Mol. Cryst. Liq. Cryst., Vol. 530: pp. 116/[272]–122/[278], 2010

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2010.495922

Color Tuning of Blue Phosphorescence: New Iridium Complexes Containing a Bipyridine Derivative and Various Ancillary Ligands

SO YOUN AHN AND YUNKYOUNG HA

Department of Information Display Engineering, Hongik University, Seoul, Korea

New blue-phosphorescent iridium complexes containing 2,6-difluoro-3-(4-methylpyridin-2-yl)pyridine (4-Me-dfpypy) and various ancillary ligands, acetylacetonate (acac) and 2-(5-tert-butyl-2H-1,2,4-triazol-3-yl)pyridine (trzl-CMe$_3$*), were synthesized and their photophysical properties were investigated. The main ligand, 4-Me-dfpypy, was designed for development of the blue light-emitting iridium complexes by introducing the electron-donating group, CH*$_3$*, at the* para *positions of the pyridine ring determining the LUMO level. The resulting iridium complexes, Ir(4-Me-dfpypy)*$_3$*, Ir(4-Me-dfpypy)*$_2$*(acac) and Ir(4-Me-dfpypy)*$_2$*(trzl-CMe*$_3$*) exhibited the blue emission at 450, 442 and 435 nm in CH*$_2$*Cl*$_2$* solution, respectively. The trzl-CMe*$_3$* ancillary ligand in the heteroleptic complex had a stronger effect on hypsochromic shift in PL of its iridium complex than acac ancillary ligand and even further than homoleptic main ligands.*

Keywords Blue; iridium complex; OLED; phosphorescence; pyridylpyridine

Introduction

Compared to fluorescent organic light-emitting devices (OLEDs), the performance of phosphorescent OLEDs is significantly better because both singlet and triplet excitons can be harvested for light emission [1,2]. While phosphorescent OLEDs with red and green iridium complexes have proven fairly straightforward to produce, the same cannot be said for saturated blue emissive materials. According to recently report [3], the CIE coordinates for a blue light-emitting iridium(III) complex, Ir(dfpypy)$_3$, where dfpypy represents 2,6-difluoro-3-(pyridin-2-yl)pyridyl ligand, were (0.14, 0.12). Since N of the pyridyl ligand is more electronegative than a C of the nonsubstituted phenyl ligand, replacement of the phenyl ring with a pyridine ring in the C∧N ligand of the iridium complex may contribute to lowering the HOMO energy levels of the complex. The resulting energy gap increase can lead to luminescence toward the saturated blue emission.

Address correspondence to Prof. Yunkyoung Ha, Department of Information Display Engineering, Hongik University, Sangsu-dong, Mapo-gu, Seoul 121-791, Korea (ROK). Tel.: (+82)2-320-1490; Fax: (+82)2-3142-0335; E-mail: ykha@hongik.ac.kr

To obtain a good blue phosphorescent material, we designed the new C∧N ligand for the blue emission color and prepared its iridium complexes in this study. An electron donating group, methyl, was introduced to the LUMO site of the pyridylpyridine (pypy)-based ligand, which may be contributed to the LUMO level increase. In addition, we introduced several ancillary ligands which were reported to contribute to blue light emission of their iridium complexes. The ancillary ligands for the iridium complexes tend to influence the perturbation degree of the metal-to-ligand charge transfer (MLCT) transition by the excited-state interaction with the cyclometallating ligand centered (LC) state, causing the fine change in emission wavelengths [4–6]. We thus synthesized the new pypy derivative and various ancillary ligands (acetylacetonate (acac) and 2-(5-tert-butyl-2H-1,2,4-triazol-3-yl)pyridine (trzl-CMe_3)) and prepared their iridium complexes, Ir(4-Me-dfpypy)$_3$, Ir(4-Me-dfpypy)$_2$(acac) and Ir(4-Me-dfpypy)$_2$(trzl-CMe_3). The photoabsorption and electrochemical properties of the complexes were investigated and their photoluminescence characteristics were studied. We compared the photophysical properties of new iridium complexes to find how the different ancillary ligands have influence on emission wavelengths of the iridium complexes.

Experimental

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}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.

Synthesis of Ligands

2,6-difluoro-3-(4-methylpyridin-2-yl)pyridine (4-me-dfpypy). The 4-Me-dfpypy ligand was prepared according to the literature [3] with the corresponding precursors 2,6-difluoropyridin-3-yl-3-boronic acid and 2-chloro-4-methylpyridine.

