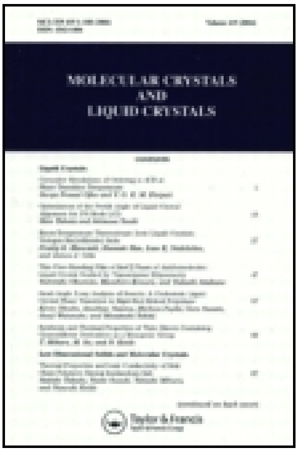

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Luminescence Comparison of Homoleptic and Heteroleptic 6-membered Iridium(III) Complexes

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The new iridium complexes, heteroleptic Ir(4-Me-2,3-dpq)$_2$(LX) (4-Me-2,3-dpq = 4-methyl-2,3-diphenylquinolinato ligand; LX = 2-(2-hydroxyphenyl)benzoxazolate (BOX) and 2-(2-hydroxyphenyl)benzothiazolate (BTZ)) and homoleptic Ir(LX)$_3$, were synthesized and their luminescence properties were investigated. The lithium salts of the ligands, BOX and BTZ, were previously applied to OLED as the blue fluoresecent dyes. These ligands can form 6-membered metallacycles with the metal center. Herein, BOX and BTZ were introduced as ligands to the iridium complexes for possible application to phosphorescent OLEDs.

According to the previously reported literature, the ancillary ligand could have a profound effect on the emitting color of its complexes depending on the relative orbital energy levels of the main ligands (C^N) and the ancillary ligand(LX). For the heteroleptic iridium complexes, 4-Me-2,3-dpq which could form a 5-membered metallacycle with the iridium center was introduced as a main ligand. We compared the luminescence and stability of the homoleptic and heteroleptic iridium complexes with respect to their structures. We investigated photoabsorption and photoluminescence properties of the iridium complexes and studied their band gaps with cyclic voltammetry. The emitting colors and the luminous efficiencies of the complexes were compared to find the involvement effect of the five- and six-membered rings in the complexes.

Keywords Organic light-emitting diode; Phosphorescence; Iridium complex; 6-membered metallacycle; Benzoxazolate ligand.

Introduction

Much attention has been paid to the phosphorescent materials for their potential application as highly efficient electroluminescent (EL) emitters in organic light emitting devices (OLEDs) [1–3]. Most of the investigations of phosphorescent materials have been focused on the heavy mental complexes [4–7]. Because the heavy metal complexes lead to strong spin-orbit coulping and singlet-triplet state mixing, high efficient electrophosphrescence can be produced in OLEDs [8].

Particularly, among many types of metal complexes, the iridium complexes have showed effective emitting colors and high bright phosphorescence at room temperature due to their relative short triplet lifetime and high quantum efficiency [9]. During the last two decades, cyclometalated Ir(III) complexes, because of their interesting photophysical

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*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 properties, have been actively studied for the material of the promising flat panel display [10–13]. OLEDs prepared with phosphors of the iridium complexes have the highest efficiency to date, giving internal quantum efficiencies approaching 100% [9,14]. Many reports showed that it is possible to tuning emitting colors by the introduction of various ligands to the iridium complexes [1,9]. Thus, we have designed and synthesized a variety of new Ir complexes, which are highly desirable to obtain the full color EL devices and to improve properties of the devices [15].

In this paper, we synthesized new homoleptic iridium complexes, Ir(BOX)$_3$ and Ir(BTZ)$_3$, and heteroleptic complexes, Ir(4-Me-2,3-dpq)$_2$(BOX) and Ir(4-Me-2,3-dpq)$_2$(BTZ). Through a comparison of the homoleptic and heteroleptic iridium complexes, we wanted to find how the different ligands have influence on the luminescence properties of the iridium complexes. We investigated the photoabsorption properties of the complexes with their UV-Vis spectra and studied the electrochemical characteristics with their cyclic voltammetric diagrams. The emitting colors of the complexes, Ir(BOX)$_{3,}$ Ir(BTZ)$_{3,}$ Ir(4-Me-2,3-dpq)$_2$(BOX) and Ir(4-Me-2,3-dpq)$_2$(BTZ), were compared to find the involvement effect of the different ancillary ligands, BOX and BTZ, to the complexes. The possible luminescence mechanism by ILET in the heteroleptic complexes was discussed.

