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Seung-Chan Lee [a] & Young Sik Kim [a b]

[a] Department of Information Display, Hongik University, Seoul, Korea

[b] Department of Science, Hongik University, Seoul, Korea

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New Blue Phosphorescent Iridium Complexes with Various Ancillary Ligands Based on Fluorinated 2-Phenyl-4-Methylpyridine

Seung-Chan Lee[1] and Young Sik Kim[1,2]
[1]Department of Information Display, Hongik University, Seoul, Korea
[2]Department of Science, Hongik University, Seoul, Korea

In this study, a series of new blue phosphorescent iridium(III) complexes with ligands of $(CF_3)_2$Meppy [$(CF_3)_2$Meppy = 2-(3′,5′-bis-trifluoromethylphenyl)-4-methylpyridine] were successfully synthesized and their photophysical properties were systematically investigated. To analyze color tuning effected by changing the ancillary ligands, we have measured UV-absorption and photoluminescence (PL) spectra and have theoretically calculated the iridium complexes with different ancillary ligands using computational methods. The maximum emission spectrum of Ir[$(CF_3)_2$Meppy]$_2$(acac), Ir[$(CF_3)_2$Meppy]$_2$(pic), Ir[$(CF_3)_2$Meppy]$_2$(taz) and Ir[$(CF_3)_2$Meppy]$_2$(N_4) were 473.5, 472, 475 and 468 nm, respectively. However, the PL efficiency was not improved by changing the picolinate ligands with other ancillary ligands, such as triazolate or tetrazolate ions.

We discuss how the ancillary ligand influences both the emission peak and the metal to ligand charge transfer (MLCT) transition efficiency.

Keywords: 2-(3′,5′-bis-trifluoromethylphenyl)-4-methylpyridine; blue; iridium complex; OLED; phosphorescence

1. INTRODUCTION

Organic light-emitting diodes (OLEDs) have attracted increasing attention in recent years and hold much promise as the next generation of flat-panel displays due to their low-voltage operation, wide-viewing angle, high contrast, and mechanical flexibility. One

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

important focus in OLED research is on its electroluminescent (EL) organic materials. Since the first discovery by Tang and co-workers [1] that organic material emits visible light in a multilayered structure when a bias voltage is applied to the structure, OLEDs and emitting materials [2–5] have developed rapidly. Luminescent materials for OLED devices are generally classified into two groups; fluorescent and phosphorescent. Recently, Forrest, Thompson and coworkers have developed phosphorescent OLEDs with an efficiency approaching 100% of the internal quantum efficiency. These OLEDs utilize both singlet and triplet excitons produced at an emitting layer doped with phosphorescent dopants [6,7].

Phosphorescent dopant using iridium, ruthenium, osmium or platinum complexes 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 is changed to spin-allowed, resulting in high phosphorescent efficiencies. Thus, iridium complexes are known to have high photoluminescence (PL) efficiency and a relatively short excited state lifetime, which minimizes quenching of the triplet emissive states [8,9]. Until now, greater success has been achieved in the development of a green, red and blue colored emitters in phosphorescent material, especially using iridium and 2-phenylpyridine-based complexes [10–13]. In addition, some phosphorescent blue emitter materials have been synthesized and reported to offer good blue emission characteristics, especially 2-phenylpiridine (ppy) with electro-withdrawing groups added to the phenyl ring or electro-donating groups added to the pyridyl ring [14–16].

In this study, $(CF_3)_2$Meppy [$(CF_3)_2$Meppy = 2-(3′,5′-bis-trifluoromethylphenyl)-4-methylpyridine] based iridium complexes were 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). A CF_3 group in the phenyl ring pulls the HOMO level of iridium complexes, and an added methyl group in the pyridyl ring pulls up the LUMO level of iridium complex, which help enlarge the energy level and tune the color to blue. In order to tune the emission band to a shorter wavelength and to improve the PL efficiency, the ancillary ligand of the iridium complex with ligands of $(CF_3)_2$Meppy has been changed from the acetylacetonate (acac) ligand to other ancillary ligands (LXs), such as picolinate (pic), pyridinetriazolate (taz) and pyridinetetrazolate (N_4) ions. To analyze the color tuning and luminescence efficiency effected by changing the ancillary ligand, we have measured UV-absorption and photo-luminescence

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(PL) spectra, and have calculated these complexes theoretically by the density functional theory (DFT) method.

