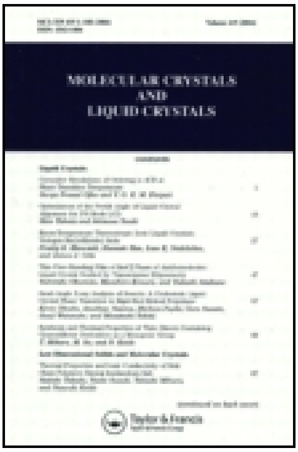

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# Deep Blue Phosphorescence of the Iridium(III) Complexes Containing *N*-Heterocyclic Carbene Ligands

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*Previously, the iridium complexes containing* N*-Heterocyclic carbene (NHC) ligands have caught attention because of their phosphorescence for organic light-emitting diodes (OLEDs). It was reported that the use of strong-field ligands such as carbenes should result in an increase of the blue phosphorescent efficiency of their metal complexes. In this study, the new NHC ligands, 1-(4-fluorophenyl)-3-methyl benzimidazolate (fpmb) and 1-naphthyl-3-methyl benzimidazolate (nmb), were introduced to the iridium complexes to develop phosphorescent dyes for OLED.*

*We investigated photoabsorption and photoluminescence (PL) properties of the iridium complexes and studied their bandgaps with cyclic voltammetry (CV). Deep blue and green phosphorescence was observed with these complexes, and the bandgaps between their highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) were correlated with CV data. We also studied the electroluminescence (EL) properties of the new iridium complexes as possible phosphors for the application to OLED.*

**Keywords** Organic light-emitting diode; Blue phosphorescence; iridium complex; carbene

## Introduction

During the past decade, organic light-emitting diodes (OLEDs) have been extensively studied because of their fundamental physical properties and possibility of application for many kinds of displays [1]. Ir(III) tricyclometallated complexes have caught attention for their phosphorescence performance for OLEDs [2–6]. For the fabrication of full color display, the colors red, green, and blue are required for the complexes, and their emission colors can be tuned by the structures of the ligands in the complexes.

In 2005, Sajoto et al. reported the iridium complexes containing phenylbenzimidazolinato and phenylimidazolinato carbene ligands that exhibit near-UV phosphorescence

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with a relatively high quantum efficiency at room temperature. One of the homoleptic cyclometallated carbene complexes, Ir(pmb)$_3$ where pmb is 1-phenyl-3-methylimidazolin-2-ylidiene, was reported with unique luminescence in the near-UV region (*ca.* 380 nm) at room temperature [1]. Such high phosphorescence is due to the strong ligand-field effect by the carbene ligands. As a result, the nonradiative $d_\pi$–$d_{\sigma^*}$ state is kept largely away from the emissive triplet state, and therefore the complexes were actually used as emissive materials for OLEDs [7,8].

The emission color of the complexes depends on the energy gap between LUMO and HOMO energy levels and the resulting luminescence is mainly determined by their ligands. Previous studies in which the benzimidazole carbene ligands were used in the complexes can help us to predict that benzimidazole ring moiety tunes the LUMO level and the other part of ligand such as a phenyl group affects the HOMO level.

In this study, we synthesize two iridium complexes. One is Ir(fpmb)$_3$ (fpmb = 1-(4-fluorophenyl)-3-methyl benzimidazolate) and the other is Ir(nmb)$_3$ (nmb = 1-naphthyl-3-methyl benzimidazolate). Both fpmb and nmb ligands have a benzimidazole ring which make the LUMO level of complexes almost same. The fpmb ligand has a fluorine-substituted phenyl ring in which F lowers the HOMO levels. Thus, Ir(fpmb)$_3$ can emit blue luminescence. Meanwhile, the nmb ligand that contains naphthalene moiety has extensive $\pi$-conjugation length and its iridium complexes may undergo a bathochromic shift in emission wavelength due to extension of $\pi$-conjugation on the ligands.