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. Mass spectra were determined on JEOL, JMS-AX505WA, HP 5890 Series II Hewlett-Packard 5890A at Seoul National University. ^{1}H NMR was taken with a 400 MHz NMR spectrometer at Sogang University in Korea.

Synthesis of Ligands and Iridium Complexes.

4-Me-2,3-dpq. 4-Methyl-2,3-diphenylquinoline was obtained from condensation reaction with 2-phenyl-acetophenone (1.96 g, 10.0 mmol) and 2-aminoacetophenone (2.46 g, 10.0 mmol) [16]. Yield: 72%

Ir(4-Me-2,3-dpq)$_2$(LX). [LX = BOX, BTZ] First, the cyclometallated iridium μ-chloro-bridged dimer, (4-Me-2,3-dpq)$_2$Ir(μ-Cl)$_2$Ir(4-Me-2,3-dpq)$_2$, was prepared according to the method reported by Nonoyama with slight modification [17]. Second, the resulting dimer and an excess of the ancillary ligands were mixed with Na$_2$CO$_3$ (500 mg) in 2-ethoxyethanol (30 mL). The mixture was refluxed for 2 h. The solution was cooled to room temperature and filtered. The obtained product was chromatographed on silica gel column with dichloromethane and purified by recrystallization.

The characterization results of the new heteroleptic iridium complexes are as follows:

[Ir(4-Me-2,3-dpq)$_2$(BOX)]: A red powder (Yield: 69%). FAB-MS: calculated 992; found 993. ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.46 (d, 1H) 7.88–7.17 (m, 20H) 6.95–6.08 (m, 13H) 2.52 (s, 3H) 2.33 (s, 3H)

[Ir(4-Me-2,3-dpq)$_2$(BTZ)]: A dark red powder (Yield: 73%). FAB-MS: calculated 1008; found 1009. ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.47 (d, 1H) 7.88–7.17 (m, 20H) 6.96–6.08 (m, 13H) 2.53 (s, 3H) 2.33 (s, 3H)

Ir(LX)$_3$. [LX = BOX, BTZ] The homoleptic complexes were prepared from the reaction of Ir(acac)$_3$ and an excess of LX by a reported procedure [18]. Ir(acac)$_3$ (1.22 g, 2.5 mmol) and LX (10 mmol) were dissolved in 50 ml of ethylene glycol and the mixture was refluxed for 24 h. 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.

The characterization results of the new homoleptic iridium complexes are as follows:

[Ir(BOX)$_3$]: A bluish green powder (Yield: 61%). FAB-MS: calculated 823; found 611(M-BOX). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, 3H) 7.86 (t, 6H) 7.53 (t, 3H) 7.46 (m, 6H) 7.14 (d, 3H) 7.09 (m, 3H)

[Ir(BTZ)$_3$]: A white powder (Yield: 53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (t, 6H) 8.06 (d, 3H) 7.54 (t, 3H) 7.43 (m, 6H) 7.06 (d, 3H) 7.02 (t, 3H)

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 100mV/s, and tetrabutylammonium hexafluorophosphate was added as an electrolyte in CH_2Cl_2 solution.

