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Synthesis and the Luminescent Study of the Iridium Complexes Containing 2,3-Diphenylquinoline Derivatives and the New Ancillary Ligand for OLED

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We previously reported that Ir(6-F-2,3-dpqx-(OMe)$_2$)$_2$(acac) (6-F-2,3-dpqx-(OMe)$_2$ = 6-fluoro-2,3-bis(4-methoxylphenyl)quinoxaline) exhibited photoluminescence (PL) and electroluminescence (EL) emission at 645 and 667 nm, respectively. To modulate the emission maxima toward the saturated red chromacity, a new main ligand and its iridium complexes were prepared, and their photophysical properties were investigated. As a main ligand, 6-OMe-2,3-dpqx-(OMe)$_2$ (6-OMe-2,3-dpqx-(OMe)$_2$ = 6-methoxy-2,3-bis(4-methoxylphenyl)quinoxaline), were designed and synthesized. Acetylacetonate (acac) and pyrazolonates (przls) were also chelated to the iridium center as an ancillary ligand. The resulting complexes prepared herein were Ir(6-OMe-2,3-dpqx-(OMe)$_2$)$_2$(acac), Ir(6-OMe-2,3-dpqx-(OMe)$_2$)$_2$(przl1) and Ir(6-OMe-2,3-dpqx-(OMe)$_2$)$_2$(przl2). The photoluminescence (PL) of these complexes were observed around 660 nm, and their electroluminescence maxima were observed around 650 nm. The PL investigation of the complexes in PMMA (PMMA = poly(methylmetacrylate)) for the polymer solution process revealed that the emission peaks became broader with the range of 600~850 nm than those of the complexes only.

Keywords: iridium complex; OLED; pyrazolone-based ancillary ligands (przl series); red phosphorescence

1. INTRODUCTION

Organic light-emitting diodes (OLEDs) involving phosphorescent compounds as an emitting dopant have been developed because they generally exhibit higher efficiencies than those containing

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conventional fluorescent materials [1–7]. The heavy transition metal complexes can provide large population of the emitting triplet state by strong spin-orbit coupling induced by the metal center, resulting in high efficiency. The iridium(III) complexes with high luminescence efficiency were also known to have relatively short excited emissive states, suitable for a phosphorescent dopant in OLEDs [8–9]. The cyclometalating ligands in the iridium complex were reported to determine the major color of phosphorescence with control of the energy gap between the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) [10–11]. Thus, modification of cyclometalating ligands by adding an electron-donating or -withdrawing group should lead to emission color tuning of their complexes.

The ancillary ligands for the iridium complexes tend to influence the perturbation degree of the metal-to-ligand charge transfer (MLCT) transition by the excited-state interaction with the cyclometalating ligand centered (LC) state, causing the minor change in emission wavelengths [12]. As recently reported [13–14], introduction of the new bulky ancillary ligand, pyrazolate, to red-emitting Eu(III) and Ir(III) complexes could result in the luminous efficiency improvement by their orbital mixing with the Ir d-orbitals. Our previous results also indicated that replacement of acac with przl in the iridium complexes could improve the emission efficiency and lead to fine-tuning of the emission wavelength [15]. Pyrazolone based ligands 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.

According to our earlier report [16] an iridium complex, Ir(6-F-2,3-dpqx-$(OMe)_2)_2$(acac), exhibited its electroluminescence (EL) emission at 667 nm with luminous efficiency of 2.39 cd/A. This luminescence was in rather deep red region, and thus increase of the band gap was required for the saturated red emission by controlling the energy levels of the HOMOs and/or LUMOs. Therefore, another cyclometallating ligand, 6-methoxy-2,3-bis(4-methoxyphenyl)quinoxaline, was prepared to tune the emission color of its iridium complexes toward the saturated red region. Additionally, for fine tuning of the emission color, the ancillary ligand, acetylacetonate (acac) was replaced with the pyrazolone-based ligands, 4-R-5-methyl-2-phenyl-2,4-dihydro-pyrazol-3-one (przl) series, where the przl ligand series have different substituents at the 4-position of the ring. As a result, new iridium complexes, Ir(6-OMe-2,3-dpqx-$(OMe)_2)_2$(acac) and Ir(6-OMe-2,3-dpqx-$(OMe)_2)_2$(przls), were synthesized and their PL properties were compared. Fabrication of OLEDs was attempted with the complexes prepared herein as an emitting dopant, and the preliminary EL spectra were obtained. Furthermore, the PMMA film spin coated with iridium complexes were fabricated and their film PLs were also studied.