## 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).

### *Synthesis of Ligands.*

**1-(4-fluorophenyl)-3-methyl benzimidazolium iodide (fpmb).** The 1-(4-fluorophenyl)-3-methyl benzimidazolium iodide was prepared according to the literature [9] with the corresponding precursor, 4-fluoroiodobenzene and benzimidazole. Yield: 45%

**Naphthyl-3-methyl benzimidazolium iodide (nmb).** This compound was prepared from the reaction of 1-iodonaphthalene and benzimidazole, according to the similar procedure described for 1-(4-fluorophenyl)-3-methyl benzimidazolium iodide (fpmb). Yield: 34%

### *Synthesis of Iridium Complexes.*

**Ir(fmpb)$_3$.** 1-(4-fluorophenyl)-3-methyl benzimidazolium iodide (0.93 g, 2.6 mmol), $IrCl_3 \cdot 3H_2O$ (0.25 g, 0.84 mmol), silver carbonate (0.37 g, 1.3 mmol), sodium carbonate (0.14 g, 1.3 mmol), and ethoxyethanol (40 mL) were heated at reflux for 20 h. After the mixture was cooled to room temperature and diluted with water, and the resultant precipitate was filtered off and washed with water and methanol. The crude product was chromatographed on silica gel column with dichloromethane and purified by recrystallization. Yield: 35%. FAB-MS: calculated 868; found 868. $^1$HNMR (DMSO, 400 MHz) : $\delta$ 8.34–6.05 (m, 21H, aromatic C-H); 3.33 (s, 9H, N-CH$_3$)

**Ir(nmb)$_3$.** This compound was prepared from the reaction of with $IrCl_3nH_2O$ and 1-naphthyl-3-methyl benzimidazolium iododide, according to the similar procedure described for Ir(fpmb)$_3$. Yield: 14%.

## Measurements

UV-visible absorption spectra were obtained from Hewlett Packard 8425A spectrometer. Photoluminescence (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 $CH_2Cl_2$ solution. Cyclic voltammograms were obtained at scan rate of 100 mV/s with Electrochemical Analyzer of CH Instruments. $^1$H NMR spectra were obtained from a 400 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.

## 3. Results and Discussion

The synthesis of the ligands and their iridium complexes was straightforward, but the overall yields were rather low presumably due to instability of the carbene ligands during the reaction. The ligands, 1-(4-fluorophenyl)-3-methyl benzimidazolium iodide and 1-naphthyl-3-methyl benzimidazolium iodide, was prepared from the reaction of benzimidazolium iodide precursor with 4-fluoroiodobenzene and 1-iodonaphthalene, according to the reported procedure [4]. Their iridium complexes were synthesized via one step, according to the procedure reported previously [7]. 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 Ir(fpmb)$_3$ and Ir(nmb)$_3$ have the strong bands appearing in the ultraviolet part of the spectrum between 230 and 280 nm. These bands are assigned to the spin-allowed $^1(\pi \rightarrow \pi^*)$ transitions of the ligands in the complexes. The weak bands from 280 nm extended to 320 nm can be assigned to the spin-allowed metal-ligand charge transfer band ($^1$MLCT). The weaker absorption bands at the longer wavelengths can be attributed to the spin-forbidden $^3$MLCT and spin-orbit coupling enhanced $^3\pi$-$\pi^*$ transition [10]. In the case of Ir(nmb)$_3$, weak absorption beyond 330 nm was also observed due to extended $\pi$-conjugation by naphthalene moiety while Ir(fmpb)$_3$ showed the shoulder peak only around 320 nm.

The photoluminescence (PL) spectra of the Ir complexes in $10^{-5}$ M $CH_2Cl_2$ solution are shown in Figure 3. The PL patterns of the complexes are different: While Ir(fmpb)$_3$ showed a sharp peak in emission, Ir(nmb)$_3$ exhibited a rather wide emission band with a shoulder peak in front. The emission maxima also occur at somewhat different wavelengths. Ir(fmpb)$_3$ and Ir(nmb)$_3$ exhibited the emission maxima at 435 and 530 nm, respectively. Ir(fmpb)$_3$ containing the electron-withdrawing fluorine (F) substituents in the phenyl ring experiences blue-shift in emission, compared to Ir(nmb)$_3$ containing naphthyl substituents. It indicates that the fluorinated phenyl ring contributes to energy gap increase by lowering the HOMO levels with electron-withdrawing substituent. On the other hand, $\pi$-conjugation effect by the naphthyl substituent in the ligand leads its iridium complex to a bathochromic shift in photoemission.