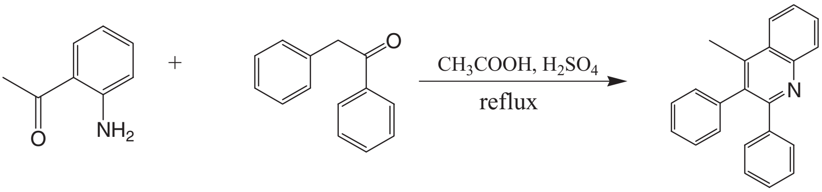
Results and Discussion

The main and ancillary ligands in the iridium complexes are known to give a major effect on determination of the emission characteristics through the MLCT. The resulting emission color and luminous efficiency of the iridium complexes could be tuned by both the main and the ancillary ligands. Herein, the homoleptic and heteroleptic complexes Ir(BOX)$_3$, Ir(BTZ)$_3$, Ir(4-Me-2,3-dpq)$_2$(BOX) and Ir(4-Me-2,3-dpq)$_2$(BTZ) were prepared, and their luminescence properties were investigated.

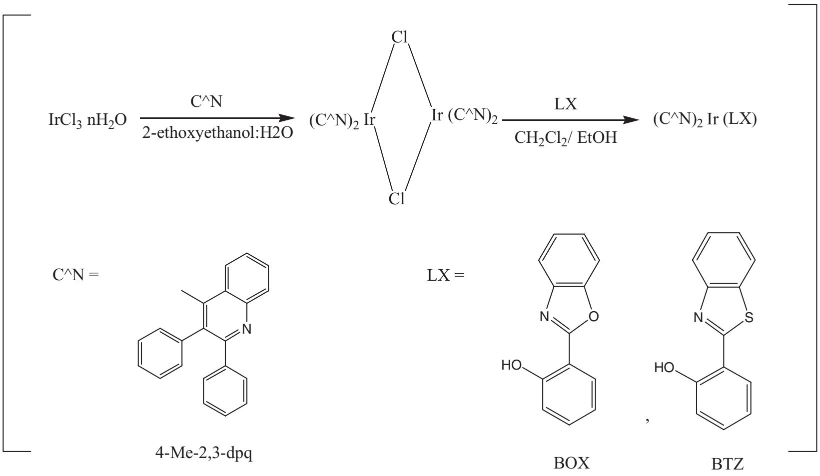
The main ligand, 4-Me-2,3-dpq, was synthesized according to the modified Suzuki coupling method [16]. The heteroleptic iridium complexes were synthesized as reported by Nonoyama reaction [17]. The homoleptic iridium complexes, Ir(LX)$_3$, (LX = BOX, BTZ) were prepared from the one-pot reaction of the main ligand with Ir(acac)$_3$. The overall synthetic schemes are illustrated in Fig. 1.

The UV-Vis absorption spectra of the complexes in CH_2Cl_2 are shown in Fig. 2. The absorption spectra of the heteroleptic complexes have intense bands appearing in the ultraviolet region between 220 and 285 nm. These bands have been assigned to the spin-allowed $^1\pi$ - π^* transitions of the ligands. The $^1\pi$ - π^* bands are accompanied by weaker and lower energy features extending from 330 to 465 nm that 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 cyclometallating ligand [19]. The absorption peaks of the homoleptic complexes around 300~365 nm were assigned to a spin-allowed metal charge transfer (^{1}MLCT) band, and the weaker absorption bands at the longer wavelengths can be attributed to the spin-forbidden ^{3}MLCT and spin-orbit coupling enhanced $^3\pi$ - π^* transition. The absorption patterns of Ir(4-Me-2,3-dpq)$_2$(BOX) and Ir(4-Me-2,3-dpq)$_2$(BTZ) are similar with absorption maxima at 270/356/433 and 273/390/485 nm, respectively, while the homoleptic iridium complexes showed absorption at the shorter wavelengths in the UV-Vis spectra. The stronger MLCT bands of the heteroleptic Ir complexes compared to those of the homoleptic ones could lead to better emission efficiency.