2-(5-tert-butyl-2H-1,2,4-triazol-3-yl)pyridine (trzl-CMe_3). This compound was prepared according to the procedure previously reported [7,8]. Yield: 68%. ^{1}H NMR (DMSO-d6, 300 MHz): δ 8.57, 8.08, 7.88, 7.44 (m, 1H each, aromatic Hs′); 1.21(s, 9H, $C(\underline{CH_3})_3$).

Synthesis of Iridium Complexes

Ir(4-Me-dfpypy)$_3$. This complex was prepared from Ir(acac)$_3$ and the 4-Me-dfpypy ligand by a reported procedure [3]. Ir(acac)$_3$ (1.22 g, 2.5 mmol) and (C∧N) 4-Me-dfpypy (2.07 g, 10 mmol) were dissolved in 50 ml of ethylene glycol and the mixture was refluxed for 24 hr. After cooling, 1 N HCl solution was added and the resulting precipitate was filtered off. The residue was purified by silica gel chromatography by using CH_2Cl_2. Yield: 18%. FAB-MS: calculated 808; found 809.

Ir(4-Me-dfpypy)$_2$(acac)[†]. The cyclometalated iridium μ-chloro-bridged dimer, *(4-Me-pypy)$_2$Ir(μ-Cl)$_2$Ir(4-Me-pypy)$_2$*, was prepared according to the method reported by Nonoyama with slight modification[9]. The resulting dimer (1.276 g, 1 mmol) and 2,4-pentadione (0.349 ml, 3.4 mmol) were mixed with Na_2CO_3 (500 mg) in 2-ethoxyethanol (30 mL). The mixture was refluxed for 4 hr. After cooling to room temperature, the solution was filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography by using CH_2Cl_2. Yield: 23%. FAB-MS: calculated 702; found 703.

Ir(4-Me-dfpypy)$_2$(trzl-CMe$_3$). This Ir(III) complex was prepared from the reaction of the corresponding dimer with the trzl-CMe$_3$ according to the procedure described above. Yield: 19%. FAB-MS: calculated 804; found 805.

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 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. Cyclic voltammograms were obtained at scan rate of 100 mV/s, and tetrabutylammonium hexafluorophosphate was added as an electrolyte in CH_2Cl_2 solution.

Results and Discussion

Synthesis of the main ligand, 4-Me-dfpypy, was straightforward, according to the modified Suzuki coupling method [3]. The ancillary ligand, trzl-CMe$_3$, was prepared from the reaction of amidrazone precursor with trimethylacetyl chloride, according to the reported procedure [7,8]. The heteroleptic iridium complexes were synthesized as reported by Nonoyama [9]. The homoleptic iridium complex, Ir(4-Me-dfpypy)$_3$, was prepared from the one-pot reaction of the main ligand with Ir(acac)$_3$. 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 heteroleptic iridium complexes, Ir(4-Me-dfpypy)$_2$(acac) and Ir(4-Me-dfpypy)$_2$(trzl-CMe$_3$), have strong absorption bands appearing in the ultraviolet region of the spectrum between 230 and 290 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 290 to 350 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 charge-transfer transitions with high lying spin-allowed transitions on the cyclometalating ligand [10]. MLCT is important with respect to the emission efficiency. The absorption spectra of Ir(4-Me-dfpypy)$_2$(acac) and Ir(4-Me-dfpypy)$_2$(trzl-CMe$_3$) have almost

---

[†] The preliminary result on quantum efficiency of its device was 0.59%. Further detail of the device characteristics will be submitted for publication.

