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New Blue Phosphorescent Iridium Complexes Containing Phenylpyridine and Triazole Ligands: Synthesis and Luminescence Studies

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The synthesis and luminescence of iridium(III) complexes containing new phenylpyridine (C^N) ligands, 4-Me-4′-F-ppy, 4-Me-4′-CF$_3$-ppy and 4-OMe-4′-CF$_3$-ppy, were studied. These ligands were designed for development of the blue light-emitting iridium complexes by introducing the electron-withdrawing group (F, CF$_3$) and the electron-donating group (Me, OMe) at the *para* positions of the phenyl and pyridine ligand rings, respectively. As an ancillary ligand, trzl-CMe$_3$ was employed where trzl-CMe$_3$ represents 2-(5-*tert*-butyl-2H-1,2,4-triazol-3-yl)pyridine. The resulting iridium complexes, Ir(4-Me-4′-F-ppy)$_2$(trzl-CMe$_3$), Ir(4-OMe-4′-CF$_3$-ppy)$_2$(trzl-CMe$_3$) and Ir(4-Me-4′-CF$_3$-ppy)$_2$(trzl-CMe$_3$) exhibited the blue emission at 472, 484 and 494 nm in CH$_2$Cl$_2$ solution, respectively. Ir(4-Me-4′-F-ppy)$_2$(trzl-CMe$_3$) showed the most hypsochromic shift in photoluminescence (PL) among the complexes prepared herein. In the electroluminescence (EL) spectra, Ir(4-Me-4′-F-ppy)$_2$(trzl-CMe$_3$) and Ir(4-Me-4′-CF$_3$-ppy)$_2$(trzl-CMe$_3$) exhibited the luminescence peak at 437 nm and 496 nm, respectively. In the aspect of blue emission color purity, Ir(4-Me-4′-F-ppy)$_2$(trzl-CMe$_3$) had the CIE coordinates of (0.176, 0.143), very close to the saturated standard blue emission.

Keywords: Iridium Complex, Blue Phosphorescence, OLED, ppy Ligand Derivatives.

1. INTRODUCTION

Development of red, green and blue emitting materials with good efficiency and pure chromacity is the most important issue for the advance of full-color display. Theoretically, the internal quantum efficiency of phosphorescent emitters can approach 100% while that of fluorescent molecules is limited to 25%.[1,2] Thus, OLEDs that involve phosphorescent compounds as an emitting material have been developed with high efficiency.[3,4] Compared to the green phosphorescent compounds, development of blue and red phosphorescent dopants has difficulties, mostly due to the problems in color purity and efficiency. Ir(F$_2$-ppy)$_2$(trzl), a blue phosphorescent emitter, was recently reported to have emission peaks at 461 nm and 492 nm, where F$_2$-ppy and trzl represent 4,6-difluorophenylpyridine and 2-(5-methyl-2H-1,2,4-triazol-3-yl)pyridine ligands, respectively. Its electroluminescence (EL) showed a maximum efficiency of 13.4 cd/A, a power efficiency at 300 cd/m^2 of 5.5 lm/W and color point of (0.168, 0.281).[5]

To obtain the blue phosphorescent material of good color purity and efficiency, we proposed two strategies on the ligand design: increasing LUMO and lowering HOMO energy levels of a ligand with respect to ppy, yielding the energy gap increase of the complex. First, withdrawing groups, F and CF$_3$, were involved in the phenyl fragment of the phenylpyridine moiety to decrease HOMO levels. Secondly, methoxy and methyl groups were included at the pyridine ring to raise the LUMO energy levels. As a result, the energy gap of the iridium complexes may increase and emission can be closer to true blue color. Considering these strategies, we synthesized the new ppy ligand derivatives and prepared their iridium complexes. For a charge balance, triazole (trzl) was introduced as an ancillary ligand for blue phosphorescent iridium complexes.[5,6] The photoabsorption and luminescence properties of the iridium complexes, Ir(4-Me-4-F-ppy)$_2$(trzl-CMe$_3$), Ir(4-Me-4-CF$_3$-ppy)$_2$(trzl-CMe$_3$) and Ir(4-OMe-4-CF$_3$-ppy)$_2$(trzl-CMe$_3$), were investigated.