We investigated the electrochemical properties of the Ir complexes by the cyclic voltammetry (CV), which reveal their positions of the HOMO/LUMO [11,12]. 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 0.41–0.48 V relative to an internal

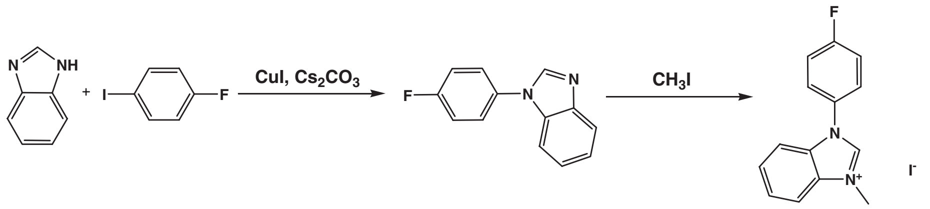
**Table 1.** Physical parameters for the complexes.

| Ir complex | $\lambda_{em}$/nm[a] | $E_{ox}$/V[b] | HOMO/eV[c] | LUMO/eV[d] | $\Delta E$/eV[d] |
|---|---|---|---|---|---|
| Ir(fmpb)$_3$ | 435 | 0.41 | −5.21 | −1.39 | 3.82 |
| Ir(nmb)$_3$ | 530 | 0.48 | −5.28 | −1.83 | 3.45 |

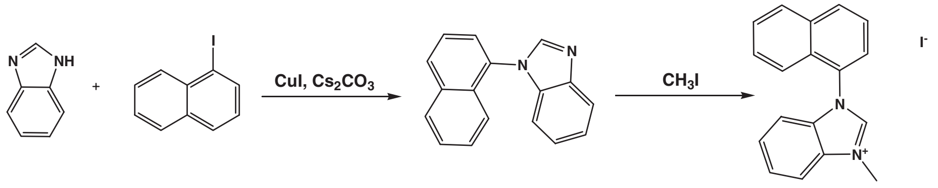
[a]Measured in $CH_2Cl_2$ solution. [b]scan rate: 100 mV/s, Electrolyte: tetrabutylammonium hexafluorophosphate. The potentials are quoted against the internal ferrocene standard. [c]Deduced from the equation HOMO $= -4.8 - E_{ox}$. [d]Calculated from the optical edge $\triangle E =$ LUMO − HOMO.

(a) The ligands, fpmb and nmb

-fpmb



-nmb



(b) The iridium complexes

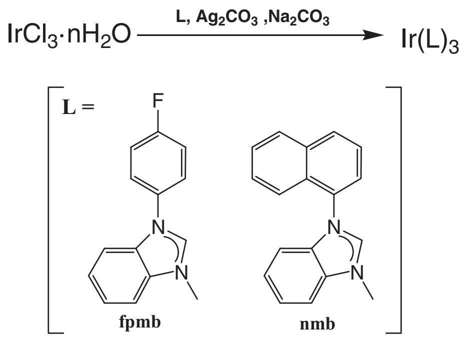


**Figure 1.** The synthesis of ligands and their iridium complexes.

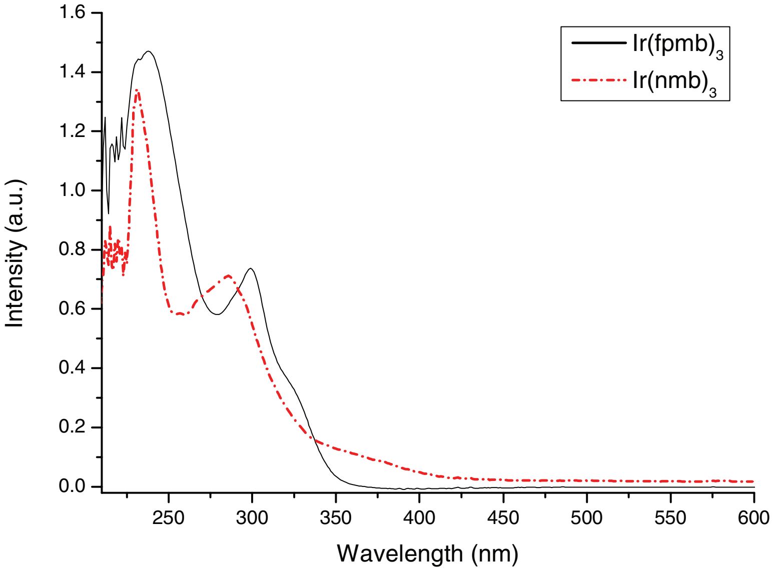


**Figure 2.** UV-Vis absorption spectra of Ir(fmpb)$_3$ and Ir(nmb)$_3$ in a $10^{-5}$ M $CH_2Cl_2$ solution.

ferrocenium/ferrocene reference ($Fc^+/Fc$). The reduction potentials of the complexes in this study were calculated to be between −1.39 and −1.83 eV, according to optical-edge estimation with their photoabsorption spectra. Using the equation $HOMO = -4.8 - E_{ox}$, the HOMO of Ir(fpmb)$_3$ was calculated to be −5.21 eV, that gives the larger energy gap ($\Delta E$) of 3.82 eV.

