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## The Blue Phosphorescent Iridium Complexes Containing New Triazole Ligands for OLEDs

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*For the application to organic light-emitting diodes (OLEDs), the blue light emitting iridium complexes containing a new triazole (trzl) ancillary ligand were prepared and their photophysical properties were studied with respect to substituent effect at the 5-position of the triazole in the complexes. As substituents, electron donating groups, CMe<sub>3</sub> and CH<sub>2</sub>OMe were introduced to the triazole ligand of the complex to investigate the electronic effect on their chromacity and efficiency. The absorption patterns of the iridium complexes, Ir(F<sub>2</sub>-ppy)<sub>2</sub>(trzl-CMe<sub>3</sub>) and Ir(F<sub>2</sub>-ppy)<sub>2</sub>(trzl-CH<sub>2</sub>OMe) prepared in this study were very similar. Their PL spectra exhibited the blue emission at 464 and 462 nm with the shoulder at 490 nm, respectively. Previously reported Ir(F<sub>2</sub>-ppy)<sub>2</sub>(trzl-Me) showed almost identical emission maxima at 461 nm with a shoulder at 492 nm. Such similar emission patterns of these complexes indicate that the ancillary ligands, derivatives of triazole, did not make significant influence on chromaticity of their iridium complexes.*

**Keywords:** blue phosphorescence; iridium complex; OLED

### 1. INTRODUCTION

The organic light emitting diodes (OLEDs) have been extensively studied for application in flat-panel displays, owing to rapid progress in material design and device fabrication in recent years. Development of pure red, green and blue emitting materials is the most important issue for the advance of full-color display. OLEDs based on phosphorescent emitters can significantly improve electroluminescence

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performance because both singlet and triplet excitons can be harvested for light emission [1–11]. Greater success has been achieved at development of a red and a green emitter in fluorescent and phosphorescent displays. However, development of the blue emitting material is especially difficult because blue luminescence need big energy gap between HOMO and LUMO of the material. Requirement of such large energy gap increase means that there should be a gradual decrease in the admixture of the ligand-centered  $\pi \rightarrow \pi^*$  and metal-to-ligand charge-transfer (MLCT) transition [12]. The net results are reduction in the  $T_1 \rightarrow S_0$  transition probability and hence a low emission quantum efficiency (QE). Moreover, increasing the energy gap toward blue emission raises the likelihood that thermal population of the higher lying  $dd$ , MLCT,  $n\pi^*$ , or even ligand-to-ligand charge-transfer states (LLCT) could be invoked, accounting for the fast quenching at room temperature [13].

Recently, it was reported that 1,2,4-triazole (trzl) could be an ancillary ligand for the iridium complexes with its strong  $\sigma$  donor and weak  $\pi$  acceptor characteristics [14]. Introduction of the new ancillary legend, 1,2,4-triazole (trzl), to the blue-green phosphorescent Ir complexes could lead to better blue chromacity in their electroluminescence (EL) devices [14]. We thus investigated modification of the ancillary trzl ligand in the iridium complexes with different substituents at the 5-position and studied the photophysical properties of the complexes chelated with the trzl.

## 2. EXPERIMENTAL SECTION

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).  $^1\text{H}$  NMR spectra were obtained from a 300 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.

### 2.1. Synthesis

#### 2.1.1. Synthesis of Ligands

*Synthesis of  $F_2$ -ppy* [15]. 4,6-difluorophenylpyridine ligand was obtained from the reaction of 1-chloropyridine with the corresponding substituted phenylboronic acids by Suzuki coupling. 2-chloropyridine

(1.035 ml, 11 mmol), 2,4-difluorophenylboronic acid (1.58 g, 10 mmol) and tetrakis(triphenylphosphine) 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  $\text{MgSO}_4$ , filtered and pumped dry. 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. Yield: 60%.

*Synthesis of ancillary ligand (trzI-CMe<sub>3</sub>, trzI-CH<sub>2</sub>OMe) (pyridine-2-yl)amidrazone (intermediate) [14].* After melting 5.2 g (0.05 mol) of 2-cyanopyridine with gentle heating, 2.65 ml (0.055 mol) of hydrazine monohydrate was added, yielding a cloudy mixture. Ethanol was added until the mixture became clear, and the resulting solution was stirred overnight at room temperature, causing a gel-like product to form. All solvents were removed under reduced pressure, and the solid was suspended in petroleum ether (50 ml), cooled in an ice bath, and filtered, washing with cold petroleum ether. The resulting amidrazone was unstable to air and water and thus used right away for the synthesis and the functionallized ancillary ligand, trzI. Yield: 73%.