2. EXPERIMENTAL DETAILS

2.1. Synthesis and Characterization

All ligands and reagents were purchased from Aldrich Co., except Ir(III) trichloride hydrate ($IrCl_3 \cdot H_2O$), 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 Ligand [L = $(CF_3)_2$Meppy]

The synthesis of the phenylpyridine ligand used Suzuki coupling [17]. 2-chloro-4-methoxypyridine (1 eq.) and 3,5-bis(trifluoromethyl)-phenylboronic acid (1.05 eq.) and tetrakistriphenylphospine palladium(0) (0.196 g, 0.17 mmol) were dissolved 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 12 hr at 105°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 pumped dry. The residue was chromatographed on a silica gel column with ethyl acetate/hexane (1:3). The product was collected and dried. (Yield 60%, orange sticky oil, MW:305.25)

2.1.2. Synthesis of Complexes: Ir$(L)_2$(acac), Ir$(L)_2$(pic), Ir$(L)_2$(pic-5M), Ir$(L)_2$(taz) and Ir$(L)_2(N_4)$

2.1.2.1. General Procedure for Cyclometalated Ir(III) μ-chloro-bridged Dimers. Cyclometalated Ir(III) μ-chloro-bridged dimers of the general formula, $(L)_2Ir(\mu\text{-}Cl)_2Ir(L)_2$, were synthesized by the method reported by Nonoyama with slight modification [18]. 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 $(L)_2Ir(\mu\text{-}Cl)_2Ir(L)_2$. The yellow to yellowish green solid was filtered and washed with ethanol.

2.1.2.2. Synthesis of Complexes; Ir$(L)_2$(acac), Ir$(L)_2$(pic) and Ir$(L)_2$(pic-5M). This chloride-bridged dimer (2 mmol) was then placed in a 50 ml two-neck flask filled with 2-ethoxyethanol (30 mL).

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2,4-pentanedione (acac) [0.68 ml, d = 0.975, 6.8 mmol (3.4 eq)], picolinic acid (pic) was added and the reaction mixture was refluxed for 24 hr at 120°C. The solution was cooled to room temperature. The yellow solid was filtered and washed with water, followed by purification by column chromatography or flash chromatography to afford a powder of $Ir(L)_2(acac)$ and $Ir(L)_2(pic)$.

2.1.2.3. Synthesis of Complexes; $Ir(L)_2(taz)$ and $Ir(L)_2(n_4)$. Synthesis of pyridinetriazole (taz) is a 2-step process from 2-cyanopyridine [19,20]. Synthesis of pyridinetetrazole (N_4) is a simple 1-step process that uses 2-cyanopyridine and sodium azide [21]. A 1 equiv amount of Cyclometalated Ir(III) μ-chloro-bridged dimers and 2.2 equiv of the corresponding taz or N_4 were stirred in 15 mL of CH_2Cl_2 and 5 mL of EtOH at room temperature or reflux for 16 h under nitrogen. Upon completion of the reaction, all solvents were removed under reduced pressure and the resulting yellow solid was chromatographed on silica gel (CC) and crystallized where appropriate.

2.2. Optical Measurements

UV-Vis absorption spectra were measured on a Hewlett Packard 8425A spectrometer. The PL spectra were obtained on Perkin Elmer LS 55B spectrometer. UV-Vis and PL spectra of iridium complexes were measured with a 10^{-5} M dilute solution in CH_2Cl_2.

2.3. Theoretical Calculations

Calculations of the electronic ground states for $Ir[(CF_3)_2Meppy]_2(acac)$, $Ir[(CF_3)_2Meppy]_2(pic)$, $Ir[(CF_3)_2Meppy]_2(taz)$ and $Ir[(CF_3)_2Meppy]_2(N_4)$ were carried out using the B3LYP density functional theory (DFT). LANL2DZ [22] and 6–31G (d) [23] basis sets were employed for Ir and the other atoms, respectively. For the calculated ground state geometries, the electronic structure was examined in terms of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs). The electronic populations on the central atom were calculated to show the significant admixture of ligand π character with the amount of iridium 5d character in the occupied molecular orbitals, related to those metal-to-ligand charge-transfer (MLCT) transitions.