2. EXPERIMENTAL DETAILS

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 Co.). Mass spectra were determined on JEOL, JMS-AX505WA, HP 5890 Series II Hewlett-Packard 5890A (capillary column) at Seoul National University, Korea.

2.1. Synthesis of Ligands

Synthesis of Prazolone Ligands (Przl1 and Przl2)

1-phenyl-3-methyl-5-pyrazolone (3.5 g, 10 mmol) was dissolved in 40 ml of dried 1,4-dioxane in a 100 ml flask. Calcium hydroxide (3.552 g) and barium hydroxide (2.064 g) were added. Acylchloride (acetyl chloride or benzoyl chloride) (11.6 mmol, 1.64 ml/1.345 ml, respectively) were dripped slowly to the solution mixture under stirring. After the reflux for 24 h, the reaction mixture was cooled and poured into a 70 ml solution of ice-cold hydrochloric acid solution [$HCl:H_2O = 3:7$ (v/v)]. The product was extracted with dichloromethane and recrystallized from acetone and water [13–14]. Yield: 60%.

6-methoxy-2,3-bis(4-methoxyphenyl)quinoxaline (6-OMe-2,3-dpqx-$(OMe)_2$)

4-Methoxy-o-phenylenediamine dihydrochloride (2.1 g, 10.0 mmol) with NaOH(0.48 g, 12 mmol) in 30 ml ethanol. The solution was heated to reflux for 5 h. The mixture was cooled at room temperature and removed water and salt. The dark purple solution was evaporated at vacuum. This step was neutralization reaction before synthesize the ligand. This ligand for emission was obtained according to Friedlander reaction [17] of neutralized 4-Methoxy-o-phenylenediamine dihydrochloride (1.38 g, 10.0 mmol) with 4,4′-dimethoxybenzil (2.70 g, 10.0 mmol) in 30 ml of glacial acetic acid. The solution was heated to reflux for 6 h at 110°C. The reaction mixture was then cooled and dripped slowly with stirring into an ice-cold solution of 50% ammonium hydroxide (160 ml). The resulting yellow precipitate was collected by filtration. The solid was column chromatographed on a silica gel column with dichloromethane and dried to obtain the product. Yield: 68%.

2.2. Synthesis of Iridium(III) Complexes

Synthesis of Ir(6-OMe-2,3-dpqx-(OMe)$_2$)$_2$(acac)

First, the cyclometallated Ir(III) μ-chloro-bridged dimer, (6-OMe-2,3-dpqx-(OMe)$_2$)$_2$Ir(μ-Cl)$_2$Ir(6-OMe-2,3-dpqx-(OMe)$_2$)$_2$ (3.88 g, 2 mmol), was prepared according to the Nonoyama method [18]. Second, the resulting dimer and 2,4-pentandione (0.698 ml, 6.8 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. Ir(6-OMe-2,3-dpqx-(OMe)$_2$)$_2$(acac) was purified by chromatography on silica gel column with dichloromethane and recrystallization from dichlorometane/hexane. Yield: 63%. FAB-MS: calculated: 1034.3; found: 1034.

Synthesis of Ir(6-OMe-2,3-dpqx-(OMe)$_2$)$_2$(przl)

Ir(6-OMe-2,3-dpqx-(OMe)$_2$)$_2$(przl) were prepared according to the method as described above. Yield: 60%.

Ir(6-OMe-2,3-dpqx-(OMe)$_2$)$_2$(przl1) : Yield 59% FAB-MS: calculated: 1150.3; found: 1150.