*2-(5-R-2H-1,2,4-triazol-3-yl)pyridine. General procedure [14].* (pyridine-2-yl)amidrazone (2.0 g, 15 mmol) and  $\text{NaCO}_3$  (1.6 g, 15 mmol) were placed in a dry flask. 15 ml of dry dimethylacetamide (DMAA) and 5 ml of dry THF were added, yielding a pale yellow suspension that was cooled to 0°C. In a separate, dry flask, 15 mmol of the appropriate acyl chloride was dissolved in 5 ml of DMAA. This solution was then added dropwise to precooled amidrazone mixture, which caused it to turn bright yellow. The mixture was slowly warmed to room temperature and stirred for additional 5 hr, yielding a thick yellow mixture. The contents were filtered and the solid was washed with water and EtOH. The resulting pale white solid was dried under vacuum.

*2-(5-tert-butyl-2H-1,2,4-triazol-3-yl)pyridine (trzI-CMe<sub>3</sub>).* Yield: 70%.  $^1\text{H}$  NMR ( $\text{DMSO-d}^6$ , 300 MHz):  $\delta$  8.57, 8.08, 7.88, 7.44 (m, 1H each, aromatic Hs'); 1.21(s, 9H, C(CH<sub>3</sub>)<sub>3</sub>)

*2-(5-(methoxymethyl)-2H-1,2,4-triazol-3-yl)pyridine (trzI-CH<sub>2</sub>-OMe).* Yield: 66%.  $^1\text{H}$  NMR ( $\text{DMSO-d}^6$ , 300 MHz):  $\delta$  8.56, 8.05, 7.85, 7.43 (m, 1H each, aromatic Hs'); 3.32 (overlapped s, 5H, CH<sub>2</sub>OCH<sub>3</sub>)

### 2.1.2. Synthesis of Ir(III) Complexes

$Ir(F_2\text{-ppy})_2(\text{trzl-CMe}_3)$ . The cyclometalated iridium  $\mu$ -chloro-bridged dimer,  $(F_2\text{-ppy})_2Ir(\mu\text{-Cl})_2Ir(F_2\text{-ppy})_2$ , was prepared according to the method reported by Nonoyama with slight modification [16]. The resulting dimer (1.2 g, 1 mmol) and  $\text{trzl-CMe}_3$  (0.687 g, 3.4 mmol) were mixed with  $\text{Na}_2\text{CO}_3$  (500 mg) in 2-ethoxyethanol (30 mL). The mixture was refluxed for 6 hr. After cooling to room temperature, the solution was filtered and concentrated under reduced pressure. Excess of water was added to induce the precipitation of an orange solid. This precipitate was filtered, followed by washing with methanol and acetone and dried under vacuum. Yield: 52%. FAB-MS: calculated 774.2; found 775.

$Ir(F_2\text{-ppy})_2(\text{trzl-CH}_2\text{OMe})$ . The iridium complexes were prepared from the reaction of the corresponding dimer with the  $\text{trzl-CH}_2\text{OMe}$ , according to the procedure described above as yellow powder. Yield: 57%. FAB-MS: calculated 762.1; found 763.

### 2.2. Optical Measurements

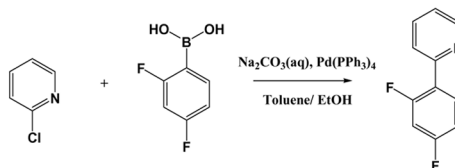
UV-Vis absorption spectra were measured on a Hewlett Packard 8425A spectrometer. PL spectra were measured on a Perkin Elmer LS 50B spectrometer. UV-Vis and PL spectra of iridium complexes were measured in  $10^{-5}$  M dilute  $\text{CH}_2\text{Cl}_2$  solution.

## 3. RESULTS AND DISCUSSION

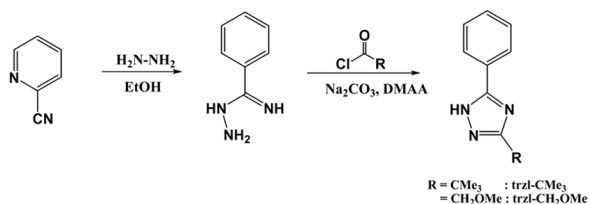
Synthesis of the main ligand, difluorophenylpyridine ( $F_2\text{-ppy}$ ), was straightforward according to the modified Suzuki coupling method [15]. The new ancillary ligand, 2-(5-R-2H-1,2,4-triazol-3-yl)pyridine, was prepared from the reaction of amidrazone intermediate with the corresponding acyl halide, according to the reported procedure [14]. Finally, the iridium complexes were synthesized as reported by Nonoyama [16]. The overall synthetic schemes are illustrated in Figure 1.

