Blue-emitting heteroleptic iridium(III) complexes based on fluorinated 2-phenyl-4-methoxypyridine

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Abstract

New iridium complexes with 2-(3',5'-bis-trifluoromethyl phenyl)-4-metoxypyridine [(CF$_3$)$_2$ppyOMe] were synthesized and characterized for blue phosphorescent materials. It was found that Ir[(CF$_3$)$_2$ppyOMe]$_2$(acac) gives blue emission at 471 nm with strong luminescence efficiency. We discuss the role played by electron withdrawing substituents and also how the ancillary ligand influences the emission peak.

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted increasing attention in recent years and are considered to hold the promise as the next generation of flat-panel displays due to their low-voltage operation, wide-viewing angle, high contrast, and mechanical flexibility. Since the first great discovery by Tang and coworkers [1] that organic material emits visible light in 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. 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 an efficiency approaching 100% of the internal quantum efficiency. These OLEDs utilize both singlet and triplet excitons produced at the emitting layer doped with 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 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 emitter in phosphorescent material, especially using iridium and ppy-based complex [10-13]. However 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 to offer good blue emission characteristics, especially 2-phenylpiridine with electro-withdrawing groups added to the phenyl ring or electro-donating groups added to the pyridyl ring [14-16].

In this study, (CF$_3$)$_2$OMeppy [(CF$_3$)$_2$OMeppy = 2-(3',5'-bistrifluoromethylphenyl)-4-metoxypyridine] 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). Furthermore, combination with the ancillary ligand of picolate (pic) and (CF$_3$)$_2$OMeppy ligand result in a broad emission band compared to its acetylacetonate (acac) analogue. To analyze the color tuning and luminescence efficiency by the substitution, we have measured UV-absorption and photo-luminescence (PL) spectra, and have calculated these complexes theoretically by the density functional theory (DFT) method.

2. Experimental

All ligands and 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 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 Synthesis of ligands [(CF$_3$)$_2$ppy and (CF$_3$)$_2$OMeppy]

Synthesis of (CF$_3$)$_2$OMeppy: A synthetic of phenylpyridine was processed using Suzuki coupling [17]. 2-chloro-4-methoxypyridine (1 eq.) and 3,5-Bis(trifluoromethyl)-phenylboronic acid (1.05 eq.) and tetrakistriphenylphospine palladium (0.196g, 0.17mmol) were dissolved in a mixture of toluene(20ml), ethanol(10ml) and 2N sodium carbonate aqueous solution(20ml). The reaction mixture was heated and refluxed for 12 hr at 110℃. The mixture was cooled to room temperature and extracted with 20ml 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 was collected and dried. (Yield 60%, orange sticky oil, MW: 321.24)

Synthesis of (CF$_3$)$_2$ppy: We used 2-chloropyridine [for synthesis of (CF$_3$)$_2$ppy] (1 eq.) and 3,5-Bis(trifluoromethyl) phenylboronic acid (1.05 eq.). The reaction and purification method is the same as (3',5'-bis-trifluoromethylphenyl)-4-metoxypyridine. [(CF$_3$)$_2$ppy: Yield 62%, red sticky oil, MW: 291.18]

2.2. Synthesis of complexes of Ir(L)$_2$(acac) and Ir[(CF$_3$)$_2$OMeppy]$_2$(pic)

Cyclometalated Ir(III) μ-chloro-bridged dimers of the general formula, (L)$_2$Ir(μ-Cl)$_2$Ir(L)$_2$, were synthesized by the method reported by Nonoyama with slight modification [18]. To a flask containing IrCl$_3$·H$_2$O (1.49g, 5mmol) and ligand (12.5mmol (2.5eq)) we 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 slowly evaporated under vacuum to obtain the crude product (L)$_2$Ir(μ-Cl)$_2$Ir(L)$_2$. The yellow to yellowish green solid was filtered and washed with ethanol.

This chloride-bridged dimer (2mmol) was then placed in a 50ml two-neck flask filled with 2-ethoxyethanol (30mL). 2,4-pentanedione [0.68ml, d = 0.975, 6.8mmol(3.4eq)](acac) or picolinic acid(pic) was added and the reaction mixture was refluxed for 24 hr at 120℃. 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) or Ir[(CF$_3$)$_2$OMeppy]$_2$(pic).

Ir[(CF$_3$)$_2$OMeppy]$_2$(acac) –Yield 45%, yellowish green powder. MW: 931.75

Ir[(CF$_3$)$_2$ppy]$_2$(acac) –Yield 48%, light yellow powder. MW: 871.69

Ir[(CF$_3$)$_2$OMeppy]$_2$(pic) –Yield 38%, yellowish green powder. MW: 954.65

2.3. Optical measurements

UV-Vis absorption spectra were measured on a Hewlett Packard 8425A spectrometer. The PL spectra were obtained on a Perkin Elmer LS 55B spectrometer. UV-Vis and PL spectra of Ir(L)$_2$(acac) were measured with a 10^{-5} M dilute solution in CH$_2$Cl$_2$.