(1) the main ligand, 4-Me-2,3dpq



(2) the heteroleptic iridium complexes



(3) the homoleptic iridium complexes

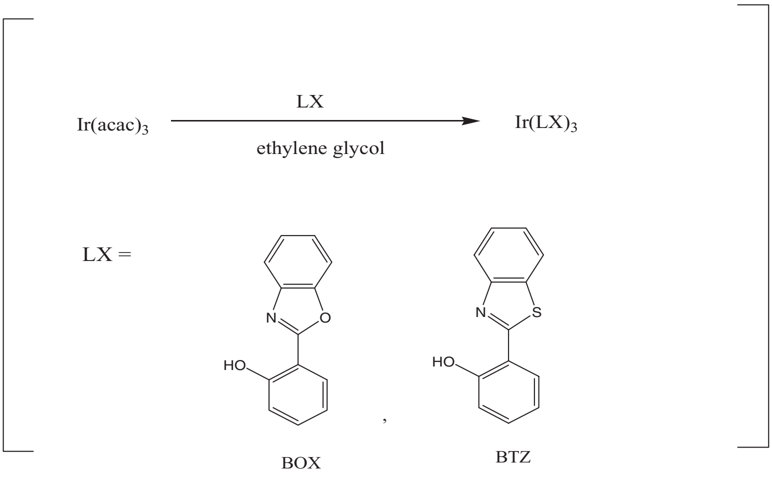


Figure 1. The synthesis of main ligands and their iridium complexes.

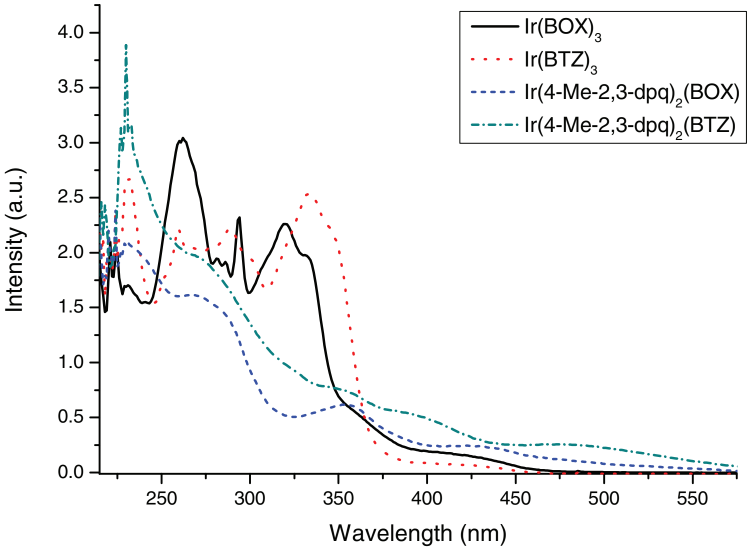


Figure 2. UV-Vis absorption spectra of the homoleptic and heteroleptic iridium complexes in a 10^{-5} M CH_2Cl_2 solution.

The photoluminescence (PL) spectra of the Ir complexes in 10^{-5} M CH_2Cl_2 solution are shown in Fig. 3. $Ir(BOX)_3$, $Ir(BTZ)_3$, $Ir(4\text{-Me-}2,3\text{-dpq})_2(BOX)$ and $Ir(4\text{-Me-}2,3\text{-dpq})_2(BTZ)$ exhibited the emission maxima at 491, 519, 618 and 656 nm, respectively. The homoleptic $Ir(BOX)_3$ showed the emission band at the shortest wavelength. The emission maxima of both homoleptic and heteroleptic complexes were substantially shifted to the

