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Seung-Chan Lee<sup>a</sup> & Young Sik Kim<sup>a b</sup>

<sup>a</sup> Department of Information Display, Hongik University, Seoul, Korea

<sup>b</sup> Department of Science, Hongik University, Seoul, Korea

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## Synthesis and Photophysical Studies of New Blue Phosphorescent Iridium Complexes of Fluorinated 2-phenyl-4-methoxypyridine

Seung-Chan Lee<sup>1</sup> and Young Sik Kim<sup>1,2</sup>

<sup>1</sup>Department of Information Display, Hongik University, Seoul, Korea

<sup>2</sup>Department of Science, Hongik University, Seoul, Korea

*In this study, a new Ir(III) complex containing 2-(3',5'-bistrifluoromethyl phenyl)-4-methoxypyridine have been synthesized and characterized for efficient blue organic light-emitting diodes (OLEDs). In order to tune photoluminescence (PL) spectra to a shorter wavelength, ppy ligand was fluorinated by  $-CF_3$  and substituted by  $-OCH_3$  group. The methoxy group substituted on the 4-position of pyridyl ring as electron donating group strongly affected the lowest unoccupied molecular orbital (LUMO) and it raised the LUMO energy and increased the energy gap. The trifluoromethyl group substituted on the 3',5'-position of phenyl ring as electron withdrawing group decreased the highest occupied molecular orbital (HOMO), and bulky  $CF_3$  groups occurs a steric hindrance of iridium complex helps decrease of self-quenching. As a result,  $Ir[(CF_3)_2OMeppy]_2(acac)$  is more blue-shifted emission at 471 nm and strong luminescence efficiency.*

**Keywords:** 2-(3',5'-bis-trifluoromethylphenyl)-4-metoxypyridine; blue; iridium complex; OLED; phosphorescence

### 1. INTRODUCTION

Electroluminescent (EL) organic materials have received much of attention due to their potential application in flat-panel displays due to the rapid progress in material design and device fabrication in recent years. One of the important parts of Organic light-emitting diode (OLED) development for full-color display is to find out materials emitting pure colors of red, green and blue [1–5]. Luminescent materials for OLED devices are generally classified into two groups;

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Address correspondence to Young Sik Kim, Department of Information Display, Hongik University, Seoul 121-791, Korea. E-mail: [youngkim@wow.hongik.ac.kr](mailto:youngkim@wow.hongik.ac.kr)

fluorescence and phosphorescence. OLEDs based on phosphorescent materials can greatly improve electroluminescence performance because both singlet and triplet excitons can be harvested for light emission. Theoretically, the internal quantum efficiency of phosphorescent emitters can approach 100%. Recently, Forrest, Thompson and coworkers have developed electrophosphorescent OLEDs with a high efficiency approaching 100% of the internal quantum efficiency, which utilize both singlet and triplet excitons produced at the emitting layer doped with the phosphorescent dopants [6,7]. A heavy metal such as Ir or Pt in their complex forms is known to induce intersystem crossing by strong spin-orbit coupling, leading to mixing of the singlet and triplet excited states. The spin-forbidden nature of radiative relaxation from the triplet excited state has then been changed to allow, resulting in high phosphorescent efficiencies. Thus, Ir complexes are known to have high photoluminescence (PL) efficiency and a relatively short excited state lifetime which minimizes quenching of triplet emissive states [8,9]. Until now, greater success has been achieved in the development of a green and red emitter in fluorescent and phosphorescent displays. However, the purely blue-emitting complex dopants are rarely found. Hence, the current effort of researchers has been focused on the syntheses of blue-emitting iridium complexes. Some phosphorescent blue emitter materials have been synthesized and reported, especially 2-phenylpyridine added some electro-withdrawing groups to the phenyl ring (fluoro, cyano group and others) or electro-donating groups to the pyridyl ring (methoxy group and others) were good blue emission characteristics [10–12].

In this study,  $\text{Ir}[(\text{CF}_3)_2\text{OMeppy}]_2(\text{acac})$  [ $(\text{CF}_3)_2\text{OMeppy} = 2\text{-(3',5'-bistrifluoromethylphenyl)-4-methoxypyridine}$ ,  $\text{acac} = \text{acetylacetonate}$ ] was successfully synthesized and fully characterized as a new blue emitting material by following the increasing energy gap between HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital). To analyze the color tuning by the substitution, we have measured UV-absorption and photoluminescence (PL) spectra of  $\text{Ir}[(\text{CF}_3)_2\text{OMeppy}]_2(\text{acac})$ . To support these effects, we have calculated these complexes theoretically by using computational method.