3. RESULTS AND DISCUSSION

In order to tune PL spectra to a shorter wavelength and to improve the luminescence efficiency by changing the ancillary ligand,

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$Ir[(CF_3)_2Meppy]_2(LX)$ were designed where the ancillary ligand LX is acac, pic, taz or N_4. The ligands, $(CF_3)_2$Meppy, were prepared by Suzuki coupling, as illustrated in Figure 1(a). Final iridium complexes were obtained via two steps. In the first step, Ir(III) μ-chloro-bridged dimers were prepared according to the Nonoyama method, as illustrated in Figure 1(b). The second step to make the final monomeric $Ir(L)_2(LX)$ complex is shown in Figure 1(c). The overall reaction yields were about $32 \sim 45\%$, respectively.

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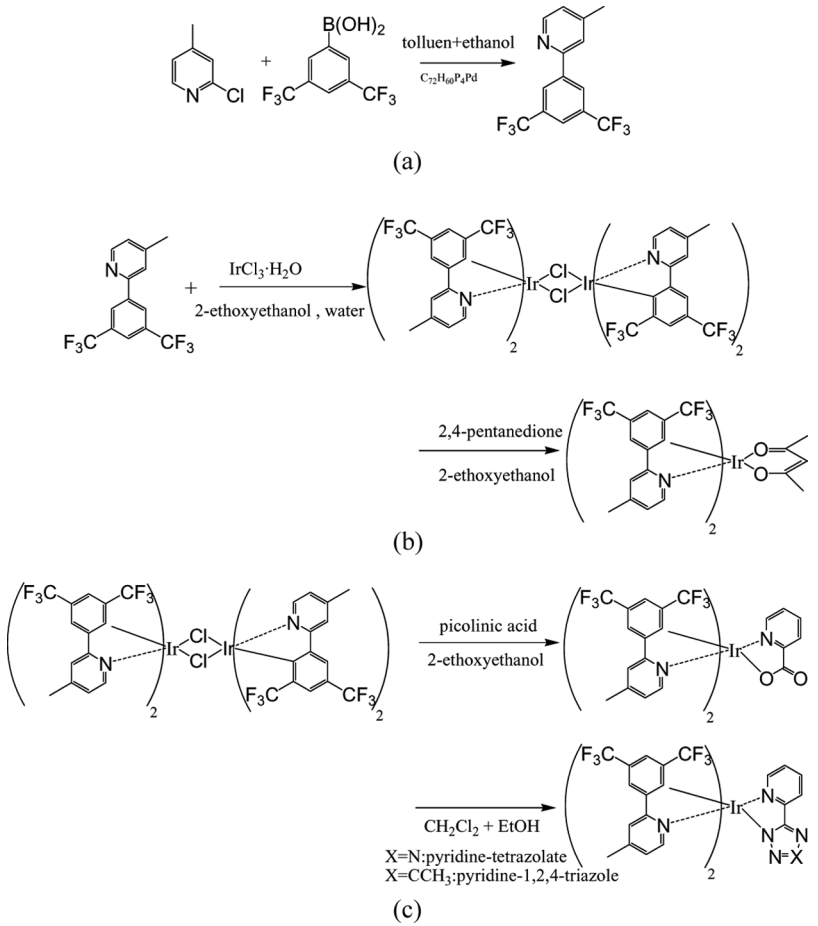

FIGURE 1 (a) Synthesis of $(CF_3)_2$Meppy ligands, (b) Synthesis of Ir(III) μ-chloro-bridged dimmers, and (c) Synthesis of Iridium complexes based on $(CF_3)_2$Meppy.

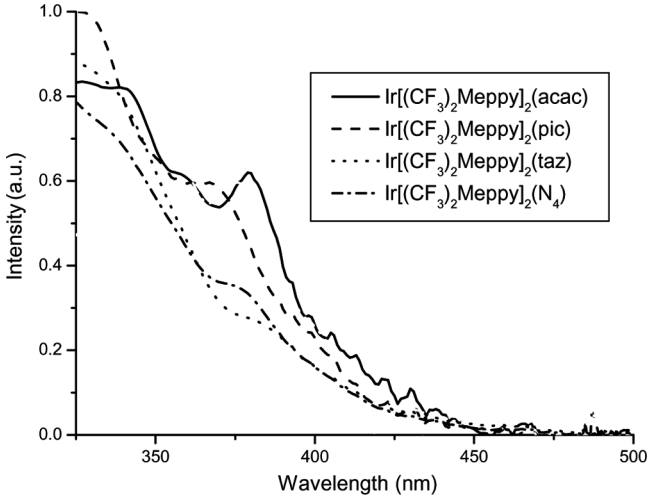

FIGURE 2 UV-Vis absorption spectrum of $Ir[(CF_3)_2Meppy]_2(acac)$, $Ir[(CF_3)_2Meppy]_2(pic)$, $[(CF_3)_2Meppy]_2(taz)$ and $Ir[(CF_3)_2Meppy]_2(N_4)$ in 10^{-5} M CH_2Cl_2 solution of room temperature.

