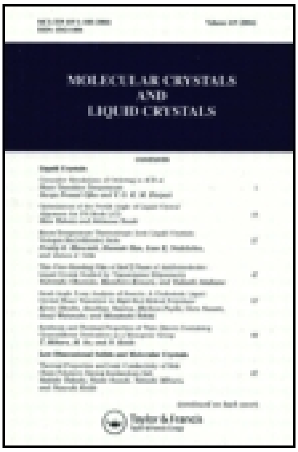

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Luminescence Comparison of Iridium(III) Complexes Containing Symmetric vs. Asymmetric Quinolinate Ligands

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We have focused our research on development of the iridium complexes, especially with respect to blue and red emission for OLED. Previously, we prepared bis-[2,3-bis(4-fluorophenyl)quinoxalinato]iridium(acetylacetonate) [Ir(2,3-dpqx-F_2)$_2$-(acac)] where the main ligand, 2,3-dpqx-F_2, itself is symmetric. The luminescence spectra of Ir(2,3-dpqx-F_2)$_2$(acac) revealed red emission with the peak at approximately 640 nm with the CIE coordinates of (0.684, 0.311). Recently, Johannes et al. *reported the iridium complexes containing fluorophenylmethylquinoxaline derivatives (fpmqx) as asymmetric main ligands and investigated their luminescence properties. Herein, we synthesized symmetric Ir(2,3-dpqx-F_2)$_2$(AL) and asymmetric Ir(fpmqx)$_2$(AL) and compared their emission patterns and characteristics where accetylacetonate (acac) and 2-(5-(trifluoromethyl)-2*H*-1,2,4-triazol-3-yl)pyridine (trzl-CH_3) were introduced as ancillary ligands(AL). We investigated the emission properties of Ir(2,3-dpqx-F_2)$_2$(AL) and Ir(fpmqx)$_2$(AL), and found that asymmetric Ir(fpmqx)$_2$(AL) showed blue-shifted photoluminescence compared with symmetric Ir(2,3-dpqx-F_2)$_2$(AL). We also estimated the energy gap between the HOMO and LUMO of the complexes with electrochemical properties measured by cyclic voltammetry.*

Keywords Asymmetric vs. symmetric ligand; iridium complex; organic light-emitting diode; red phosphorescence

Introduction

As phosphorescent materials of organic light emitting devices (OLEDs), iridium(III) complexes are attracting much attention because of their high efficiency and chemical stability. These complexes are easy to process as small molecules in ultra-high vacuum processes, which make them good candidates for OLED applications [1–5]. In addition, they have ability to harvest both singlet and triplet excitons, achieving nearly 100% internal quantum efficiency [6–8]. Such high efficiency is due to strong spin orbit coupling by the heavy metal iridium center, which allows fast energy transfer from singlet to triplet states and also removes the forbidden character of radiative transition to ground states, leading to efficient phosphorescence for these

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complexes [9]. However, it is difficult to the goal of achieving three primary colors with high color purity. Compared to green phosphorescent iridium complexes, development of the orange- and red-emitting complexes presents a particular challenge because their luminescence quantum yield tends to be low due to the smaller energy gap [10,11].

Recently, Johannes *et al.* reported the iridium complexes containing fluorophenylmethylquinoxaline derivatives (fpmqx) as asymmetric main ligands and investigated their luminescence properties [2]. In this study, we prepared the iridium complexes, Ir(2,3-dpqx-F_2)$_2$(AL) and Ir(fpmqx)$_2$(AL), where symmetric 2,3-dpqx-F_2, asymmetric fpmqx, and AL (acac and trzl-CH_3) represent the ligands of 2,3-bis(4-fluorophenyl)quinoxaline, 2-(4-fluorophenyl)-3-methylquinoxaline, acetylacetonate and 2-(5-methyl-4*H*-1,2,4-triazol-3-yl-pyridine, respectively. We compared the effect of the symmetric and asymmetric C^N ligands on luminescence of their complexes. Electrochemical characterization of iridium complexes was also performed to investigate their luminescence color and energy gap between HOMO and LUMO. It was found that the asymmetric complexes exhibit the shorter emission wavelengths than the symmetric ones. Furthermore, introduction of two different ancillary ligands to the iridium complexes revealed their effects to photoabsorption, photoemission and electrochemical properties and thereby the emission color tuning of the complexes.