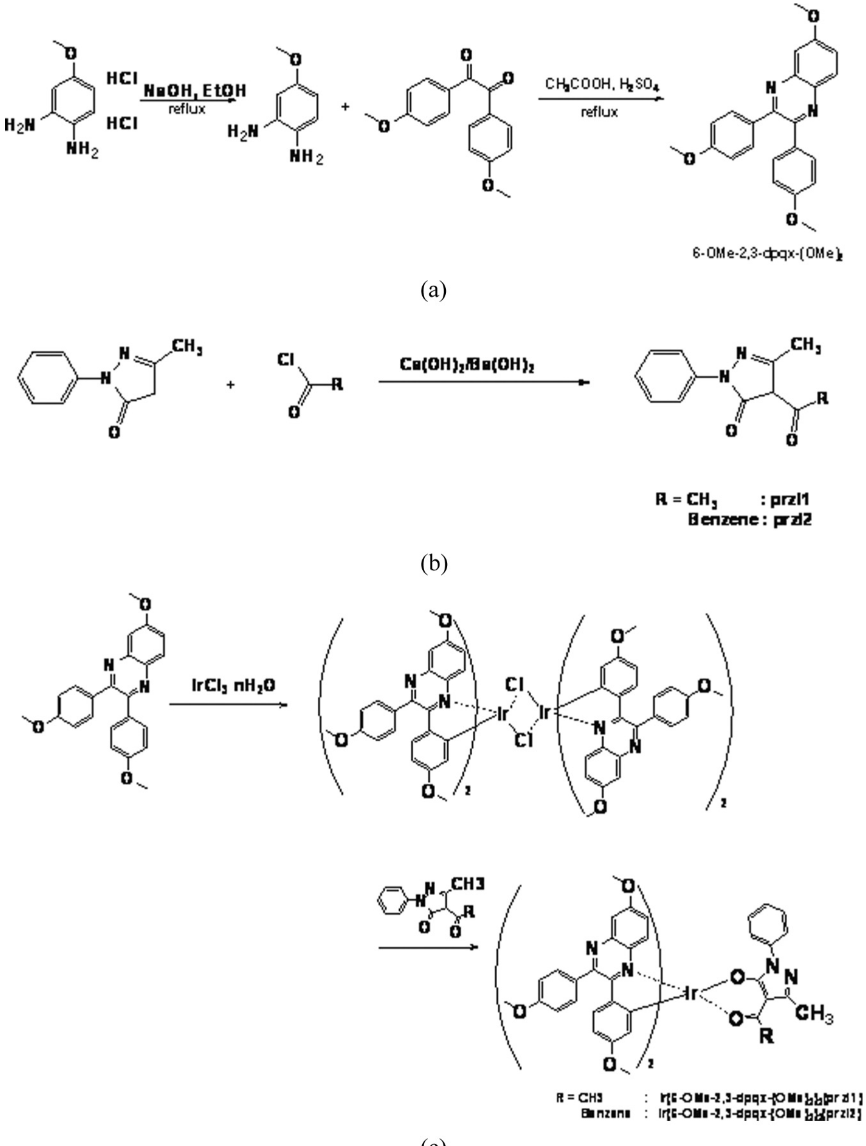
Ir(6-OMe-2,3-dpqx-(OMe)$_2$)$_2$(przl2) : Yield 61% FAB-MS: calculated: 1212.3; found: 1212.

2.3. 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 and in the PMMA film. The film was prepared by spin-coating of PMMA solution containing 10 wt% Ir complexes in 1,2-dichloroetane onto the glass substrate and the following solvent evaporation.

3. RESULTS AND DISCUSSION

The main ligand, 6-OMe-2,3-dpqx-(OMe)$_2$, was synthesized according to Friedlander Reaction, as illustrated in Figure 1(a). A series of przl, 4-R-5-methyl-2-phenyl-2,4-dihydro-pyrazol-3-one (R = methyl (przl1), phenyl (przl2)) were prepared as shown in Figure 1(b). Two kinds of R groups were chosen to study the electronic and steric effects of the R at przl in the iridium complexes on the luminescence properties. The synthetic method of the iridium complexes, Ir(6-OMe-2,3-dpqx-(OMe)$_2$)$_2$(acac or przl), involved two steps, formation of the dimer and the following coordination of przl-based ligands, as summarized in Figure 1(c).



(a)

(b)

(c)

FIGURE 1 Synthetic scheme of the ligands and iridium complexes.