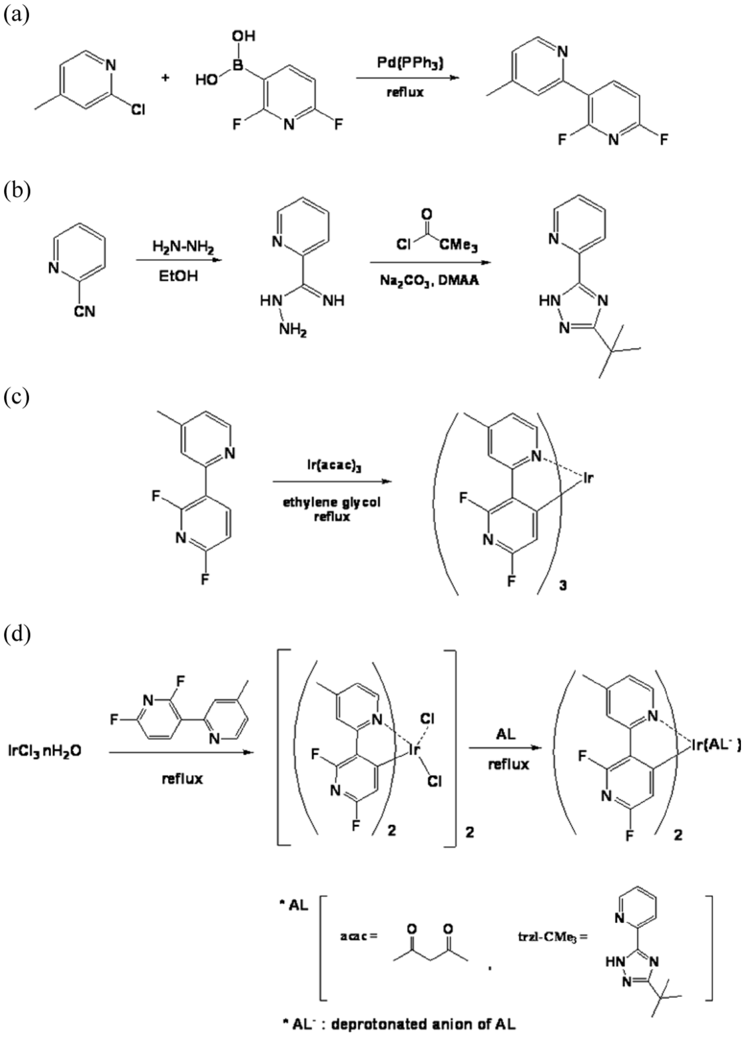

Figure 1. The synthesis of 4-Me-dfpypy, trzl-CMe$_3$ and their iridium complexes.

identical pattern, whereas that of Ir(4-Me-dfpypy)$_3$ shows different features. The MLCT band of Ir(4-Me-dfpypy)$_3$ has relatively low intensity and the absorption spectra of this homoleptic iridium complex has mostly the spin-allowed $^1(\pi \rightarrow \pi^*)$ transitions of the ligands between 245 and 310 nm. The result that the MLCT bands of the heteroleptic Ir complexes have lager absorption intensity than that of the homoleptic Ir complex could lead to better emission efficiency in heteroleptic Ir complexes.

The photoluminescence (PL) spectra of the Ir complexes in 10^{-5} M CH$_2$Cl$_2$ solution are shown in Figure 3. Ir(4-Me-dfpypy)$_3$, Ir(4-Me-dfpypy)$_2$(acac) and Ir(4-Me-dfpypy)$_2$(trzl-CMe$_3$) exhibited the emission maxima at 450, 442 and 435 nm, respectively. The emission peaks of Ir(4-Me-dfpypy)$_2$(trzl-CMe$_3$) was the most bluish due to the trzl-CMe$_3$ ancillary ligand which has the strong electron-withdrawing ability, in turn, resulting in the deep blue emission.

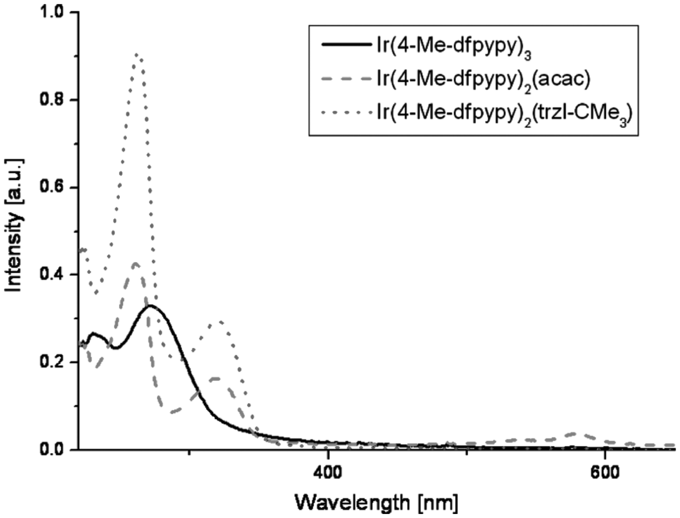

Figure 2. UV-Vis absorption spectra of the iridium complexes.