The UV-Vis absorption of the complexes in solution has been measured as shown in Figure 2. Both ^{1}MLCT and ^{3}MLCT peaks are observed for these complexes. CF_3 groups, substituted on the 3′,5′-position of phenyl ring as electron withdrawing groups, tune the MLCT absorption peak to bluish. In addition, the methyl group substituted on the 4-position of the pyridyl ring as an electron donating group strongly affected the lowest unoccupied molecular orbital (LUMO) and raised the LUMO energy and increased the energy gap. The bands in the range of 360−380 nm can be assigned to a spin-allowed meta-ligand charge transfer band (^{1}MLCT). Weak absorption at 420−470 nm was attributed to the previously spin-forbidden ^{3}MLCT transition. In particular, ^{1}MLCT absorption peaks of $Ir[(CF_3)_2Meppy]_2(acac)$ and $Ir[(CF_3)_2Meppy]_2(pic)$ were stronger than were other iridium complexes. The ancillary ligand of pic destabilizes MLCT energy mainly by changing the HOMO energy level. The HOMO energy may be lowered by strong ancillary ligands, which cause a large d-orbital energy splitting. Therefore, $Ir[(CF_3)_2Meppy]_2(pic)$ has an about 10 nm blue-shifted ^{1}MLCT absorption band compared to that of $Ir[(CF_3)_2Meppy]_2(acac)$. The ^{1}MLCT absorption spectra of $Ir[(CF_3)_2Meppy]_2(taz)$ and $Ir[(CF_3)_2Meppy]_2(N_4)$ show a small absorption extinction coefficient. In the case of $Ir[(CF_3)_2Meppy]_2(taz)$ and $Ir[(CF_3)_2Meppy]_2(N_4)$, the blue-shifting power of an anionic nitrogen based ancillary ligand destabilizes t_{2g}

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energy level of 5d orbital of the iridium atom to a greater extent. Thus, the MLCT state is created by mixing between the iridium atom and the ancillary ligand instead of the luminescent $(CF_3)_2$Meppy ligand. This reduces the MLCT transition efficiency and calculated HOMO and LUMO energy levels of iridium complexes as shown in Figure 3.

The PL spectra of iridium complexes in CH_2Cl_2 also reflected their mechanism. As shown in Figure 4, the maximum emission spectrum of Ir[$(CF_3)_2$Meppy]$_2$(acac), Ir[$(CF_3)_2$Meppy]$_2$(pic), Ir[$(CF_3)_2$Meppy]$_2$(taz) and Ir[$(CF_3)_2$Meppy]$_2$(N_4) were 473.5, 472, 475 and 468 nm, respectively. The substitution of CF_3 groups at the ortho and para positions on the iridium atom blue-shifted the emission spectrum. This shift is attributed to the fact that the HOMO level is lower than that of the ppy ligand, as judged from their electrochemical properties. In addition, methyl groups in the pyridyl ring pull up the LUMO level of iridium complex and help increase the energy level and tune the color to blue. Interestingly, the HOMO level of pic is a destabilized MLCT mixing state of iridium complex that leads to pull down of the total HOMO level. The ancillary ligand of pic destabilizes MLCT energy mainly by changing the HOMO energy level, which causes a large d-orbital energy splitting. Therefore, the MLCT absorption band of Ir[$(CF_3)_2$Meppy]$_2$(pic) gives more ligand-centered (LC) characteristics than does Ir[$(CF_3)_2$Meppy]$_2$(acac). Both MLCT mixing and LC