Experimental

All reagents were purchased from Aldrich Co. and Strem 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 with the use of silica gel (230-mesh, Merck).

Synthesis of Ligands

2,3-dpqx-F_2. The symmetric 2,3-bis-(4-fluorophenyl)quinoxaline was obtained according to Friedlander Reaction [12] with the corresponding precursor, 2-phenylacetophenone (1.96 g, 10.0 mmol) and 4,4′-difluorobenzil (2.46 g, 10.0 mmol). Yield: 70%.

Fpmqx. The asymmetric 2-(4-fluorophenyl)-3-methylquinoxaline was obtained from the reaction of 1-(4-fluorophenyl)propane-1,2-dione and 1,2-diaminobenzene. The synthesis of 1-(4-Fluorophenyl)propane-1,2-dione (fppd) was as follows: First, to a 100 ml round bottom flask containing 4-fluoropropiophenone (4.0 g, 26.3 mmol) and aluminum chloride (52 mg, 0.4 mmol) in 20 ml dry diethyl ether, bromine (3.2 ml, 63.1 mmol) was added dropwise at 0°C over 10 min. The dark red suspension was heated to reflux with stirring for 21 h. After cooling to room temperature, the solvent was removed under reduced pressure. The resulting oil was mixed with a solution of sodium methoxide (3.83 g, 71.0 mmol) in 30 ml of dry methanol, and the mixture was stirred at 0°C over 15 min. Followed by addition of 8.2 ml of concentrated hydrochloric acid, the overall mixture was warmed slowly to room temperature and stirred for 1.5 h. The precipitate was filtered off and washed repeatedly with diethyl ether. The combined filtrate was concentrated and extracted with chloroform. The organic phases were dried with anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography to obtain yellow oil. The resulting 1-(4-fluorophenyl)propane-1,2-dione (2.44 g, 14.7 mol) was reacted with 1,2-diaminobenzene (1.91 g, 17.6 mol) and iodine (0.37 g, 1.5 mmol) in 15 ml of acetonitrile. The reaction mixture was stirred for 10 min at room temperature. The solvent was removed under reduced pressure, and the crude product was purified by flash chromatography to yield a yellow solid (88%).

Synthesis of Iridium Complexes

The iridium complexes with an ancillary ligand, acetylacetonate (acac) or 2-(5-methyl-4H-1,2,4-triazol-3-yl)pyridine (trzl-CH_3) was prepared from the reaction of the cyclometalated iridium μ-chloro-bridged dimer, $(C\^{}N)_2Ir(\mu\text{-}Cl)_2Ir(C\^{}N)_2$, with the corresponding ancillary ligand, according to the method reported by Nonoyama with slight modification [13].

Ir(2,3-dpqx-F_2)$_2$(AL) (AL = acac, trzl-CH_3). (2,3-dpqx-F_2)$_2$Ir(μ-Cl)$_2$Ir(2,3-dpqx-F_2)$_2$ (1.73 g, 1.9 mmol) and an excess of the ancillary ligands were mixed with Na_2CO_3 (500 mg) in 2-ethoxyethanol (30 mL). The mixture was refluxed for 2 h. The solution was cooled to room temperature and the red solid was filtered. The obtained product was chromatographed on silica gel column with dichloromethane and purified by recrystallization.

Ir(2,3-dpqx-F_2)$_2$(acac). Yield: 69%. FAB-MS: calculated 926; found 926. ^{1}HNMR($CDCl_3$, 400 MHz) : δ 8.20–6.04 (m, 22H, aromatic C-H); 5.3, 4.7 (S, 2H, acac-CH3); 1.6 (S, 1H, acac-H). Anal. Calc. for $C_{45}H_{29}F_4IrN_4O_2$: C, 58.37; H, 3.16; N, 6.05. Found: C, 56.97; H, 3.18; N, 5.87%.

Ir(2,3-dpqx-F_2)$_2$(trzl-CH_3). Yield: 62%. FAB-MS: calculated 986; found 986. ^{1}HNMR($CDCl_3$, 400 MHz) : δ 8.09–6.36 (m, 24H, aromatic C-H); 1.20 (S, trzl-CH_3, 3H). Anal. Calc. for $C_{48}H_{29}F_4IrN_8$: C, 58.47; H, 2.96; N, 11.36. Found: C, 56.76; H, 3.18; N, 10.15%.