We also attempted to investigate their PL in PMMA (poly(methylmethacrylate)) film for the polymer light-emitting device (PLED) fabrication. PMMA was chosen as a host because its non-emitting property within the visible range could provide the PL of the iridium complexes only [11]. The solid PL peak of the Ir(4-Me-dfpypy)$_3$, Ir(4-Me-dfpypy)$_2$(acac) and Ir(4-Me-dfpypy)$_2$(trzl-CMe$_3$) in the PMMA had emission maxima at 449, 437 and 415/446 nm, respectively, as shown in Figure 4. The solid PL spectra of Ir complexes have a shoulder, which appeared at shorter wavelength than maximum peak. However both the solid and the solution PLs showed the similar aspects in emission maxima. It means that the emission process in both the solution and the solid is similar without the significant quenching.

We investigated electrochemical properties of the Ir complexes by the cyclic voltammetry (CV), which reveal their positions of the HOMO/LUMO [12,13].

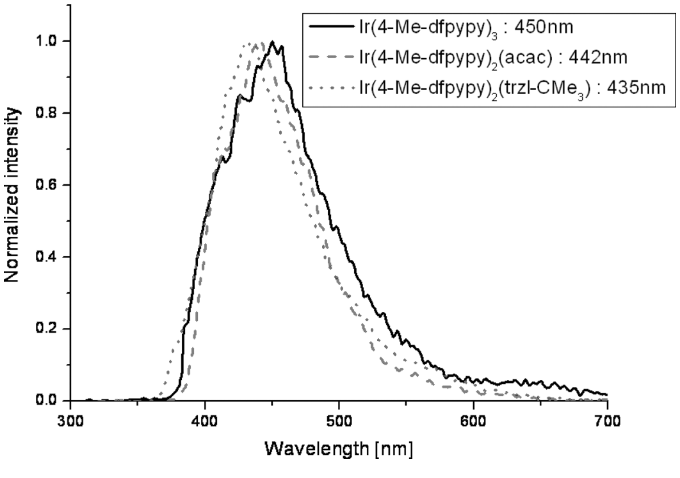

Figure 3. PL spectra of the iridium complexes in a 10^{-5} M CH_2Cl_2 solution.

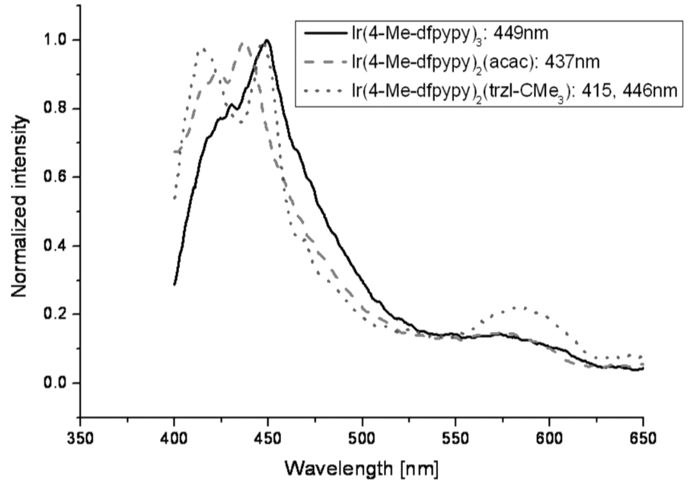

Figure 4. PL spectra of the iridium complexes in a PMMA film.

Table 1. Physical parameters for the complexes

Ir complex	λ_{abs}/ nm[a]	λ_{em}/ nm[a]	E_{ox}/ V[b]	HOMO/ eV[c]	LUMO/ eV[d]	ΔE/ eV[d]
Ir(4-Me-dfpypy)$_3$	270	450	0.74	−5.54	−2.77	2.77
Ir(4-Me-dfpypy)$_2$(acac)	257, 318	442	0.68	−5.48	−2.64	2.84
Ir(4-Me-dfpypy)$_2$(trzl-CMe$_3$)	260, 316	435	0.67	−5.47	−2.46	3.01

[a] Measured in CH_2Cl_2 solution.
[b] Scan rate: 100 mV/s, Electrolyte: tetrabutylammonium hexafluorophosphate. The potentials are quoted against the internal ferrocene standard.
[c] Deduced from the equation HOMO = −4.8 − E_{ox}.
[d] Calculated from the optical edge ΔE = LUMO − HOMO.