2. EXPERIMENTAL DETAILS

All reagents were purchased from Aldrich Co., except Ir(III) trichloride hydrate (IrCl$_3$ · H$_2$O), which was purchased from Strem Co. and used without further

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purification. All reactions were carried out under a nitrogen or argon atmosphere. Solvents were dried by standard procedures. Column chromatography was performed with the use of silica gel (230-mesh, Merck Co). ^{1}H NMR spectra were obtained from an NMR spectrometer of 600 MHz at Seoul National University. 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

2.1.1. Synthesis of 4-Me-4′-CF_3-ppy

2-(4′-(trifluoromethyl)phenyl)-4-methylpyridine ligand was obtained from the reaction of 2chloro-4-methylpyridine with 4-trifluoromethyl-phenylboronic acid by Suzuki coupling. 2chloro-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 2 N 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 $MgSO_4$. After removal of $MgSO_4$, the solvent was evaporated and the residue was chromatographed on a silicagel column with ethyl acetate/hexane (1:3). The product was collected and dried in vacuum to yield a light yellow liquid with 57% yield.

2.1.2. Synthesis of 4-Me-4′-F-ppy

2-(4′-fluorophenyl)-4-methylpyridine ligand was synthesized from the reaction of 4-fluorophenylboronic acid with 2chloro-4-methylpyridine, according to the procedure mentioned above. Yield: 60%.

2.1.3. Synthesis of 4-OMe-4′-CF_3-ppy

2-(4′-(trifluoromethyl) phenyl)-4-methoxypyridine ligand was synthesized from the reaction of 4-trifluoromethyl-phenylboronic acid with 2-chloro-4-methoxypyridine, according to the procedure mentioned above. Yield: 60%.

2.1.4. Synthesis of Trzl-CMe_3

The ancillary tetrazolone ligand was prepared according to the literature.[5] Yield: 70%. ^{1}H NMR (DMSO-d^6, 300 MHz): δ 8.57, 8.08, 7.88, 7.44 (m, 1H each, aromatic Hs′); 1.21(s, 9H, $C(CH_3)_3$) ppm.

2.2. Synthesis of Iridium(III) Complexes

2.2.1. Synthesis of Ir($C^\wedge N$)$_2$(Trzl-CMe_3)

To a flask containing $IrCl_3 \cdot H_2O$ (1.49 g, 5 mmol) and a cyclometallating ligand ($C^\wedge N = $ 4-Me-4′-F-ppy, 4-Me-4′-CF_3-ppy or 4-OMe-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, cooled to room temperature and slowly evaporated. The resulting yellow solid was filtered and washed with ethanol to give the chloride-bridged dimer, $(C^\wedge N)_2Ir(\mu\text{-}Cl)_2Ir(C^\wedge N)_2$. The dimer (2 mmol) was then placed in a 50 ml two-neck flask filled with 2-ethoxyethanol (30 mL). 2-(5-tert-butyl-2H-1,2,4-triazol-3-yl)pyridine (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 precipitate was filtered, washed with methanol and acetone and dried under vacuum.

Ir(4-Me-4′-CF_3-ppy)$_2$(trzl-CMe_3), Yield: 47%. FAB-MS: calculated 866.2; found 867. ^{1}H NMR (DMSO, 600 MHz): δ8.26–6.37 (m, 16H, aromatic Hs′); 2.54, 2.51 (s, 3H each, CH_3); 1.25 (s, 9H, $C(CH_3)_3$) ppm.

Ir(4-Me-4′-Fppy)$_2$(trzl-CMe_3), Yield: 52%. FAB-MS: calculated 766.2; found 767. ^{1}H NMR (DMSO, 600 MHz): δ8.07–5.75 (m, 16H, aromatic Hs′); 2.47, 2.45 (s, 3H each, CH_3); 1.26 (s, 9H, $C(CH_3)_3$) ppm.

Ir(4-OMe-4′-CF_3ppy)$_2$(trzl-CMe_3), Yield: 49%. FAB-MS: calculated 898.8; found 899. ^{1}H NMR (DMSO, 600 MHz): δ8.11–6.43 (m, 16H, aromatic Hs′); 3.99, 3.96 (s, 3H each, OCH_3); 1.26 (s, 9H, $C(CH_3)_3$) ppm.