The UV-Vis absorption spectra of the complexes in CH_2Cl_2 are shown in Figure 2. The strong absorption bands between 200 and 400 nm in the ultraviolet region are assigned to the spin-allowed

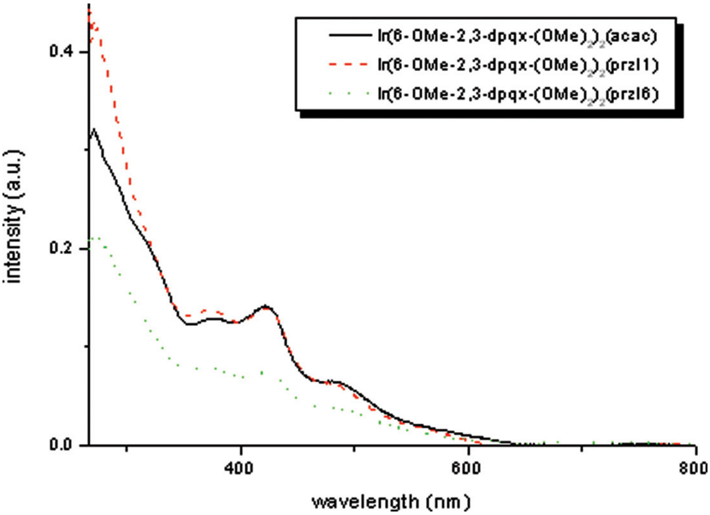


FIGURE 2 UV-Vis absorption spectra of the iridium complexes in a 10^{-5} M CH_2Cl_2 solution.

$^1\pi$-π^* transition of the cyclometalating 6-OMe-2,3-dpqx-$(OMe)_2$ ligand in the complexes. The weak bands between 400 and 450 nm in the visible region can be assigned to the spin-allowed metal-to-ligand charge transfer band (^{1}MLCT), and the weaker absorption bands at the longer wavelengths can be attributed to the spin-forbidden ^{3}MLCT and spin-orbit coupling enhanced $^3\pi$-π^* transition. The formally spin-forbidden ^{3}MLCT gains the intensity by mixing with the higher-lying ^{1}MLCT transition through the strong spin-orbit coupling by the iridium center. The absorption patterns of these complexes are similar with few differences in the peak wavelengths, suggesting that change of the ancillary ligand does not make significant contribution to the absorption process. The absorption spectra of those in PMMA film have similar patterns and the absorption peaks appeared at 425, 430, and 480 nm (Fig. 3).

The photoluminescence (PL) spectra of the Ir complexes in 10^{-5} M CH_2Cl_2 solution are shown in Figure 4. The emission maxima for Ir(6-OMe-2,3-dpqx-$(OMe)_2)_2$(acac), Ir(6-OMe-2,3-dpqx-$(OMe)_2)_2$(przl1) and Ir(6-OMe-2,3-dpqx-$(OMe)_2)_2$(przl2) appeared at 667, 661, and 658 nm, respectively. There is no substantial difference in PL emission by changing the ancillary ligands in the complexes. The PL spectra are only slightly shifted within 10 nm upon the ancillary ligand variation in the complexes.

Such PL peaks of Ir(6-OMe-2,3-dpqx-$(OMe)_2)_2$(acac or przl) around 660 nm should be noted. According to our previous result, the emission

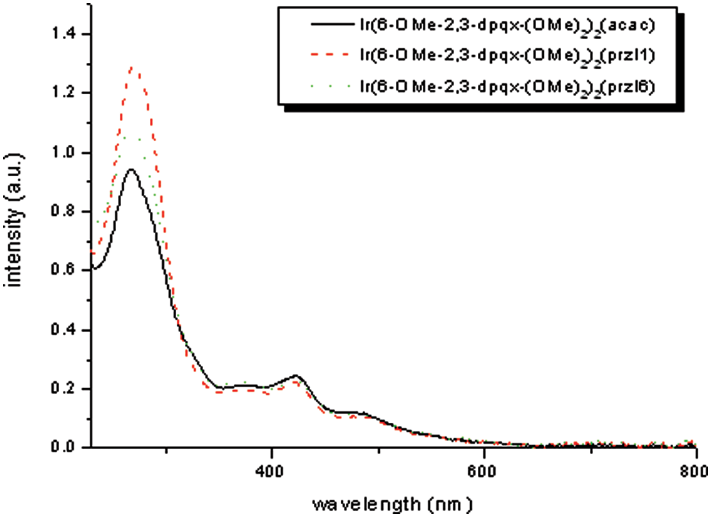


FIGURE 3 UV-Vis absorption spectra of PMMA film containing the Ir complexes.

maxima of Ir(6-F-2,3-dpqx-(OMe)$_2$)$_2$(acac) occurs at 645 nm. Substitution of an electron withdrawing F for an electron donating OMe group at 6-position in the LUMO site of the complex is supposed

