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The New Iridium(III) Pyridyltetrazolate Complexes for Blue Phosphorescence

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A series of new blue-phosphorescent iridium complexes containing phenypyridine (ppy) derivatives and pyridyltetrazole were synthesized and their photophysical and electroluminescent properties were investigated. In the complex, the phenyl moiety which is mostly the highest occupied molecular orbital (HOMO) site was modified with the electron-withdrawing groups F and CF_3*. By doing so, the emission maxima were expected to shift hypsochromically due to the HOMO level decrease. Furthermore, addition of the modest electron donating group,* CH_3*, to the pyridyl moiety in the ligand could slight raise the lowest unoccupied molecular orbital (LUMO) level of the complex. Therefore, the energy gap increase of the main ligands, phenylpyridine derivatives, might lead to blue emission of their iridium complexes. Previously reported pyridyltetrazole, an ancillary ligand, were also introduced to the iridium complexes for efficient blue phosphorescence and charge balance. The complexes prepared herein exhibited the blue emission at 467 and 486 nm with a shoulder peak at the longer wavelengths, respectively. We also investigated the luminescence properties of the complexes in a polymer film of PMMA (poly(methylmetacrylate)) for their application to the solution process. The photoemission of the complex in PMMA showed similar pattern with that of the complex itself.*

Keywords: blue phosphorescence; iridium complex; OLED; phenylpyridyl-based ligands; pyridyltetrazole

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INTRODUCTION

Phosphorescent transition-metal complexes have been extensively utilized in the light-emitting diodes (OLEDs). Among the transition metal complexes, particularly, the iridium(III) complexes were known to have high efficiency and broad color versatility from blue to red [1–3]. The strong spin-orbit coupling from the iridium center can lead to the intersystem crossing from the singlet to the triplet state, which forms the mixed excited state. These mixed excited states of the complex are attributed to its emitting ligands (C^N) and ancillary ligand, and thus the emitting color can be easily tuned by the structure modification or substituents in the iridium complexes [4–9].

For the full color display, red, green and blue emitting material are needed, but development of blue phosphors showing the pure color purity and high efficiency have lagged behind compared with the red, green phosphors [10]. Recently, iridium complexes involving the 2-phenylpyridine(ppy)-based ligands and tetrazole were reported and showed the blue to green emission, depending on the substituted position at ppy in the complexes [11,12]. Using this concept, we designed the new C^N ligand for the blue emission color. The energy gap of these new ligands can be controlled by introducing the electron withdrawing/donating groups to the HOMO site in the ppy-based ligand. The electron-withdrawing group (F and CF_3) at the 4-position of the phenyl ring can lead to lower the energy of the complex HOMO. Methyl group was introduced into the 4-position of pyridine ring which may slightly be contributed to the LUMO level increase. Furthermore, we employed the pyridyltetrazole ligand having the strong electron-withdrawing ability, which leads to the deep blue emission and high efficiency. In our paper, the synthesis and the luminescent properties of the substituted ppy-based iridium complexes were investigated and the substituent effects were compared with the unsubstitued one.

EXPERIMENTAL SECTION

Synthesis and Characterization

All reagents were purchased from Aldrich Co., except Ir(III) trichloride hydrate ($IrCl_3 \cdot H_2O$) and Ir(III) acetylacetonate, which were 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).

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

Synthesis of Ligand

Synthesis of 4-Me-4-F-ppy

4-methyl-4-fluorophenylpyridine ligand was obtained from the reaction of 2-chloro-4-methylpyridine with 4-fluorophenylboronic acid by Suzuki coupling [13]. 2-chloro-4-methylpyridine (0.968 g, 11 mmol), 4-fluorophenyl-boronic acid (1.40 g,10 mmol) and tetrakistriphenylphospine palladium(0) (0.196 g, 0.17 mmol) were placed in a mixture of toluene (20 ml), ethanol (10 ml) and 2N sodium carbonate aqueous solution (20 ml). The reaction mixture was heated to reflux for 8 hr at 135°C. The mixture was cooled to room temperature and extracted with 20 ml of ethyl acetate. The organic fraction was dried over anhydrous $MgSO_4$, filtered and the solvent was evaporated. The residue was chromatographed on a silica-gel column with ethyl acetate/hexane (1:3). The product was collected and dried in vacuum to yield a light yellow liquid with 60% yield.