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 55 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.

2.4. Fabrication of the EL Devices

The configuration of the devices was ITO/4,4′bis[*N*-(naphthyl)-*N*-phenyl-amino]biphenyl (NPB) (50 nm)/8% Ir complex in 4,4,*N*,*N*′-dicarbazolebiphenyl (CBP) (30 nm)/4,7-diphenyl-1,10-phenanthroline (Bphen) (30 nm)/lithium quinolate (Liq) (2 nm)/Al (100 nm). The OLEDs were fabricated by high vacuum (5×10^{-7} torr) thermal deposition of the materials onto an indium tin oxide (ITO)-coated glass substrate. The current density–voltage (J–V) characteristics of the OLEDs were measured with a source measure unit (Kiethley 236). Their luminance and CIE chromaticity coordinates were measured using a chromameter (MINOLTA CS-100A). The EL spectra of the devices were measured by IVL-200 of JBS international Co., Ltd. All measurements were performed in ambient conditions under DC voltage bias.

3. RESULTS AND DISCUSSION

The synthesis of the C^N ligand, an ancillary ligand and their iridium complexes was straightforward. The ligands (C^N), 4-Me-4′-CF_3-ppy, 4-Me-4′-F-ppy and 4-OMe-4′-CF_3-ppy, were prepared by the Suzuki coupling, as illustrated in Figure 1(a). The ancillary ligand, trzl-CMe_3, was prepared from the reaction of amidrazone precursor with trimethylacetyl chloride, according to the reported procedure.[5] Ir$(C^\wedge N)_2$(trzl-CMe_3) were synthesized via the chloride bridged dimer, according to Nonoyama method.[8] 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 the complexes have intense bands, appearing at the