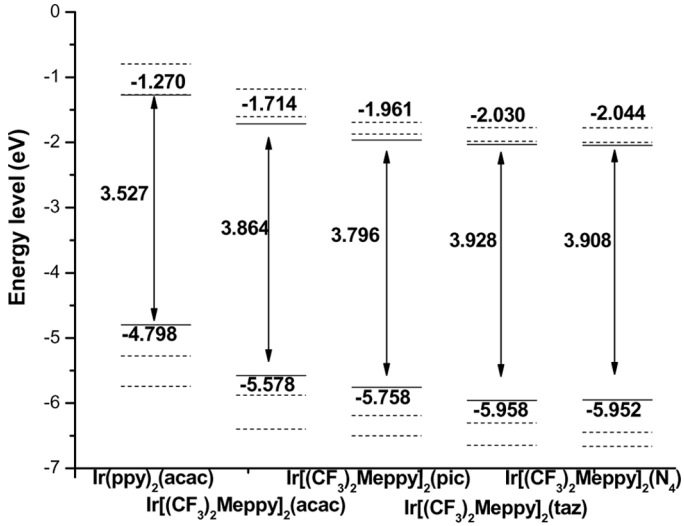

FIGURE 3 Calculated energy level of Ir[$(CF_3)_2$Meppy]$_2$(acac), Ir[$(CF_3)_2$ Meppy]$_2$(pic), Ir[$(CF_3)_2$Meppy]$_2$(taz) and Ir[$(CF_3)_2$Meppy]$_2$(N_4).

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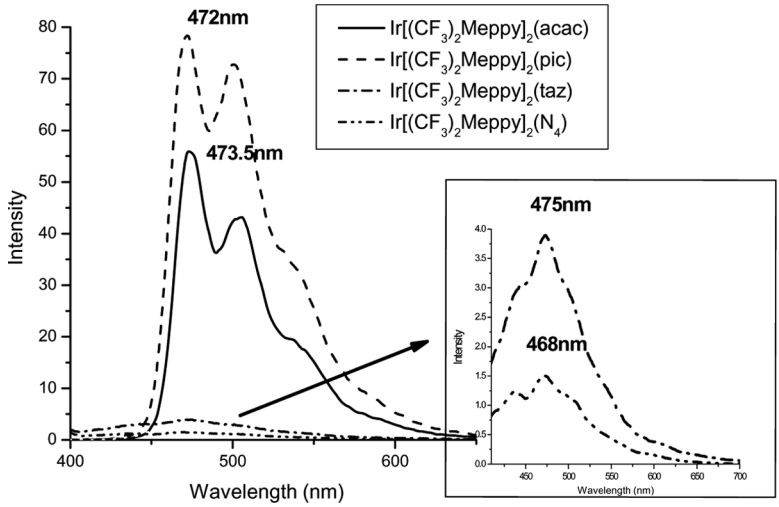

FIGURE 4 PL spectrum of $Ir[(CF_3)_2Meppy]_2(acac)$, $Ir[(CF_3)_2Meppy]_2(pic)$, $Ir[(CF_3)_2Meppy]_2(taz)$ and $Ir[(CF_3)_2Meppy]_2(N_4)$ in 10^{-5} M CH_2Cl_2 solution of room temperature.

characteristics bring about PL efficiency improvement. This effect also strongly influences LUMO level, pulling down the LUMO level brings about a narrow band gap, and achieves a red-shifted PL wavelength compared with $Ir[(CF_3)_2OMeppy]_2(acac)$.

In order to examine which ligand mainly contributes to the MLCT transition process of $Ir[(CF_3)_2Meppy]_2(pic)$, and $Ir[(CF_3)_2Meppy]_2(N_4)$, the d-orbital characteristics of HOMOs and LUMOs were investigated after geometry optimization of the molecular structure of this complex using the density functional theory (DFT). In Figure 5, contour plots of the three highest HOMOs and three lowest LUMOs of $Ir[(CF_3)_2Meppy]_2(pic)$ and $Ir[(CF_3)_2Meppy]_2(N_4)$, are compared. These orbitals are important because dominant excitations and emissions mainly occur due to the electronic transition among these orbitals. Most of the electron population of $Ir[(CF_3)_2Meppy]_2(pic)$ is localized in the mixing state between the 5d orbital of the centric Ir atom and the $(CF_3)_2Meppy$ ligand where most of the electron population is localized mainly in the N_4 ancillary ligand. It is concluded that the three HOMOs of $Ir[(CF_3)_2Meppy]_2(pic)$ and $Ir[(CF_3)_2Meppy]_2(N_4)$ have different characteristics with respect to the electron population, as the former has mainly the MLCT state between metallic character of the 5d orbital of the centric iridium atom and the luminescent $(CF_3)_2Meppy$ ligand while the latter has the MLCT character with