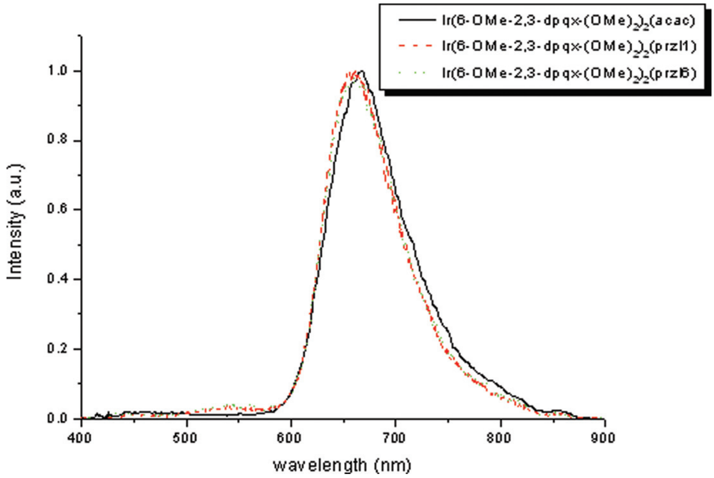


FIGURE 4 PL spectra of the iridium complexes in a 10^{-5} M CH_2Cl_2 solution.

to cause band gap increase by raising the LUMO levels, resulting in hypsochromic shift. However, the results indicate otherwise. The PL of the complexes containing 6-OMe substituted ligands exhibit slightly red-shifted peaks. On the other hand, comparison of EL spectra of these complexes reveals that Ir(6-OMe-dpqx-$(OMe)_2)_2$(acac or przl) has the maxima around 650 nm, blue-shifted from the EL peaks of Ir(6-F-dpqx-$(OMe)_2)_2$(acac) at 660 nm as expected, *vide infra*. Therefore, we conclude that the substituents at 6-position of the dpqx ligand in the complex do not influence the emission wavelengths significantly, contrary to our prediction.

Their electroluminescence (EL) properties are also investigated (Fig. 6). The configuration of the EL device is ITO/ NPB/ CBP:Ir complex 8%/BPhen/Liq/Al. The maximum EL wavelengths of Ir(6-OMe-2,3-dpqx-$(OMe)_2)_2$(acac) and Ir(6-OMe-2,3-dpqx-$(OMe)_2)_2$ (przl2) are 655 and 646 nm, blue-shifted from their PLs and that of r(6-F-2,3-dpqx-$(OMe)_2)_2$(acac) as mentioned above. Nonetheless, the EL patterns of the device for Ir(6-OMe-2,3-dpqx-$(OMe)_2)_2$(acac) are consistent with the corresponding PL patterns in solution, suggesting that the same exciting states are generated during photo- and electrical excitation. Detailed EL investigation was not possible due to the low volatility of the iridium complexes containing 6-OMe-2,3-dpqx-(OMe) and przl ligands.

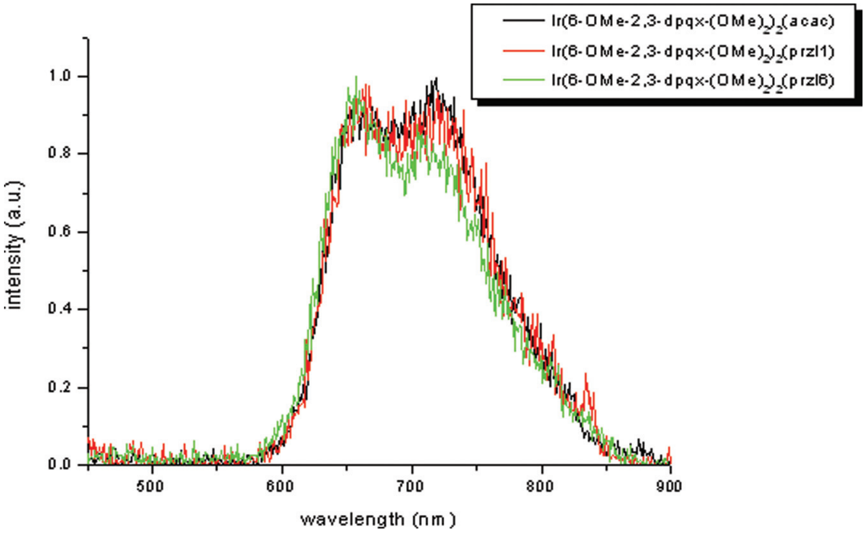


FIGURE 5 PL spectra of PMMA film containing the Ir complexes.