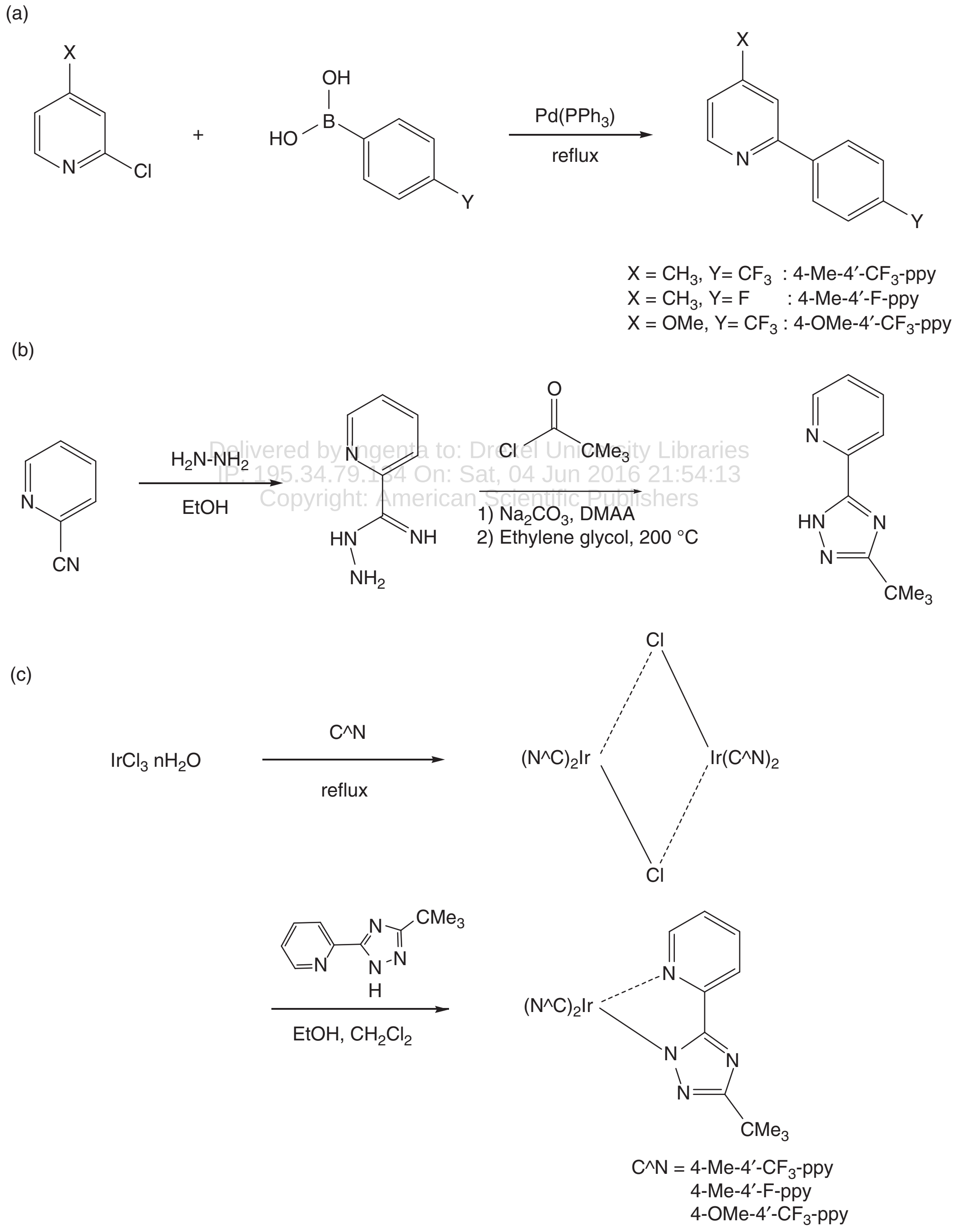

Fig. 1. The synthesis of substituted ppy ligands, triazole and their iridium complexes.

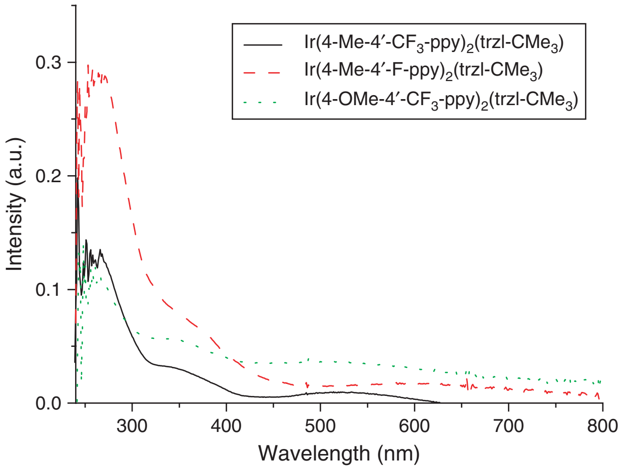

Fig. 2. UV-Vis absorption spectra of the iridium complexes.

ultraviolet region of the spectrum between 200 and 310 nm. These bands are assigned to the spin-allowed $^1(\pi \rightarrow \pi^*)$ transitions of the ligands in the complexes. The weak bands from 320 nm extended to 400 nm can be assigned to the spin-allowed metal-ligand charge transfer band (^{1}MLCT), and the weaker absorption bands at the longer wavelengths than 450 nm are attributed to the spin-forbidden ^{3}MLCT.[9] The intensities of the MLCT bands were lower than those of red or green phosphorescent emitters because the large energy gap causes reduction of the MLCT transitions.[10]

The photoluminescence (PL) spectra of the iridium complexes in 10^{-5} M CH_2Cl_2 solution are shown in Figure 3. The PL patterns of the complexes are similar, but the emission maxima occur at somewhat different wavelengths. The PL peaks for Ir(4-Me-4′-CF$_3$-ppy)$_2$(trzl-CMe$_3$), Ir(4-Me-4′-F-ppy)$_2$(trzl-CMe$_3$) and Ir(4-OMe-4′-CF$_3$-ppy)$_2$(trzl-CMe$_3$) appeared at 494, 472 and 484 nm. The less intense shoulder peaks at the longer wavelengths were also observed at 514, 493 and 505 nm, respectively, which cause green tint in blue phosphorescence of the complexes. Ir(4-Me-4′-F-ppy)$_2$(trzl-CMe$_3$) shows the most hypsochromic shift in emission among the Ir(III) complexes prepared herein. The complex having the electron-withdrawing fluorine (F) substituents in phenyl ring experiences more blue-shift in emission than the complex containing trifluoromethyl (CF$_3$) substituents. It indicates that the fluorinated phenyl ring contributes more to the energy gap increase by lowering the HOMO levels of the complex than the trifluoromethyl susbstituted analog.[11] Both methyl (Me) and methoxy (OMe) substituents have electron-donating properties, and the emission peak of Ir(4-OMe-4′-CF$_3$-ppy)$_2$(trzl-CMe$_3$) is blue-shifted, compared with that of Ir(4-Me-4′-CF$_3$-ppy)$_2$(trzl-CMe$_3$). It could be attributed to the difference of resonance and inductive effects by the substituents.[12] The methoxy substituent has a resonance effect with the π-system, leading to easy transfer of the electrons while the methyl substituent has only an inductive effect on the σ-system.