Ir(fpmqx)$_2$(AL) (AL = acac, trzl-CH_3). (fpmqx)$_2$Ir(μ-Cl)$_2$Ir(fpmqx)$_2$(0.80 g, 0.57 mmol), an excess of the ancillary ligands and potassium *tert*-butoxide (0.16 g, 1.42 mmol) in 20 ml of dry dichloromethane and 6 ml of dry ethanol was stirred at room temperature for 20 h. The solvent was removed under reduced pressure and the crude product purified by flash chromatography [2].

Ir(fpmqx)$_2$(acac). Yield: 78%. FAB-MS: calculated 766; found 766. ^{1}HNMR($CDCl_3$, 400 MHz): δ 8.24–6.14 (m, 14H, aromatic C-H); 4.55 (s, 1H, CH3); 3.32, 3.14 (s, 2H, acac-CH3); 1.47 (d,1H, acac-H). Anal. Calc. for $C_{35}H_{27}F_2IrN_4O_2$: C, 54.89; H, 3.55; N, 7.32. Found: C, 50.47; H, 3.52; N, 6.67%.

Ir(fpmqx)$_2$(trzl-CH_3). Yield: 77%. FAB-MS: calculated 826; found 826. ^{1}HNMR($CDCl_3$, 400 MHz) : δ 8.46–6.36 (m, 16H, aromatic C-H); 4.83 (s, 1H, CH3); 2.38 (t, 1H, trzl-CH3). Anal. Calc. for $C_{38}H_{27}F_2IrN_8$: C, 55.26; H, 3.30; N, 13.57. Found: C, 48.75; H, 3.36; N, 11.22%.

Measurements

UV-visible absorption spectra were obtained from Hewlett Packard 8425A spectrometer. Photoluminescence (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. Cyclic voltammograms were obtained at scan rate of 100 mV/s with Electrochemical Analyzer of CH Instruments. ^{1}HNMR spectra were obtained from a 400 MHz NMR at Sogang University, and mass spectra were determined on JEOL, JMS-AX505WA, HP 5890 Series II Hewlett-Packard 5890A (capillary column) at Seoul National University in Korea.

Results and Discussion

For the new iridium complexes we prepared two different main ligands, 2,3-dpqx-F_2 which is symmetric itself and fpmqx which is asymmetric, according to the modified Suzuki coupling method [14]. We also introduced two different ancillary ligands, acac and trzl-CH_3 to the iridium complexes. The ancillary ligand, trzl-CH_3, which was previously developed for fine tuning of the emission color and luminescence efficiency [15] was prepared from the reaction of amidrazone precursor with acetyl chloride, according to the reported procedure [15,16]. The iridium complexes were synthesized via two steps, as reported by Nonoyama [13]. The overall synthetic schemes are illustrated in Figure 1.

The UV-Vis absorption spectra of the complexes in CH_2Cl_2 are shown in Figure 2. The absorption spectra of iridium complexes, Ir(2,3-dpqx-F_2)$_2$(acac) and Ir(2,3-dpqx-F_2)$_2$(trzl-CH_3), containing symmetric main ligands have resemblance in the absorption patterns. Those of iridium complexes, Ir(fpmqx)$_2$(acac) and Ir(fpmqx)$_2$(trzl-CH_3), containing asymmetric fpmqx ligands are also similar each other. First, Ir(2,3-dpqx-F_2)$_2$(acac) and Ir(2,3-dpqx-F_2)$_2$(trzl-CH_3) have strong absorption appearing in the ultraviolet region of the spectrum between 230 and 310 nm. These bands have been assigned to the spin-allowed $^1(\pi \rightarrow \pi^*)$ transitions of the main ligands. The $^1(\pi \rightarrow \pi^*)$ bands are accompanied by weaker and lower energy features extending into the visible region from 320 to 420 nm. These absorption bands have been assigned to the allowed MLCT transitions. The high intensity of the MLCT bands has been attributed to effective mixing of these charge-transfer transitions with high lying spin-allowed transitions on the cyclometalating ligand [17]. MLCT is important with respect to the emission efficiency. The weak absorptions at the longer wavelengths than 420 nm are presumably due to the forbidden ^{3}MLCT transitions. Secondly, the absorption spectra of Ir(fpmqx)$_2$(acac) and Ir(fpmqx)$_2$(trzl-CH_3) also have almost identical patterns each other. The spin-allowed $^1(\pi \rightarrow \pi^*)$ transitions of the ligands appeared below 310 nm. The MLCT bands of the Ir complexes containing 2-(5-methyl-4*H*-1,2,4,-triazol-3-yl)pyridine (trzl-CH_3) shown from 310 to 400 nm have higher absorption intensity than those of the Ir acetylacetonate complexes. Relatively strong absorption in that region could lead to improvement of emission efficiency in the iridium complexes.