## 2. EXPERIMENTAL DETAILS

### 2.1. Synthesis

All ligands and reagents were purchased from Aldrich Co., except  $\text{Ir(III)}$  trichloride hydrate ( $\text{IrCl}_3 \cdot \text{H}_2\text{O}$ ), which was 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).

### 2.1.1. Synthesis of Ligands [ $L = (CF_3)_2ppy, (CF_3)_2OMeppy$ ]

**Synthesis of  $(CF_3)_2OMeppy$ .** A synthetic of phenylpyridine process use Suzuki coupling [13]. 2-chloro-4-methoxypyridine (1 eq.) and 3,5-Bis(trifluoromethyl)phenylboronic acid (1.05 eq.) and tetrakis(triphenylphosphine) palladium (0) (0.196 g, 0.17 mmol) were dissolved in the 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 12 hr at 105°C. The mixture was cooled to room temperature and extracted with 20 ml of ethyl acetate. The organic fraction were dried over anhydrous  $MgSO_4$ , filtered and pumped dry. The residue was chromatographed on a silica gel column with ethyl acetate/hexane (1:3). The product were collected and dried. (Yield 60%, orange sticky oil, MW:321.24)

**Synthesis of  $(CF_3)_2ppy$ .** We use 2-bromo pyridine (Aldrich Co. Product number = B80100) (1 eq.) and 3,5-Bis(trifluoromethyl) phenylboronic acid (1.05 eq.). The reaction and purification method is same to (3',5'-bis-trifluoromethylphenyl)-4-metoxypyridine. (Yield 62%, red sticky oil, MW:291.18)

### 2.1.2. Synthesis of Complexes $Ir(L)_2(acac)$

Cyclometalated Ir(III)  $\mu$ -chloro-bridged dimers of the general formula,  $(L)_2Ir(\mu-Cl)_2Ir(L)_2$ , were synthesized by the method reported by Nonoyama with slight modification [14]. To a flask containing  $IrCl_3 \cdot H_2O$  (1.49 g, 5 mmol) and ligand (12.5 mmol (2.5 eq)) was added a 3:1 mixture of 2-ethoxyethanol and water. The mixture was refluxed for 15 hr and cooled to room temperature. The solution mixture was evaporated under vacuum slowly to obtain the crude product  $(L)_2Ir(\mu-Cl)_2Ir(L)_2$ . The yellow to yellowish green solid was filtered and washed with ethanol. This chloride-bridged dimer (2 mmol) was then placed in 50 ml two-neck flask filled with 2-ethoxyethanol (30 mL). 2,4-pentanedione (0.68 ml,  $d = 0.975$ , 6.8 mmol (3.4 eq)) was added and the reaction mixture was refluxed for 2 hr at 135°C. The solution was cooled to room temperature and poured into 30 ml of 2 N HCl. The yellow solid was filtered and washed with water, followed by purification by silica gel column chromatography using  $CH_2Cl_2$  to afford a powder of  $Ir(L)_2(acac)$ .

**$Ir[(CF_3)_2OMeppy]_2(acac)$**  – Yield 45%, yellowish green powder. MW: 931.75

***Ir[(CF<sub>3</sub>)<sub>2</sub>ppy]<sub>2</sub>(acac)*** – Yield 48%, light yellow powder. MW: 871.69

***Ir(F<sub>2</sub>ppy)<sub>2</sub>(acac)*** – Yield 52%, light yellow powder. MW: 671.67

## 2.2. Optical Measurements

UV-Vis absorption spectra were measured on Hewlett Packard 8425 A spectrometer. The PL spectra were obtained on Perkin Elmer LS 50B spectrometer. UV-Vis and PL spectra of Ir(L)<sub>2</sub>(acac) were measured with a 10<sup>-5</sup> M dilute solution in CH<sub>2</sub>Cl<sub>2</sub>.