The UV-Vis absorption spectra of the complexes in  $\text{CH}_2\text{Cl}_2$  are shown in Figure 2. The absorption spectra of these compounds have intense bands appearing in the UV part of the spectrum between 230 and 350 nm. These bands have been assigned to the spin-allowed  $^1(\pi \rightarrow \pi^*)$  transitions of the ligands. The  $^1(\pi \rightarrow \pi^*)$  bands are accompanied by weaker and lower energy features extending into the visible region from 350 to 400 nm. These absorption bands have been assigned to both allowed and spin-forbidden MLCT transitions. The high intensity of the MLCT bands has been attributed to effective mixing of these

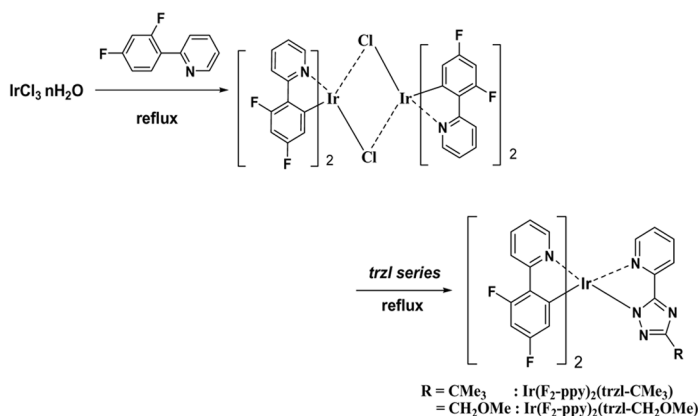
(1) the emitting ligand, F<sub>2</sub>-ppy