The detailed CV data were summarized in Table 1. The oxidation potentials which indicate the HOMOs of the complexes were irreversible in the range of 0.67 – 0.74 V relative to an internal ferrocenium/ferrocene reference (Fc^+/Fc). Using the equation HOMO = −4.8 − E_{ox}, the HOMO of Ir(4-Me-dfpypy)$_3$ was calculated to be −5.54 eV, the lowest among the complexes studied herein, but the overall HOMO differences among the complexes were less than 0.1 eV only. On the other hand, the reduction potentials of the iridium complexes were not clearly shown in the electrochemical windows and thus their LUMOs were estimated from their optical edges. The reduction potentials of the complexes in this study were calculated to be between −2.46 and −2.77 eV. Ir(4-Me-dfpypy)$_2$(trzl-CMe$_3$) has the largest energy gap (ΔE) of 3.01 eV, which consists with emission spectra having the shortest emission wavelength in PL.

Conclusions

Herein we report the detailed synthesis and photophysical properties of the phosphorescent iridium(III) complexes having a 4-Me-dfpypy ligand and various ancillary ligands. The iridium complexes, Ir(4-Me-dfpypy)$_3$, Ir(4-Me-dfpypy)$_2$(acac) and Ir(4-Me-dfpypy)$_2$(trzl-CMe$_3$), prepared in this study exhibited the blue emission at 450, 442 and 435 nm, respectively. The Ir(4-Me-dfpypy)$_2$(trzl-CMe$_3$) showed the most bluish emitting light and had the largest energy gap due to the trzl-CMe$_3$ ligand having the strong electron-withdrawing ability. Further studies are undergoing on device fabrication using these complexes as a blue-emitting material to compare electroluminescence characteristics such as CIE coordinates and luminescence efficiencies.

Acknowledgments

This work was supported by National Research Foundation of Korea Grant funded by the Korean Government (2009-0065382).

References

[1] Baldo, M. A., O'Brien, D. F., You, Y., Shoustikov, A., Sibley, S., Thompson, M. E., & Forrest, S. R. (1998). *Nature*, *395*, 151.

[2] Chopra, N., Lee, J., Zheng, Y., Eom, S.-H., Xue, J., & So, F. (2009). *ACS Appl. Mater. Interfaces*, *1*, 1169.

[3] Lee, S. J., Park, K.-M., Yang, K., & Kang, Y. (2009). *Inorg. Chem.*, *48*, 1030.

[4] Li, J., Djurovich, P. I., Alleyne, B. D., Yousufuddin, M., Ho, N. N., Tomas, J. C., Peters, J. C., Bau, R., & Thompson, M. E. (2005). *Inorg. Chem.*, *44*, 1713.

[5] Chen, L. Q., You, H., Yang, C. L., Ma, D. G., & Qin, J. G. (2007). *Chem. Commun.*, 1352.

[6] Chang, C. J., Yang, C. H., Chen, K., Chi, Y., Shu, C. F., Ho, M. L., Yeh, Y. S., & Chou, P. T. (2007). *Dalton Trans*, 1881.

[7] Orselli, E., Kottas, G. S., Konradsson, A. E., Coppo, P., Fröhlich, R., De Cola, L., van Dijken, A. M., Büchel, M., & Börner, H. (2007). *Inorg. Chem.*, *46*, 11082.

[8] Ahn, S. Y., & Ha, Y. (2009). *Mol. Cryst. Liq. Cryst.*, *504*, 59.

[9] Nonoyama, M. (1975). *J. Organomet. Chem.*, *86*, 263.

[10] Holmes, R. J., D'Andrade, B. W., Forrest, S. R., Ren, X., Li, J., & Thompson, M. E. (2003). *Appl. Phys. Lett.*, *83*, 3818.

[11] Lee, J., Chu, H. Y., Kim, S. H., Do, L. M., Zyung, T., & Hwang, D. H. (2003). *Opt. Mater.*, *21*, 205.

[12] Thomas, K. R. J., Velusamy, M., Lin, J. T., Chien, C., Tao, Y., Wen, Y. S., Hu, Y., & Chou, P. (2005). *Inorg. Chem.*, *44*, 5677.

[13] Zhao, Q., Jiang, C., Shi, M., Li, F., Yi, T., Cao, Y., & Huang, C. (2006). *Organnometallics*, *25*, 3631.