Synthesis of 4-Me-4-CF_3-ppy

4-methyl-4-trifluoromethyl-phenylpyridine ligand was synthesized through the procedure mentioned above with 4-trifluoromethylphenylboronic acid, instead of 4-fluorophenylboronic acid. The product was obtained in a 60% yield.

Synthesis of Complexes

The cyclometalated Ir(III) μ-chloro-bridged dimer, $(C^\wedge N)_2Ir(\mu\text{-}Cl)_{2\text{-}2}Ir(C^\wedge N)$ was synthesized by the method reported by Nonoyama with slight modification [14].

Synthesis of 5-(2′-Pyridyl)tetrazole

5-(2′-pyridyl)tetrazole is prepared by the previously reported method [15] 2-cyanopyridine (9.63 ml, 0.1 mole) and sodium azide (8.581 g, 0.132 mole) were added to *n*-butyl alcohol (40 ml) and glacial acetic acid (7.6 ml, 0.132 mole) and the mixture was refluxed for 4 days. Sodium azide (1.95 g) and glacial acetic acid (3.8 ml) were added to the refluxing mixture and continuously refluxed for another 2 days. The resulting product was diluted with 100 ml of water and *n*-butyl alcohol solvent was removed. The clear aqueous solution was acidified with hydrochloric acid. The white powder was obtained in 90% yield.

^1H NMR(ppm): δ 8.82 (md, aromatic H, 2H); 8.25 (md, aromatic H, 2H); 8.11 (mt, aromatic H, 2H);7.67 (mt, aromatic H, 2H).

Ir(4-Me-4-F-ppy)$_2$(ttzl), Ir(4-Me-4-CF$_3$-ppy)$_2$(ttzl)

Synthesis of Ir(4-Me-4-R-ppy)$_2$(ttzl). To a flask containing $IrCl_3 \cdot H_2O$ (1.49 g, 5 mmol) and a cyclometalating ligand (C^N = 4-Me-4-F-ppy or 4-Me-4-CF_3-ppy, 12.5 mmol (2.5 eq)) was added a 3:1 mixture of 2-ethoxyethanol and water. The mixture was refluxed for 16 hr and cooled to room temperature. The solution mixture was slowly evaporated to obtain the crude product $(C^\wedge N)_2Ir(\mu\text{-}Cl)_2Ir(C^\wedge N)_2$. The yellow solid was filtered and washed with ethanol. This chloride-bridged dimer (2 mmol) was then placed in a 50 ml two-neck flask filled with 2-ethoxyethanol (30 mL). 5-(2′-pyridyl)tetrazole (6.8 mmol (3.4 eq)) was added and the reaction mixture was refluxed for 4 hr at 135°C. The solution was cooled to room temperature and poured into 10 ml of water. The yellow solid was filtered and washed with water, followed the recrystallization with CH_2Cl_2/n-hexane.

Ir(4-Me-4-F-ppy)$_2$(ttzl) FAB-MS: calculated 711, found 712.

Ir(4-Me-4-CF_3-ppy)$_2$(ttzl): FAB-MS: calculated 811, found 812.

Optical Measurement

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 the iridium complexes were measured in 10^{-5} M dilute CH_2Cl_2 solution and in the PMMA film. The PMMA film was fabricated by the spin-coating onto the glass substrate with 10 wt% Ir complexes of PMMA in 1,2-dichloroetane solution and following solvent evaporation.