(2) the ancillary ligands (AL), trzl-CMe<sub>3</sub>, trzl-CH<sub>2</sub>OMe

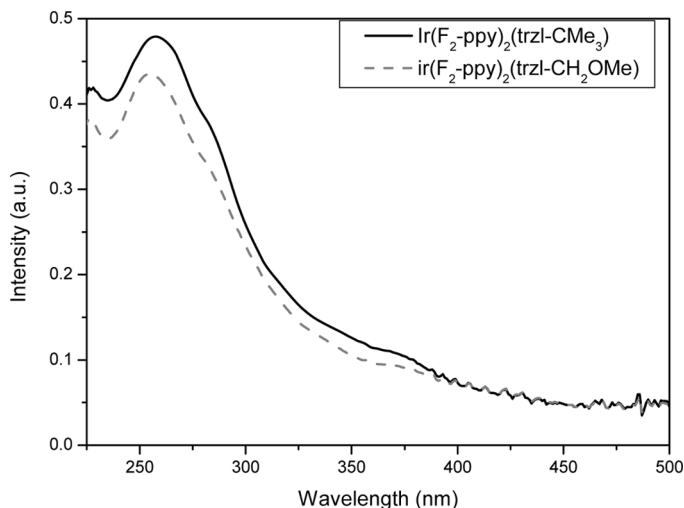


(3) the iridium complexes



**FIGURE 1** The synthesis of F<sub>2</sub>-ppy, triazoles and their iridium complexes.

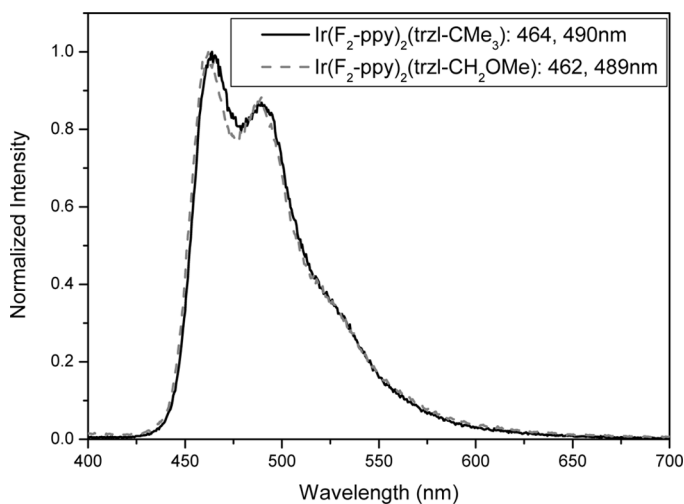
charge-transfer transitions with higher lying spin-allowed transitions on the cyclometalating ligand [17]. As previously stated, large energy gap leads to reduction of the MLCT transition, and as a result the intensity of MLCT band is lower than those of red and green phosphorescent emitters. In detail, absorption peaks Ir(F<sub>2</sub>-ppy)<sub>2</sub>(trzl-CMe<sub>3</sub>) appeared at 258, 280, 362 and 380 nm and those for Ir(F<sub>2</sub>-ppy)<sub>2</sub>(trzl-CH<sub>2</sub>OMe) were shown at 257, 282, 358, 370 and 389 nm. For comparison, the absorption of the previously reported Ir(F<sub>2</sub>-ppy)<sub>2</sub>(trzl-CH<sub>3</sub>) appeared at 258, 282, 343, 374 and 451 nm [14]. The absorption patterns of Ir(F<sub>2</sub>-ppy)<sub>2</sub>(trzl-CMe<sub>3</sub>) and Ir(F<sub>2</sub>-ppy)<sub>2</sub>(trzl-CH<sub>2</sub>OMe) were



**FIGURE 2** UV-Vis absorption spectra of  $\text{Ir}(\text{F}_2\text{-ppy})_2(\text{AL})$  ( $\text{AL} = \text{trzl-CMe}_3$ ,  $-\text{CH}_2\text{OMe}$ ).

very similar except for blue shifting of the absorption peaks in the visible region, compared with those of  $\text{Ir}(\text{F}_2\text{-ppy})_2(\text{trzl-CH}_3)$ .

The photoluminescence (PL) spectra of the Ir complexes in  $10^{-5}\text{M}$   $\text{CH}_2\text{Cl}_2$  solution are shown in Figure 3. The PL spectra of complexes



**FIGURE 3** PL spectra of  $\text{Ir}(\text{F}_2\text{-ppy})_2(\text{AL})$  in a  $10^{-5}\text{M}$   $\text{CH}_2\text{Cl}_2$  solution.



have almost identical emitting pattern at the same emitting wavelengths within experimental errors.  $\text{Ir}(\text{F}_2\text{-ppy})_2(\text{trzI-CMe}_3)$  and  $\text{Ir}(\text{F}_2\text{-ppy})_2(\text{trzI-CH}_2\text{OMe})$  exhibited the emission maxima at 464 and 462 nm, respectively and a second less intense peak at 490 and 489 nm, respectively. The emission color of the complexes is a cyan-blue because of these secondary peaks. For comparison, the emission peak of  $\text{Ir}(\text{F}_2\text{-ppy})_2(\text{trzI-CH}_3)$  appeared similar at 461 and 492 nm [14]. These results indicate that the substituent effect at the 5-position of the triazole is negligible in PL color of their complexes. However, we expect that the ancillary ligands might allow luminous efficiency increase of their complexes owing to involvement of the bulky substituent,  $\text{CMe}_3$  and  $\text{CH}_2\text{OMe}$ , since the steric bulkiness could reduce T-T annihilation. Meanwhile, the CIE coordinates of the previously  $\text{Ir}(\text{F}_2\text{-ppy})_2(\text{trzI-CH}_3)$  was (0.168, 0.281), which indicates more saturated blue emission than (0.17, 0.34) by well known FLrpic [18]. Further studies are in progress on the devices containing the complexes prepared herein with respect to EL spectra, luminous efficiency and CIE coordinates.

#### 4. CONCLUSION

Herein we report the detailed synthesis and photophysical properties of the phosphorescent iridium complexes having a trzl ancillary ligand with a different substituent. The iridium complexes,  $\text{Ir}(\text{F}_2\text{-ppy})_2(\text{trzI-CMe}_3)$  and  $\text{Ir}(\text{F}_2\text{-ppy})_2(\text{trzI-CH}_2\text{OMe})$ , prepared in this study exhibited the blue emission at 464 and 462 nm with the shoulder at 490 nm, respectively. These PL results were quite similar to those of  $\text{Ir}(\text{F}_2\text{-ppy})_2(\text{trzI-CH}_3)$  at 461 nm with the shoulder at 492 nm, indicating that the substituents at 5-position of the ancillary trzl ligand did not make significant contribution to both absorption and PL process of their iridium complexes. Further studies are undergoing on device fabrication to compare EL properties of these new Ir complexes with those of  $\text{Ir}(\text{F}_2\text{-ppy})_2(\text{trzI-CH}_3)$ .

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