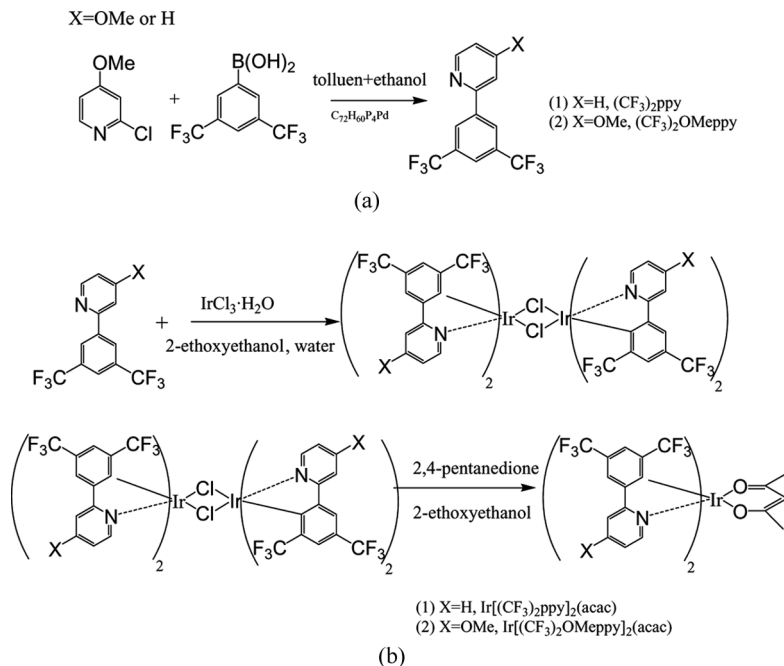
## 2.3. Theoretical Calculations

Calculations on the electronic ground states Ir[(CF<sub>3</sub>)<sub>2</sub>OMeppy]<sub>2</sub>(acac), Ir[(CF<sub>3</sub>)<sub>2</sub>ppy]<sub>2</sub>(acac), Ir(ppy)<sub>2</sub>(acac) and Ir(F<sub>2</sub>ppy)<sub>2</sub>(acac) were carried out using the B3LYP density functional theory (DFT). LANL2DZ [15] and 6-31G (d) [16] basis sets were employed for Ir and the other atoms, respectively. For the calculated ground state geometries, the electronic structure is examined in terms of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs).

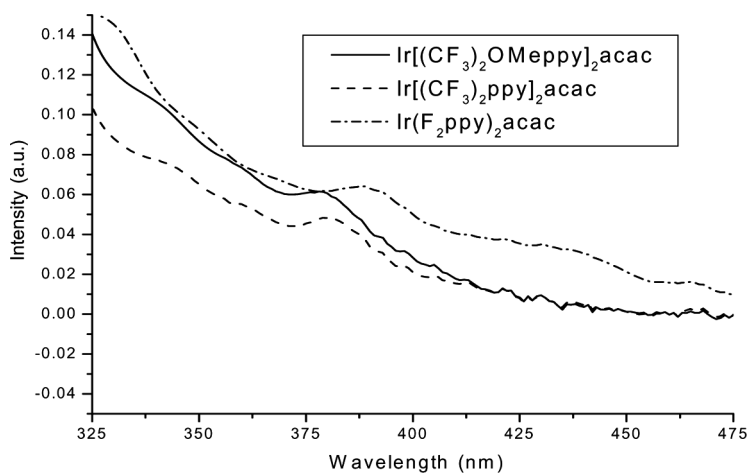
## 3. RESULTS AND DISCUSSION

The ligands, (CF<sub>3</sub>)<sub>2</sub>OMeppy, (CF<sub>3</sub>)<sub>2</sub>ppy and F<sub>2</sub>ppy were prepared by the Suzuki coupling [13], as illustrated in Figure 1(a). The bis-cyclo-metallated Ir(III) complexes containing these ligands and an ancillary ligand (acac) were prepared. Ir(L)<sub>2</sub>(acac) were obtained via two steps. In the first step, Ir(III)  $\mu$ -chloro-bridged dimer were prepared according to Nomoyama method [14]. The second step to make the final monomeric Ir(L)<sub>2</sub>(acac) complex with 2,4-pentandione requires a short reaction time compared to that reported previously. Synthesis of iridium complexes is shown in Figure 1(b). The overall reaction yields were about 40%.

