acac). As shown in Fig. 5, the FWHM (Full Width at Half Maximum) of the complex containing przl was broader than that of the complex containing acac, leading to the lower color purity toward red emission. The Commission Internationale de L'Eclairage (CIE) coordinates of Ir(4-Me-2,3-dpq)₂(acac), Ir(4-Me-2,3-dpq)₂(przl-C₆H₅), Ir(4-Me-2,3-dpq)₂(przl-C₆H₄CH₃) and Ir(4-Me-2,3-dpq)₂(przl-C₆H₄Cl) were (0.644, 0.352), (0.629, 0.370), (0.635, 0.380) and (0.629, 0.367), respectively.

On the other hand, the luminous efficiencies were improved upon change of an ancillary ligand to the bulky przl, as we suggested. The luminous efficiency maxima of the device containing Ir(4-Me-2,3-dpq)₂(przl-C₆H₅) and Ir(4-Me-2,3-dpq)₂(przl-C₆H₄CH₃) were 11.38 and 10.10 cd/A, respectively, compared to 8.10 cd/A at the device of Ir(4-Me-2,3-dpq)₂(acac). In the case of Ir(4-Me-2,3-dpq)₂(przl-C₆H₄Cl), the efficiency was the lowest among the complexes prepared herein. We attribute such low efficiency to involvement of Cl substituent which might cause the excited state of its complex to lose the energy by a non-radiative pathway. The overall electroluminescence properties of the iridium complexes were summarized in Table 2.

We also prepared Ir(4-Me-2,3-dpq)₂(przl-C₆N₄NMe₂) and tried to compare the EL efficiencies. However, the attempts to fabricate the EL device containing Ir(4-Me-2,3-dpq)₂(przl-C₆H₄NMe₂) as a dopant were failed. The failure of device fabrication could be attributed to the relatively large molecular weight of this complex. It has more than 1000 g/mol of the molecular weights and thus may be too non-volatile to be sublimed.

4. Conclusion

We studied the effect of the new ancillary pyrazoline-based ligands on the photophysical, electrochemical, electroluminescent properties of their iridium complexes. We focused on the question whether the iridium complex involving a bulky przl ligand might lead to affect the emission color and device performance. The PL peaks of the complexes synthesized in this study appeared around 600 nm, regardless of the ancillary ligand. The UV and electrochemical patterns of the complexes of acac and of pyrazolone-based ligands were also similar, indicating that the new ancillary ligands and their substituents did not make significant change in the absorption and emission process of their complexes. The devices of Ir(4-Me-2,3-dpq)₂(przl-C₆H₅) and Ir(4-Me-2,3-dpq)₂(przl-C₆H₄CH₃) exhibited the better electroluminescent performance with a luminous efficiency of 11.38 and 10.10 cd/A than that of Ir(4-Me-2,3-dpq)₂(acac), supporting that the bulky ancillary li-

gands in the complex could contribute to reduction of T–T-annihilation. This finding indicates that there is no visible charge transfer between the ancillary ligand and the cyclometalating ligand, and therefore, the ancillary ligands, acac and przls, did not change the photophysical properties of their complexes significantly.

Acknowledgement

This work was supported by the Korea Research Foundation (KRF-2008-531-C00036).

Appendix A. Supplementary material

CCDC 723680 contains the supplementary crystallographic data for compound Ir(4-Me-2,3-dpq)₂(przl-C₆H₄Cl). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.06.003](https://doi.org/10.1016/j.jorganchem.2009.06.003).

References

- B.A. Baldo, D.F. O'Brian, Y. You, A. Shoustikov, S. Sibley, M.E. Thompson, S.R. Forrest, *Nature* 395 (1998) 151.
- B.A. Baldo, S. Lamansky, P.E. Burrows, M.E. Thompson, S.R. Forrest, *Appl. Phys. Lett.* 75 (1999) 4.
- M.A. Baldo, M.E. Thompson, S.R. Forrest, *Nature* 403 (2000) 750.
- M. Ikai, S. Tokito, Y. Sakamoto, T. Suzuki, Y. Taga, *Appl. Phys. Lett.* 79 (2001) 156.
- F.C. Chen, Y. Yang, M.E. Thompson, J. Kido, *Appl. Phys. Lett.* 80 (2002) 2308.
- Y. You, K.S. Kim, T.K. Ahn, D. Kim, S.Y. Park, *J. Phys. Chem. C* 111 (2007) 4052.
- A. Kohler, J.S. Wilson, R.H. Friend, *Adv. Mater.* 14 (2002) 701.
- A.B. Tamayo, B.D. Alleyne, P.I. Djurovich, S. Lamansky, I. Tsyba, N.N. Ho, R. Bau, M.E. Thompson, *J. Am. Chem. Soc.* 125 (2003) 7377.
- S.-J. Yeh, M.-F. Wu, C.-T. Chen, Y.-H. Song, Y. Chi, M.-h. Ho, S.-F. Hsu, C.H. Chen, *Adv. Mater.* 17 (2005) 285.
- M. Shi, F. Li, T. Yi, D. Zhang, H. Hu, C. Huang, *Inorg. Chem.* 44 (2005) 8929.
- Q. ZhaO, C.Y. Jiang, M. Shi, F.Y. Li, T. Yi, Y. Cao, C.H. Huang, *Organometallics* 259 (2006) 3631.
- G.Y. Park, Y. Ha, *Synth. Met.* 158 (2008) 120.
- E.C. Riesgo, X. Jin, R.P. Thummel, *J. Org. Chem.* 61 (1966) 3017.
- M. Nonoyama, *J. Organomet. Chem.* 86 (1975) 263.
- G.M. Sheldrick, *SADABS*, Program for Absorption Correction, University of Göttingen, 1996.
- Bruker, *SHELXTL*, Structure Determination Software Programs, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1997.
- Crystallographic data for Ir(4-Me-2,3-dpq)₂(przl-C₆H₄Cl): C₆₁H₄₄ClIrN₄O₂, FW = 1092.65, T = 296(2) K, orthorhombic, Pca2₁, purple, 0.28 × 0.24 × 0.20 mm, block, a = 29.8646(8) Å, b = 14.8162(4) Å, c = 24.1281(6) Å, V = 10676.2(5) Å³, Z = 8, D_{cal} = 1.360 g cm⁻³, μ = 2.596 mm⁻¹, F(0 0 0) = 4384, T_{min} = 0.5301, T_{max} = 0.6247, No. of reflections measured = 113 762, No. of unique reflections = 16 489, No. of reflections with I > 2σ(I) = 14 056, No. of parameters refined = 1202, GOF = 1.055, R₁ = 0.0311, wR₂ = 0.0685.
- H.S. Lee, J.H. Seo, M.K. Choi, Y.K. Kim, Y. Ha, *J. Phys. Chem. Solids* 69 (2008) 1305.
- F.H. Allen, J.E. Davies, J.J. Galloy, O. Johnson, O. Kennard, C.F. Macrae, E.M. Mitchell, G.F. Mitchell, J.M. Smith, D.G. Watson, *J. Chem. Inf. Comput. Sci.* 31 (1991) 187.
- J. Ding, J. Gao, Q. Fu, Y. Cheng, D. Ma, L. Wang, *Synth. Met.* 155 (2005) 539.
- B. Schmid, F.O. Garces, J.R. Watts, *Inorg. Chem.* 33 (1994) 33.
- K.R.J. Thomas, M. Velusamy, J.T. Lin, C. Chien, Y. Tao, Y.S. Wen, Y. Hu, P. Chou, *Inorg. Chem.* 44 (2005) 5677.