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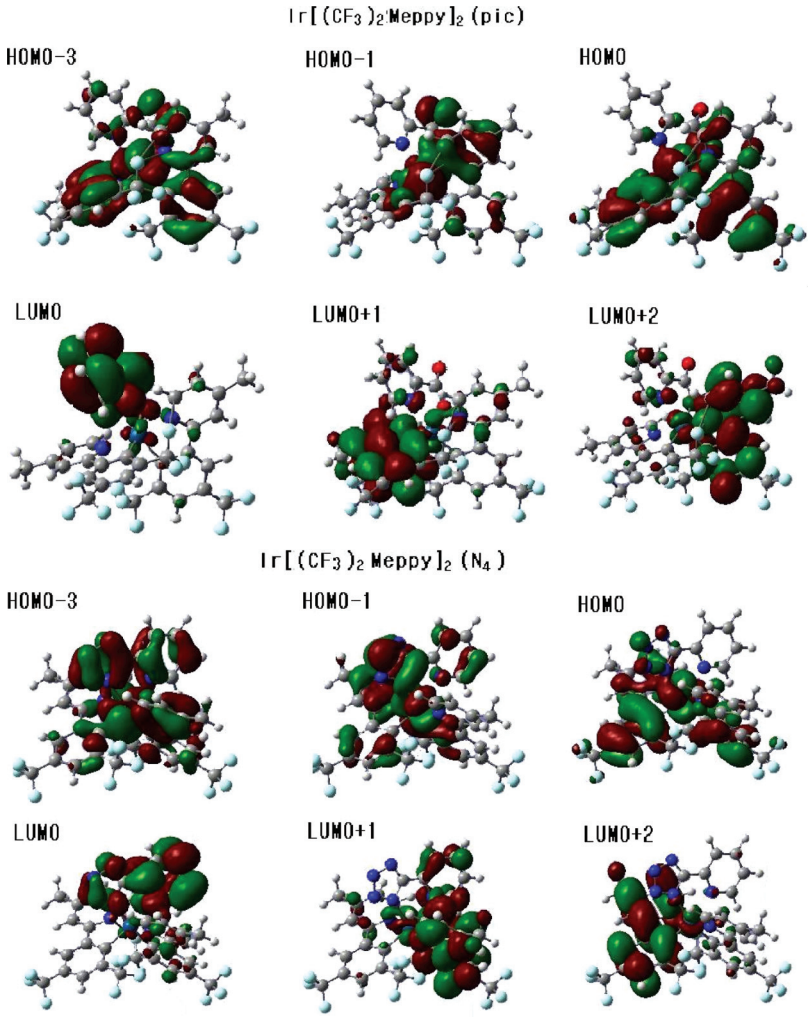

FIGURE 5 the d-orbital characteristics of HOMOs and LUMOs of Ir[$(CF_3)_2$ Meppy]$_2$(pic) and Ir[$(CF_3)_2$Meppy]$_2$(N_4).

the ancillary ligand instead. Therefore, it is expected that Ir[$(CF_3)_2$ Meppy]$_2$(pic) may have high phosphorescence emitting characteristics.

4. CONCLUSIONS

In summary, we synthesized and measured optical properties of the phosphorescent $(CF_3)_2$Meppy based iridium complex in order to find

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a new blue emitting material for application in OLEDs. The maximum PL spectrum of Ir[$(CF_3)_2$Meppy]$_2$(acac), Ir[$(CF_3)_2$Meppy]$_2$(pic), Ir[$(CF_3)_2$ Meppy]$_2$(taz) and Ir[$(CF_3)_2$Meppy]$_2$(N_4) were 473.5, 472, 475 and 468 nm, respectively. Significant improvements in the PL efficiency of the new $(CF_3)_2$Meppy based iridium complexes were achieved in the blue-shifted luminance spectrum by changing ancillary ligands, which gave good luminance efficiency due to the effect of steric hindrance. Ir[$(CF_3)_2$Meppy]$_2$(pic) has stronger PL efficiency due to destabilized electron mixing between the Iridium atom and the pic ligand. It was suggested that the Ir[$(CF_3)_2$Meppy]$_2$(pic) would be a good radiation characteristic blue dopant for new phosphorescent OLEDs.

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