The solution UV-Vis absorption complexes have been measured as shown in Figure 2. The interesting characteristic of the MLCT absorption spectra for Ir[(CF<sub>3</sub>)<sub>2</sub>ppy]<sub>2</sub>(acac) resembles that of Ir[(CF<sub>3</sub>)<sub>2</sub>OMeppy]<sub>2</sub>(acac). Both <sup>1</sup>MLCT and <sup>3</sup>MLCT peaks are observed for these complexes. MLCT absorption peaks of Ir[(CF<sub>3</sub>)<sub>2</sub>ppy]<sub>2</sub>(acac) are observed at 381, 397, and 406 nm. While, MLCT absorption peaks of Ir[(CF<sub>3</sub>)<sub>2</sub>OMeppy]<sub>2</sub>(acac) are observed at 378, 393, and 405 nm. On the other hand, Ir(F<sub>2</sub>ppy)<sub>2</sub>(acac)'s absorption peaks are observed at 388, 405, 422 and 430 nm. CF<sub>3</sub> groups substituted on the 3',5'-position



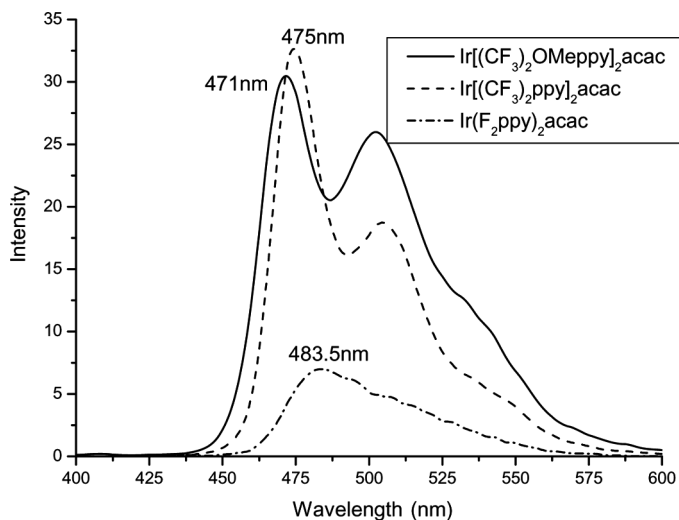
**FIGURE 1** (a) Synthesis of  $(\text{CF}_3)_2\text{ppy}$  and  $(\text{CF}_3)_2\text{OMeppy}$  ligands; (b) Synthesis of Iridium complexes of  $\text{Ir}[(\text{CF}_3)_2\text{ppy}]_2(\text{acac})$  and  $\text{Ir}[(\text{CF}_3)_2\text{OMeppy}]_2(\text{acac})$ .



**FIGURE 2** UV-Vis absorption spectrum of  $\text{Ir}[(\text{CF}_3)_2\text{OMeppy}]_2(\text{acac})$ ,  $\text{Ir}[(\text{CF}_3)_2\text{ppy}]_2(\text{acac})$  and  $\text{Ir}(\text{F}_2\text{ppy})_2(\text{acac})$  in  $10^{-5}\text{M}$   $\text{CH}_2\text{Cl}_2$  solution of room temperature.

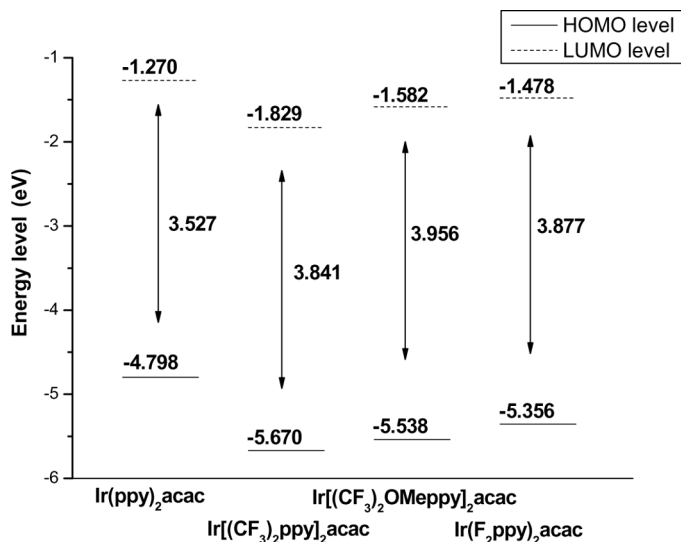
of phenyl ring as electron withdrawing group, tune the MLCT absorption peak to bluish. F atom of  $\text{Ir}(\text{F}_2\text{ppy})_2(\text{acac})$  have similar effect the MLCT absorption peak. In addition, in the case of  $\text{Ir}[(\text{CF}_3)_2\text{OMeppy}]_2(\text{acac})$ , the methoxy group substituted on the 4-position of pyridyl ring as electron donating group strongly affected the lowest unoccupied molecular orbital (LUMO) and it raised the LUMO energy and increased the energy gap.  $\text{Ir}[(\text{CF}_3)_2\text{ppy}]_2(\text{acac})$  and  $\text{Ir}[(\text{CF}_3)_2\text{OMeppy}]_2(\text{acac})$ 's MLCT peaks are 7 nm and 12 nm blue-shifted than  $\text{Ir}(\text{F}_2\text{ppy})_2(\text{acac})$ , respectively. It is suggest that  $\text{CF}_3$  groups are more strong withdrawing force than F groups, while  $\text{F}_2\text{ppy}$  ligands shows more strong MLCT peaks. And methoxy group of  $\text{Ir}[(\text{CF}_3)_2\text{OMeppy}]_2(\text{acac})$  helps more blue-shifted (6–7 nm) MLCT absorption spectrum than  $\text{Ir}[(\text{CF}_3)_2\text{ppy}]_2(\text{acac})$ .