2.4. Theoretical Calculation

Calculations on the electronic ground states of iridium complexes were carried out using the B3LYP density functional theory (DFT). LANL2DZ and 6-31G(d) basis sets were employed for iridium and the other atoms, respectively. For 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$_3$)$_2$OMeppy and (CF$_3$)$_2$ppy were synthesized as illustrated in Fig. 1.
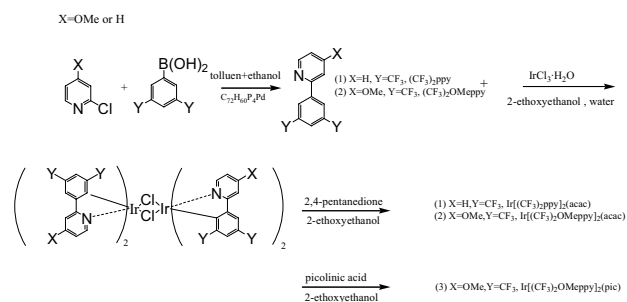

Fig. 1. Synthesis of ppy-based iridium complexes

The bis-cyclometalated Ir(III) complexes containing these ligands and an ancillary ligand were prepared. Ir(L)$_2$(acac) were obtained via two steps. In the first step, a Ir(III) μ-chloro-bridged dimer was prepared according to Nonoyama method. The second

step to make the final monomeric Ir(L)₂(acac) complex with 2,4-pentandione requires a short reaction time compared to that reported previously. Synthesis of iridium complexes is shown in Fig. 1. The overall reaction yields were about 38-48%, respectively.

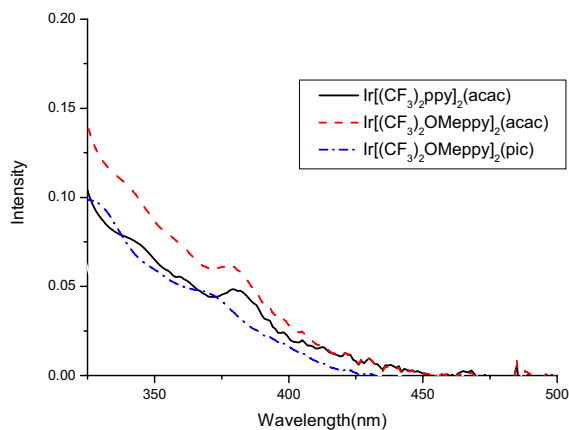The solution UV–Vis absorption complexes have been measured as shown in Fig. 2.

Fig. 2. UV-vis absorption spectra of Ir[(CF₃)₂ppy]₂ (acac), Ir[(CF₃)₂OMeppy]₂(acac) and Ir[(CF₃)₂ OMeppy]₂(pic)

Interestingly, the MLCT absorption spectra for Ir[(CF₃)₂ppy]₂(acac) resembles that of Ir[(CF₃)₂ OMeppy]₂(acac). Both ¹MLCT and ³MLCT peaks are observed for these complexes. The bands in the range 360 – 420 nm can be assigned to a spin-allowed meta-ligand charge transfer band (¹MLCT). Weak absorption at 420 – 470 nm was attributed to the previously spin-forbidden ³MLCT transition. CF₃ groups, MLCT absorption spectra of Ir[(CF₃)₂OMeppy]₂(acac) and Ir[(CF₃)₂ppy]₂(acac) shows similar. CF₃ groups substituted on the 3',5'-position of phenyl ring as electron withdrawing group, tune the MLCT absorption peak to bluish. In addition, in the case of Ir[(CF₃)₂OMeppy]₂(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. Thus, the MLCT absorption band of Ir[(CF₃)₂OMeppy]₂ (acac) is ~ 4 nm blue-shifted rather than that of Ir[(CF₃)₂ppy]₂(acac). However, the MLCT absorption band of Ir[(CF₃)₂OMeppy]₂ (pic) gives a weak MLCT characteristics. 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, it gives more ligand-centered (LC) character. This effect also strongly influence LUMO level, achieve narrow band gap compare with Ir[(CF₃)₂OMeppy]₂(acac). Calculated HOMO and LUMO energy levels of iridium complexes are shown in Fig. 3.
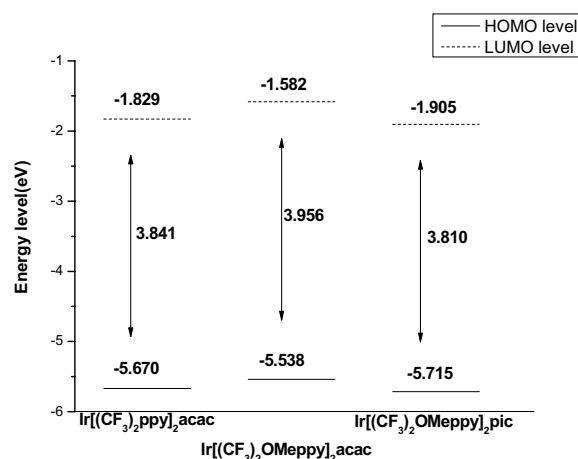