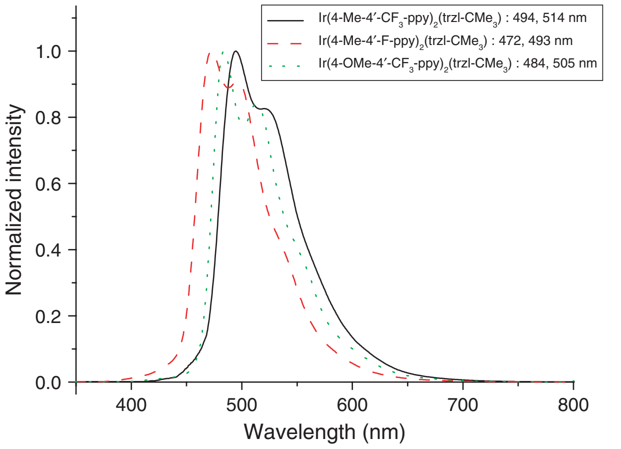

Fig. 3. PL spectra of the iridium complexes in a 10^{-5} M CH_2Cl_2 solution.

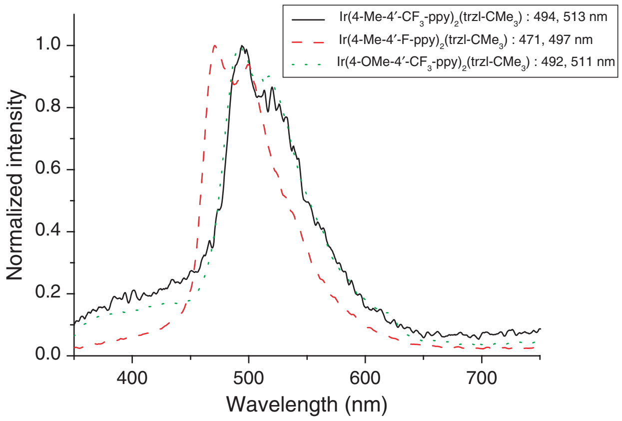

Fig. 4. PL spectra of the iridium complexes in a PMMA film.

We also attempted to investigate their PL in PMMA (poly(methylmethacrylate)) film for the polymer light-emitting device (PLED) fabrication. The films were

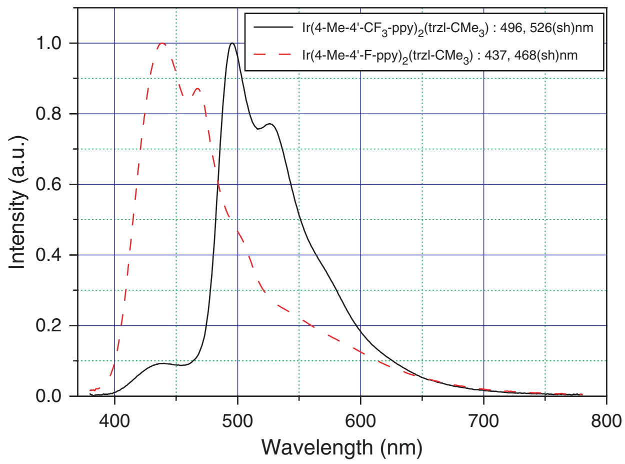

Fig. 5. EL spectra of the iridium complexes.

Table I. Characteristics of OLED devices of the iridium complexes.