The PL spectra of iridium complexes in  $\text{CH}_2\text{Cl}_2$  also reflected their absorption patterns. As shown in Figure 3, the maximum emission spectrum of  $\text{Ir}[(\text{CF}_3)_2\text{OMeppy}]_2(\text{acac})$  and  $\text{Ir}[(\text{CF}_3)_2\text{ppy}]_2(\text{acac})$  were 471 and 475 nm. In the case of  $\text{Ir}[(\text{CF}_3)_2\text{OMeppy}]_2(\text{acac})$  and  $\text{Ir}[(\text{CF}_3)_2\text{ppy}]_2(\text{acac})$ , the substitution of  $\text{CF}_3$  groups at the ortho and para positions to the iridium atom blue shifted the emission spectrum. This shift is attributed to the fact that the HOMO level is lower than that ppy ligand as judged from their electrochemical properties. Calculated HOMO and LUMO energy levels of iridium complexes are



**FIGURE 3** PL spectrum of  $\text{Ir}[(\text{CF}_3)_2\text{OMeppy}]_2(\text{acac})$ ,  $\text{Ir}[(\text{CF}_3)_2\text{ppy}]_2(\text{acac})$  and  $\text{Ir}(\text{F}_2\text{ppy})_2(\text{acac})$  in  $10^{-5}$  M  $\text{CH}_2\text{Cl}_2$  solution of room temperature.





**FIGURE 4** Calculated HOMO and LUMO energy level of  $\text{Ir(ppy)}_2\text{(acac)}$ ,  $\text{Ir}[(\text{CF}_3)_2\text{ppy}]_2\text{(acac)}$ ,  $\text{Ir}[(\text{CF}_3)_2\text{OMeppy}]_2\text{(acac)}$ , and  $\text{Ir(F}_2\text{ppy)}_2\text{(acac)}$ .

shown in Figure 4.  $\text{CF}_3$  or F group in the phenyl ring pull the HOMO level of iridium complexes, and added methoxy group in the pyridyl ring up the LUMO level of iridium complex, it helps enlarge energy level and tune the color to blue. Moreover,  $\text{CF}_3$  group in the phenyl ring is stronger electron withdrawing than F group, it realize more blue-shifted emission wavelength.

In the view of the luminance efficiency, the bulky  $\text{CF}_3$  groups in phenyl ring occurs a steric hindrance of iridium complex, less self-quenching effects, increasing luminance efficiency. Even F groups of ppy shows stronger MLCT, F groups are can't prevent self-quenching effect, less luminance efficiency than  $\text{CF}_3$  groups in phenyl ring. As a result,  $\text{Ir}[(\text{CF}_3)_2\text{OMeppy}]_2\text{(acac)}$  can decrease a self-quenching and achieve good luminance efficiency compared to  $\text{Ir(F}_2\text{ppy)}_2\text{(acac)}$ .

#### 4. CONCLUSIONS

In summary, we synthesized and measured optical properties of the phosphorescent  $\text{Ir}[(\text{CF}_3)_2\text{OMeppy}]_2\text{(acac)}$  in order to find a new blue emitting material for the application in OLEDs. The PL of device with  $\text{Ir}[(\text{CF}_3)_2\text{OMeppy}]_2\text{(acac)}$  showed the strongest emission spectra with maximum at 471 nm. Significant improvements of the new blue iridium complex,  $\text{Ir}[(\text{CF}_3)_2\text{OMeppy}]_2\text{(acac)}$ , were achieved in the

blue-shifted luminance spectrum and good luminance efficiency due to effect of steric hindrance. It was suggested that the Ir[(CF<sub>3</sub>)<sub>2</sub>OMep-py]<sub>2</sub>(acac) be a good radiation characteristic blue dopant for new phosphorescent OLEDs.

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