The photoluminescence (PL) spectra of the Ir complexes in 10^{-5} M CH_2Cl_2 solution are shown in Figure 3. Ir(2,3-dpqx-F_2)$_2$(acac), Ir(2,3-dpqx-F_2)$_2$(trzl-CH_3), Ir(fpmqx)$_2$(acac) and Ir(fpmqx)$_2$(trzl-CH_3) exhibited the emission maxima at 650, 620 and 631, 615 nm, respectively. The complexes containing asymmetric main ligands, Ir(fpmqx)Ir(fpmqx)$_2$(trzl-CH_3), showed PL emission at shorter wavelengths. We attribute such hypsochromic shift by the complexes of fpmqx in PL partly to the less conjugation in the main ligands. Though the fluorophenyl group in 2,3-dpqx-F_2 ligand can partially be tilted from the main plane of the ligand, it may still contribute to the elongation of conjugation, resulting in lower energy gap of the iridium complexes, as pointed out by Johannes, *et al.* [2]. Furthermore, substitution of the fluorophenyl group with the methyl group can reduce the rotational movement of the fluorophenyl group which may cause nonradiative pathway of the iridium

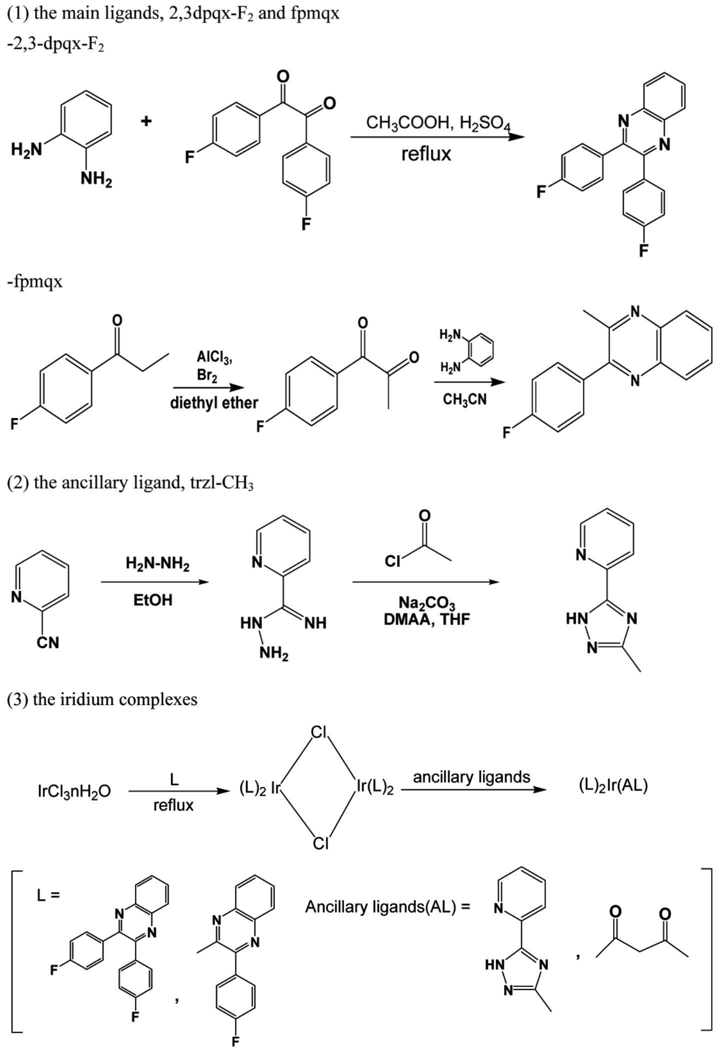
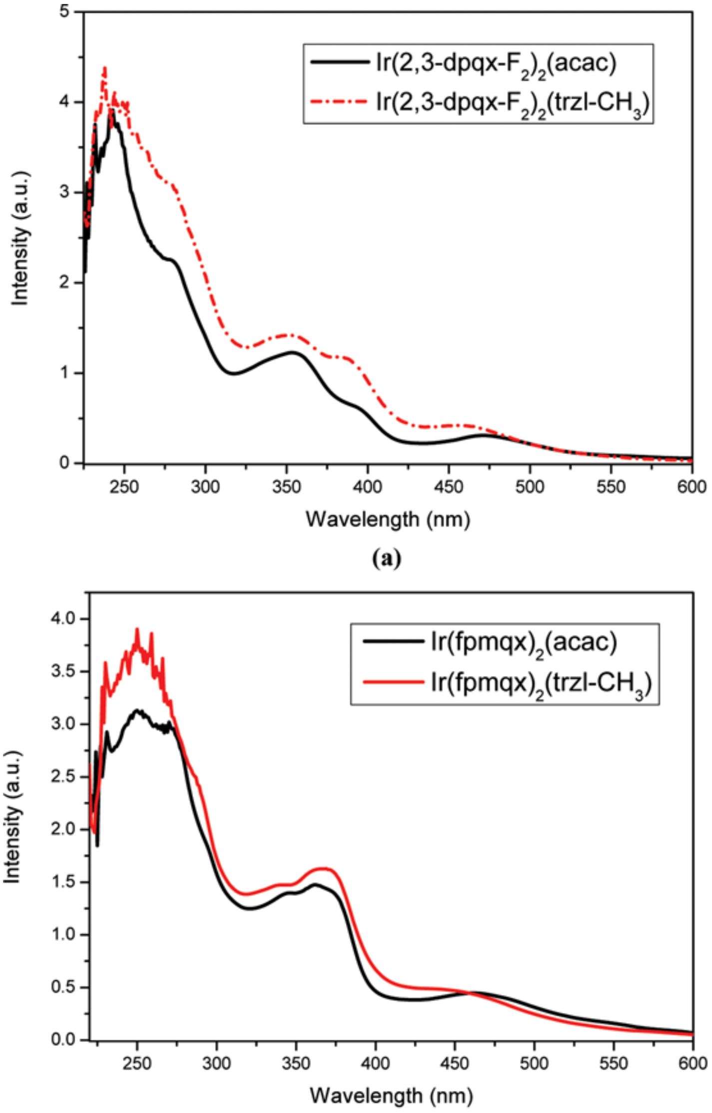


Figure 1. The synthesis of main ligands, ancillary ligands and their iridium complexes.

complexes. The effect of ancillary ligands on the luminescence characteristics of their iridium complexes was also investigated. The blue shifts of 16~30 nm by the complexes containing the trzl-CH_3 ancillary