Fig. 3. Calculated energy level of Ir[(CF₃)₂ppy]₂ (acac), Ir[(CF₃)₂OMeppy]₂(acac) and Ir[(CF₃)₂ OMeppy]₂(pic)

The PL spectra of iridium complexes in CH₂Cl₂ also reflected their absorption patterns. As shown in Fig. 4, the maximum emission spectrum of Ir[(CF₃)₂OMeppy]₂(acac) and Ir[(CF₃)₂ppy]₂(acac) were 471 and 475 nm. Ir[(CF₃)₂OMeppy]₂(pic) has two peak, 471 and 498 nm, respectively. In the case of Ir[(CF₃)₂OMeppy]₂(acac) and Ir[(CF₃)₂ppy]₂(acac), the substitution of CF₃ groups at the ortho and para positions to the iridium atom 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. And the methoxy group in the pyridyl ring pulls LUMO level, these effect increase energy gap, emitted more blue-shifted luminance spectrum.

Iridium complexes based on (CF₃)₂OMeppy ligand iridium complexes also exhibit high solution phosphorescence relative quantum yields. The relative quantum yields of Ir [(CF₃)₂ppy]₂(acac), Ir[(CF₃)₂OMeppy]₂(acac), and Ir[(CF₃)₂ppy]₂(pic) were 0.92, 0.88 and 1.39, respectively.
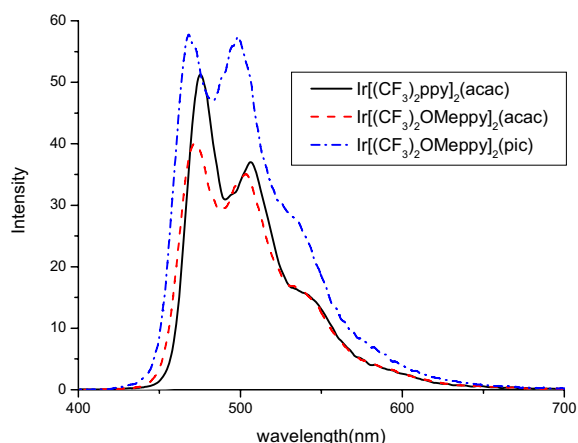
Fig. 4. PL spectra of Ir[(CF$_3$)$_2$ppy]$_2$ (acac), Ir[(CF$_3$)$_2$OMeppy]$_2$(acac), Ir[(CF$_3$)$_2$ OMeppy]$_2$(pic)

The bulky CF$_3$ groups in phenyl ring occurs a steric hindrance of iridium complex, less self-quenching effects, increasing luminance efficiency. Especially, nitrogen atom of Ir[(CF$_3$)$_2$OMeppy]$_2$(pic) destabilize electron mixing affect HOMO level leads to maximize MLCT, achieve highest PL efficiency.

4. Summary

In summary, we synthesized and measured optical properties of the phosphorescent Ir[(CF$_3$)$_2$OMeppy]$_2$ (acac) and Ir[(CF$_3$)$_2$OMeppy]$_2$(pic) in order to find a new blue-emitting material for application in OLEDs. The PL of the device with Ir[(CF$_3$)$_2$OMeppy]$_2$(acac) and Ir[(CF$_3$)$_2$OMeppy]$_2$(pic) showed the strongest emission spectra with maxima at 471 nm. Significant improvements of these new blue iridium complexes, especially Ir[(CF$_3$)$_2$OMeppy]$_2$(acac), were achieved in the blue-shifted luminance spectrum, and the good luminance efficiency was mainly due to the effect of steric hindrance. Also Ir[(CF$_3$)$_2$OMeppy]$_2$(pic) has stronger PL efficiency due to destabilized electron mixing between Iridium atom and pic ligand. We suggest that the Ir[(CF$_3$)$_2$OMeppy]$_2$(acac) and Ir[(CF$_3$)$_2$OMeppy]$_2$(pic) might serve as a good radiation characteristic blue dopant for new phosphorescent OLED materials.

5. Acknowledgements

6. References

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