RESULTS AND DISCUSSION

As previous reported [11,12], luminescent properties of the iridium complexes containing the ppy-based ligands were varied depending on the substituted position in the ligand. It was known that the electron density on the phenyl ring is high at their 4-position, and the presence of an electron withdrawing group might lead to the bathochromic shift due to the relatively weak π donation from 4-position. Thus, the electron withdrawing (F, CF_3) groups were added to the 4-position of the phenyl ring to lower the energy level of HOMO in the complexes effectively. Additionally, the electron donating group was introduced at the 4-position of the pyridine ring which are contributed to the energy of LUMO determination. The ancillary ligand was known to have a minor effect on the excited state of the complex. The introduction of pyridyltetrazole ligand having the strong electron withdrawing characteristics might lead to lower the energy level of the HOMO slightly. Thus, the new iridium complexes containing the modified ppy-based ligands and pyridyltetrazole were designed and synthesized for the true blue emission.

The main ligand (L), 4-Me-4-F-ppy and 4-Me-4-CF_3-ppy were prepared according to the modified Suzuki coupling method [13], as illustrated in Figure 1(a). The ancillary ligand, pyridyltetrazole (ttzl),

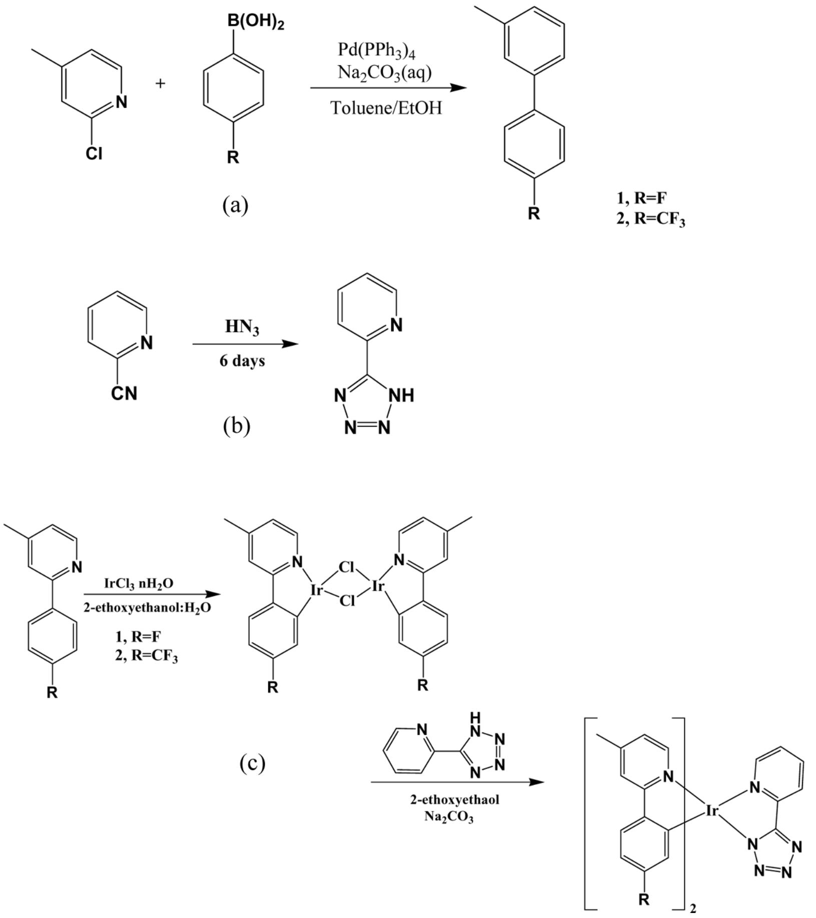

FIGURE 1 Synthetic scheme of the derivatized ppy-based ligands, tetrazole and their iridium complexes.

was prepared according to the previously reported procedure as depicted in Figure 1(b). The synthetic method of iridium complexes $Ir(L)_2(przl)$ involved two steps, formation of the dimer and the following coordination of ttzl, as summarized in Figure 1(c).