ligand were observed. Such hypsochromic shift by the ancillary ligand can be attributed to involvement of electron withdrawing N atom to the ancillary ligand skeleton. In fact, this blue shift by ancillary ligand substitution is more than expected. The ancillary ligands are usually known to involve in fine tuning of emission color by their complexes. However, up to 30 nm shift upon ancillary ligand change from acac to trzl-CH_3 was observed in Ir(2,3-dpqx-F_2)$_2$(AL).

We investigated electrochemical properties of the Ir complexes by the cyclic voltammetry (CV), which reveal their positions of the HOMO/LUMO [11,12]. The detailed CV data were summarized in Table 1. The oxidation potentials which indicate the HOMOs of the complexes were irreversible in the range of 0.45–0.78 V



(a)

(b)

Figure 2. UV-Vis absorption spectra of (a) Ir(2,3-dqpx-F$_2$)$_2$(AL) and (b) Ir(fpmqx)$_2$(AL) in a 10^{-5} M CH$_2$Cl$_2$ solution (AL = acac, trzl-CH$_3$).

relative to an internal ferrocenium/ferrocene reference (Fc$^+$/Fc). The reduction potentials of the complexes in this study were calculated to be between −2.53 and −2.93 eV. Using the equation HOMO = −4.8 − E_{ox}, the HOMO of Ir(fpmqx)$_2$-(trzl-CH$_3$) was calculated to be −5.52 eV, that has the largest energy gap (ΔE) of 2.85 eV, which consists with emission spectra having the shortest emission wavelength in PL.