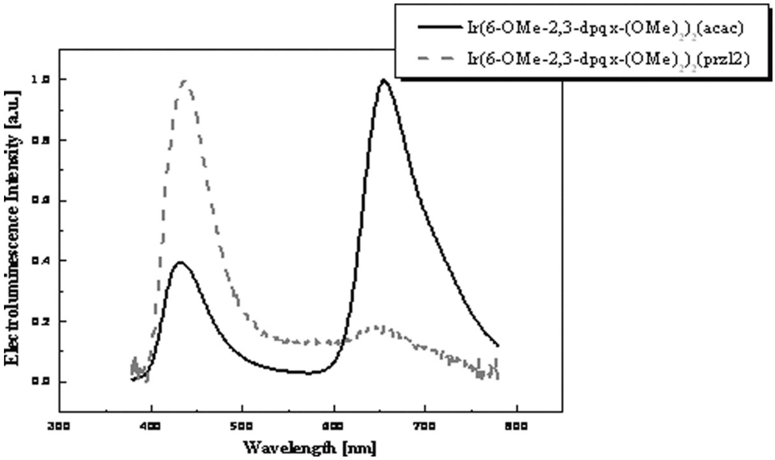


FIGURE 6 EL spectra of the Ir complexes.

Instead, we attempted to investigate their PLs in PMMA(poly (methylmethacrylate)) film for the polymer light-emitting device (PLED) application. PMMA is chosen as a host because its non-emitting property within the visible range could provide the PL of the iridium complex only. The PMMA film is fabricated by spin-coating of 10 wt% Ir complexes in PMMA onto the glass substrate. As depicted in Figure 5, The PL maxima of the PMMA film for Ir(6-OMe-2,3-dpqx-(OMe)$_2$)$_2$(acac), Ir(6-OMe-2,3-dpqx-(OMe)$_2$)$_2$(przl1) and Ir(6-OMe-2,3-dpqx-(OMe)$_2$)$_2$(przl2) appear at 657/719(sh) nm, 665/713(sh) nm and 657/704(sh) nm, respectively. PL spectra in PMMA film of the complexes show broader emission than those of the complexs in solution with the shoulder peaks in longer wavelengths as listed above. We attribute such emission at the longer wavelengths to formation of excimers. The interaction between the dopants may cause excimer formation through some extension of dopant dimeric units with strong π-π interaction. The emission from the excimers could be shown in the longer wavelengths than that of the complex itself, yielding the red-shifted and broadened the PL emission [19–20]. Further investigation of the complexes in other polymeric films such as PVK is in progress for the PLED application.

4. CONCLUSION

We designed and prepared the iridium complexes involving the ligand of dpqx derivatives and an acac or a przl as an ancillary ligand.

The UV-Vis spectra of the complexes containing acac and przl-based ligands were similar, indicating that variation of ancillary ligands did not make significant contribution to absorption process. The PL emission in solution of the iridium complex containing acac as an ancillary ligand were slightly shifted within 10 nm, from those of pyrazolone-based iridium complexes. Such shift, however, was not significant, and thus the effect by the ancillary ligands was found to be negligible within the experimental errors. The PL spectra of the complexes dispersed in the PMMA film were red-shifted and broadened with the shoulder peaks, compared with their corresponding solution spectra, suggesting formation of dopant excimers in the film. The EL devices of $Ir(6\text{-}OMe\text{-}2,3\text{-}dpqx\text{-}(OMe)_2)_2(acac)$ and $Ir(6\text{-}OMe\text{-}2,3\text{-}dpqx\text{-}(OMe)_2)_2(przl2)$ were fabricated and their EL spectra showed the peaks around 650 nm. Overall, $Ir(6\text{-}OMe\text{-}dpqx\text{-}(OMe)_2)_2$(acac or przl) studied herein and previously reported $Ir(6\text{-}F\text{-}dpqx\text{-}(OMe)_2)_2(acac)$ did not show substantial difference in both PL and EL spectra. Thus, it was concluded that substituent variation at 6-position of the dpqx ligand and change of ancillary ligands in the iridium complexes did not significantly influence the emission wavelengths of the complexes.

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