The UV-Vis absorption spectra of the complexes in CH_2Cl_2 are shown in Figure 2. The strong absorption bands between 250 and 280 nm in the ultraviolet region are assigned to the spin-allowed $^1\pi$-π^* transition of the cyclometalating 4-Me-4-F-ppy and 4-Me-4-CF_3-ppy ligand in the complexes. The weak bands between 280 and 350 nm in the visible region can be assigned to the spin-allowed metal-to-ligand charge transfer (^{1}MLCT) band. 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. In general, the ligand-centered (LC) $^3\pi$-π^* transition tends to predominate in the admixture of the LC and MLCT transitions as a transition has higher energy. Therefore, the weaker MLCT bands at the longer wavelengths could be buried under LC transition. The formally spin-forbidden ^{3}MLCT transition gains the intensity by mixing with the higher-lying ^{1}MLCT transition through the strong spin-orbit coupling on the iridium center. The absorption patterns of these complexes are similar, suggesting that substituent change of its main ligands does not make significant contribution to the absorption process.

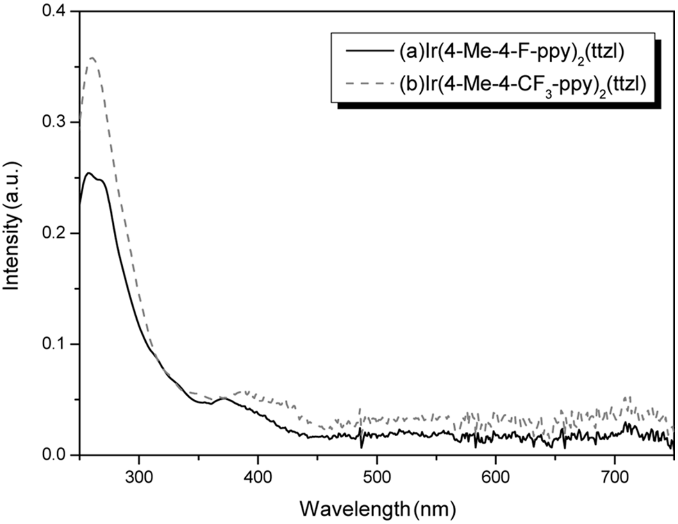

FIGURE 2 UV-Vis absorption spectra of $Ir(4\text{-}Me\text{-}4\text{-}R\text{-}ppy)_2(ttzl)$ ($R = F$, CF_3).

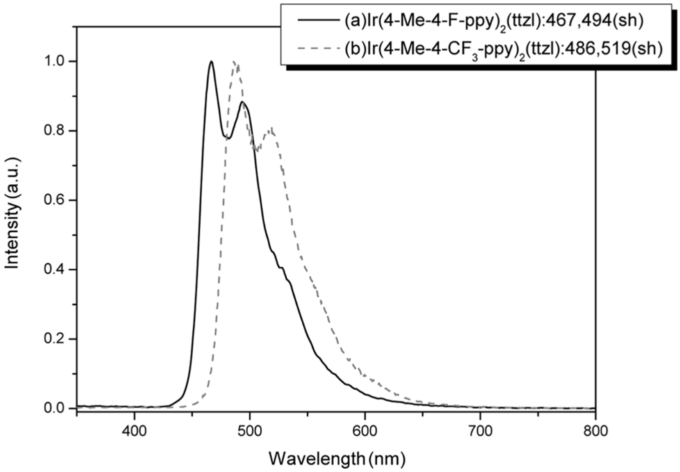

FIGURE 3 PL spectra of Ir(4-Me-4-R-ppy)$_2$(ttzl) (R = F, CF_3).