Dopant	EL λ_{max} (nm) of devices	Max. luminance (cd/m^2)	Max. Luminous efficiency (cd/A)	Max. Power efficiency (lm/W)	CIE coordinates
Ir(4-Me-4′-CF$_3$-ppy)$_2$(trzl-CMe$_3$)	496/526(sh)	10850	12.49	7.79	(0.259, 0.526)
Ir(4-Me-4′-F-ppy)$_2$(trzl-CMe$_3$)	437/468(sh)	870.7	1.09	0.86	(0.176, 0.143)

made by the spin-coating method with 1,2-dichloroethane solution of the complexes and PMMA mixture. PMMA was chosen as a host because its non-emitting property within the visible range could make the emission peak of the iridium complex shown only. Ir(4-Me-4′-F-ppy)$_2$(trzl-CMe$_3$) and Ir(4-Me-4′-CF$_3$-ppy)$_2$(trzl-CMe$_3$) in PMMA exhibited PL maxima at 471/497(sh) and 494/513(sh) nm, respectively (Fig. 4). The emission range of these complexes in the PMMA film were somewhat broader than those in solution, but both the film and the solution states showed the similar aspects in emission maxima. It means that the emission process in both the solution and the film is similar without the significant quenching. On the other hand, the PL maxima of the PMMA film of Ir(4-OMe-4′-CF$_3$-ppy)$_2$(trzl-CMe$_3$) occurred at 492/511(sh) nm, compared with that of its solution at 484/505(sh) nm. The peaks of the films became broader and underwent somewhat red-shift from its solution PL, presumably due to quenching by aggregation.

The EL devices were fabricated and their EL performances of the new complexes were investigated. The EL spectra of Ir(4-Me-4′-CF$_3$-ppy)$_2$(trzl-CMe$_3$) and Ir(4-Me-4′-F-ppy)$_2$(trzl-CMe$_3$) showed the emission peaks at 496/526(sh) nm and 437/468(sh) nm, respectively, as shown in Figure 5. The CIE coordinate of the devices containing Ir(4-Me-4′-F-ppy)$_2$(trzl-CMe$_3$) as a light-emitting dopant was (0.176, 0.143), being shifted toward the saturated blue emission, compared with (0.259, 0.526) of Ir(4-Me-4′-CF$_3$-ppy)$_2$(trzl-CMe$_3$). However, the maximum efficiency of device with Ir(4-Me-4′-F-ppy)$_2$(trzl-CMe$_3$) was much lower than that of Ir(4-Me-4′-CF$_3$-ppy)$_2$(trzl-CMe$_3$). Because the increase of energy gap means that decrease of MLCT transition, we presume that decrease of MLCT transition due to energy gap increase leads to reduction in the $T_1 \rightarrow S_0$ transition and thereby causes a low emission quantum efficiency.[10, 13] The electrical and optical characteristics are summarized in Table I.

4. CONCLUSION

Herein, we report the detailed syntheses and the luminescence properties of the phosphorescent iridium(III) complexes containing the substituted ppy ligands and a trzl ancillary ligand. The iridium complexes, Ir(4-Me-4′-CF$_3$-ppy)$_2$(trzl-CMe$_3$) and Ir(4-OMe-4′-CF$_3$-ppy)$_2$(trzl-CMe$_3$) exhibited the blue-green emission at 494 and 484 nm with the shoulder at 514 and 505 nm, respectively. The emission of Ir(4-Me-4′-F-ppy)$_2$(trzl-CMe$_3$) appeared at 472 nm with a shoulder peak at 493 nm in its solution PL, which was blue-shifted most among the complexes in this study. Although there were some differences between the PL of the solutions and of the films, the PLs had similar emission patterns. EL emission of Ir(4-Me-4′-CF$_3$-ppy)$_2$(trzl-CMe$_3$) and Ir(4-Me-4′-F-ppy)$_2$(trzl-CMe$_3$) appeared at 496/526(sh) and 437/468(sh) nm, respectively, especially, the CIE coordinate of Ir(4-Me-4′-F-ppy)$_2$(trzl-CMe$_3$) was (0.176, 0.143), very close to that of the saturated standard blue emission.

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