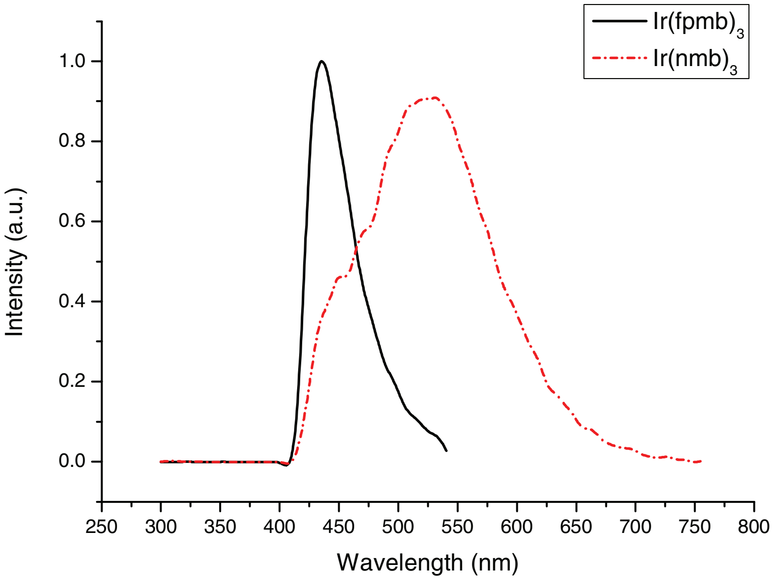


**Figure 3.** PL spectra of Ir(fmpb)$_3$ and Ir(nmb)$_3$ in a $10^{-5}$ M $CH_2Cl_2$ solution.

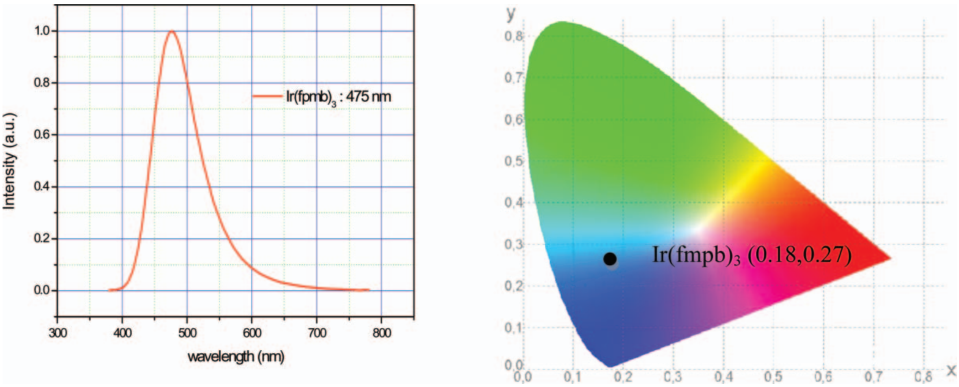


**Figure 4.** (a) EL spectra and (b) CIE coordinates of Ir(fmpb)$_3$.

The electroluminescent (EL) device containing Ir(fpmb)$_3$ as a phosphorescent dopant was fabricated and its performances were investigated. The EL spectra of Ir(fpmb)$_3$ showed the emission peak at 475 nm with the CIE coordinates of (0.18, 0.27), as shown in Figure 4. The patterns of its EL spectra were mostly consistent with the PL results, indicating that emission was originated from the iridium complex in the emitting layer. However, the EL maxima of 475 nm was red-shifted, compared with the PL maxima of 435 nm and we attribute this shift to involvement of solvent $CH_2Cl_2$ in the measurement of solution PL spectra.

## Conclusions

The iridium complexes chelated with *N*-Heterocyclic carbene (NHC) ligands were synthesized and their luminescence properties were investigated. Ir(fmpb)$_3$ and Ir(nmb)$_3$ prepared in this study exhibited the blue and green emission at 435 and 530 nm, respectively. We expected that Ir(fpmb)$_3$ might exhibit blue luminescence since the fpmb ligand has a fluorine-substituted phenyl ring in which F lowers the HOMO levels, leading to the large band-gap of its iridium complex. As a result, Ir(fpmb)$_3$ showed deep blue emission at 435 nm in PL spectra and CIE coordinates of (0.18, 0.27) in EL. On the other hand, Ir(nmb)$_3$ showed a red shift on photoemission due to $\pi$-conjugation effect of the ligand in the complex.

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