The photoluminescence (PL) spectra of the Ir complexes in 10^{-5} M CH_2Cl_2 solution are depicted in Figure 3. The emission maxima for Ir(4-Me-4-F-ppy)$_2$(ttzl) and Ir(4-Me-4-CF_3-ppy)$_2$(ttzl) appeared at 467 and 486 nm, respectively, indicating the hypsochromic effect from the emission of unsubstituted irdium complex (Ir(ppy)$_3$) [16] at 510 nm, as expected. However, the complexes show other peaks at the longer wavelength, resulting in the bluish-green emission. Ir(4-Me-4-F-ppy)$_2$(ttzl) and Ir(4-Me-4-CF_3-ppy)$_2$(ttzl) also have less intense shoulder bands at the longer wavelengths than their main peaks. In other literatures [17–19], such phenomena were also observed with iridium triazolate complexes. It was suggested that the broad and additional peaks in PL spectra might be attributed to ^{3}MLCT and interligand $\pi\pi^*$ transitions (LLCT) between F- or CF_3-substituted phenyl groups and pyridyl moieties. The PL patterns of these two complexes are similar, but the emission maxima were somewhat different.

Both fluoro and trifluoromethyl substituents have electron withdrawing property, but the PL of Ir(4-Me-4-CF_3-ppy)$_2$(ttzl) was hypsochromically shifted compared with that of Ir(4-Me-4-F-ppy)$_2$(ttzl). It might be attributed to the resonance and inductive effect [1]. First, the fluoro substituent was directly bonded with the electron cloud of the phenyl ring, which can effectively withdraw the electron density and stabilize the HOMO level. On the other hand, the inductive effect through the σ bond between the fluoro and the methyl substituent at the phenyl ring might cause rather weak withdrawing effect, which

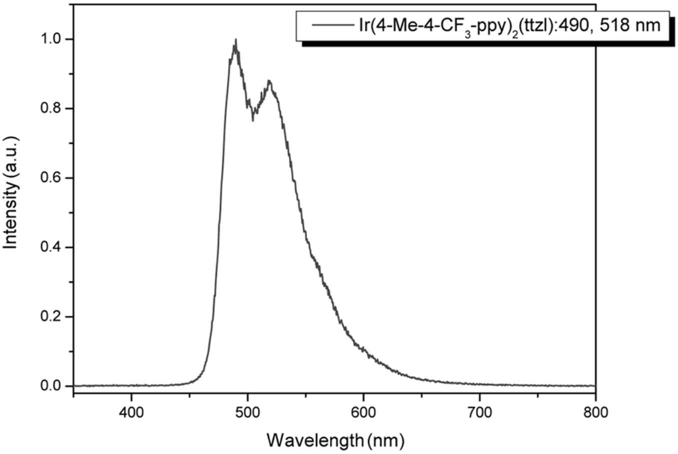

FIGURE 4 PL spectrum of Ir(4-Me-4-CF$_3$-ppy)$_2$(ttzl) on the PMMA film.

can be a decisive factor in the less hypsochromic shift by Ir(4-Me-4-CF$_3$-ppy)$_2$(ttzl).

Additionally, we attempted to investigate the PL spectrum of Ir(4-Me-4-CF$_3$-ppy)$_2$(ttzl) 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 complexes only. As depicted in Figure 4. The PL maxima of the PMMA film for Ir(4-Me-4-CF$_3$-ppy)$_2$(ttzl) appear at 490/518(sh) nm. PL spectra of the complex film in PMMA show similar aspect and its maximum wavelength is comparable to its solution PL. Thus, it is suggested that the emission process in the solution and the film is similar without the formation of the aggregation which may cause the broad and bathochromically shifted spectrrum. The energy transfer seems fast and efficient from the host, PMMA, to the dopant, the iridium complex, since the emission from the iridium complex is clearly observed without quenching. Further investigation of the complexes in other polymeric films such as PVK is in progress for the PLED application.

CONCLUSION

The new iridium complexes containing the ppy-based ligands and pyridyltetrazole were prepared and their luminescence properties of the iridium complexes were investigated. Considering the UV patterns of the iridium complexes discussed in this study, we could suggest that the substituent in the ppy-based ligand did not show a significant effect on the modulating the emission wavelength of the complex. Furthermore, the PL in the solution and the film had similar patterns and maximum emitting wavelength, suggesting the iridium complexes were eligible to be an emission source in the solution process as well as vacuum deposition for OLEDs. Further study is in progress on the film fabrication with other materials, and their photophysical properties are investigated.

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