Further studies are undergoing on device fabrication using these complexes as red phosphorescent materials to compare electroluminescence characteristics such

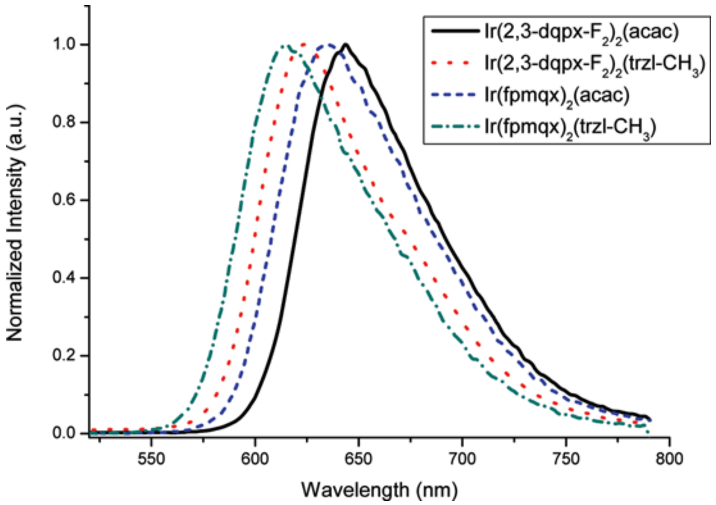


Figure 3. PL spectra of Ir(2,3-dqpx-F$_2$)$_2$(AL) and Ir(fpmqx)$_2$(AL) in a 10^{-5} M CH_2Cl_2 solution (AL = acac, trzl-CH$_3$).

Table 1. Physical parameters for the complexes

Ir complex	λ_{em}/nm[a]	E_{ox}/V[b]	HOMO/eV[c]	LUMO/eV[d]	ΔE/eV[d]
Ir(2,3-dpqx-F$_2$)$_2$(acac)	650	0.62	−5.42	−2.83	2.59
Ir(2,3-dpqx-F$_2$)$_2$(trzl-CH$_3$)	620	0.45	−5.25	−2.53	2.72
Ir(fpmqx)$_2$(acac)	631	0.5	−5.30	−2.61	2.69
Ir(fpmqx)$_2$(trzl-CH$_3$)	615	0.78	−5.58	−2.75	2.83

[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 $\text{HOMO} = -4.8 - E_{ox}$.

[d] Calculated from the optical edge $\Delta E = \text{LUMO} - \text{HOMO}$.

as CIE coordinates and luminescence efficiencies of the iridium complexes containing symmetric vs. asymmetric main ligands.

Conclusions

We reported the detailed synthesis and photophysical properties of the phosphorescent iridium complexes having symmetric 2,3-dpqx-F$_2$ ligands and an asymmetric fpmqx ligands, and directly compared their luminescence properties. We also employed two different ancillary ligands and investigated the effect of the ancillary ligand on the luminescence of their complexes. The iridium complexes, Ir(2,3-dpqx-F$_2$)$_2$(acac), Ir(2,3-dpqx-F$_2$)$_2$(trzl-CH$_3$) and Ir(fpmqx)$_2$(acac) Ir(fpmqx)$_2$(trzl-CH$_3$), prepared in this study exhibited the red emission at 650, 620, 631 and 615 nm respectively.

We expected that the iridium complexes which contain asymmetric main ligands might exhibit the blue shift compared to the iridium complexes containing the symmetric ones. As a matter of fact, the hypsochromic shift by the complexes with asymmetric fpmqx ligands was observed and such blue shift can be explained by substitution of the conjugated phenyl ring with a non-conjugated methyl fragment. The ancillary ligand also served an important role in determining the luminescence wavelength. Ir(fpmqx)$_2$(trzl-CH$_3$) showed the most blue shift on emission and had the largest energy gap due to the trzl-CH$_3$ ancillary ligand having the electron-withdrawing ability.

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