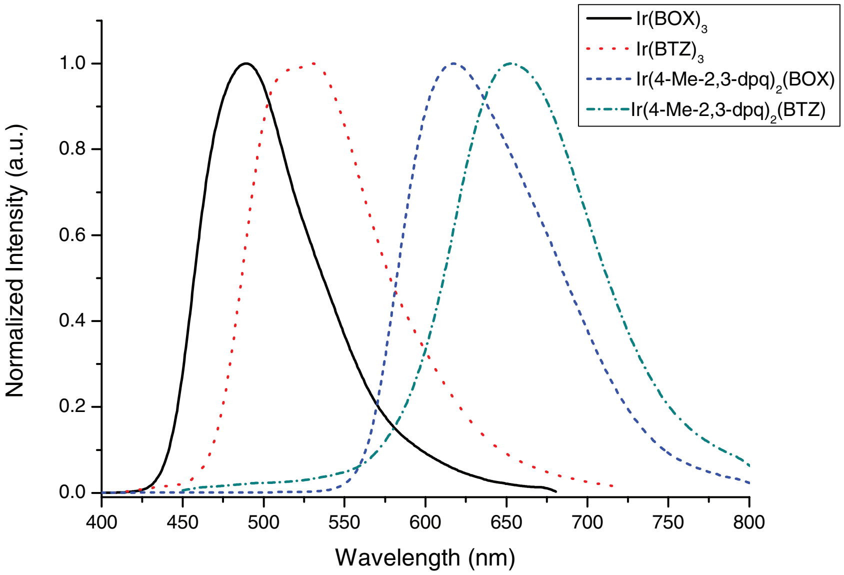


Figure 3. PL spectra of the homoleptic and heteroleptic iridium complexes in a 10^{-5} M CH_2Cl_2 solution.

Table 1. Physical parameters for the iridium complexes.

Ir complex	λ_{em}/nm[a]	E_{ox}/V[b]	HOMO/eV[c]	LUMO/eV[d]	ΔE/eV[d]
$Ir(BOX)_3$	491	0.67	−5.47	−2.33	3.14
$Ir(BTZ)_3$	519	0.17	−4.97	−1.94	3.03
$Ir(4\text{-}Me\text{-}2,3\text{-}dpq)_2(BOX)$	617.5	0.35	−5.15	−2.46	2.69
$Ir(4\text{-}Me\text{-}2,3\text{-}dpq)_2(BTZ)$	656	0.29	−5.09	−2.54	2.55

[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.

longer wavelength upon the change of the ligands from BOX to BTZ. Therefore, it could be inferred that the new ancillary ligands, BOX and BTZ, had a significant effect on the lowest excited state of its iridium complexes and thus their emitting color.

We also investigated the electrochemical properties of the iridium complexes by the cyclic voltammetry (CV), which reveal their positions of the HOMO/LUMO [20,21]. Detailed CV data were summarized in Table 1. The oxidation potentials which indicate the HOMOs of the complexes were irreversible in the range of 0.17−0.67 V relative to an internal ferrocenium/ferrocene reference (Fc^+/Fc). The reduction curves of all complexes were not clearly observed up to −2.2 V. Therefore, the LUMOs of the complexes were calculated from their respective absorption spectra, using the optical edge and band gap equation ($\Delta E = E_{ox} - E_{red}$). Their estimated reduction potentials were −2.33, −1.94, −2.17, −2.46 and −2.56 eV for $Ir(BOX)_3$, $Ir(BTZ)_3$, $Ir(4\text{-}Me\text{-}2,3\text{-}dpq)_2(BOX)$ and $Ir(4\text{-}Me\text{-}2,3\text{-}dpq)_2(BTZ)$, respectively. $Ir(BOX)_3$ has the largest energy gap (ΔE) of 3.14 eV, which consists with the emission spectra having the shortest emission wavelength in PL. The further detailed CV data were summarized in Table. I. The resulting ΔEs ($E_{ox} - E_{red}$) of the complexes were well correlated with their HOMO and LUMO data.

We expected that the heteroleptic iridium complexes could have the possibility of inter-ligand energy transfer (ILET) in the process of luminescence. In the complexes containing 4-Me-2,3-dpq as a main ligand, most of emission peaks were shown at about 600nm [15]. Meanwhile, the heteroleptic iridium complexes prepared herein appeared at 618 and 656 nm, which were significantly red-shifted. Thus, the ancillary ligands, BOX and BTZ, did seem to be involved in the luminescent process through ILET mechanism with the main ligand, 4-Me-2,3-dpq, in the complexes. Especially, $Ir(4\text{-}Me\text{-}2,3\text{-}dpq)_2(BTZ)$ showed the most red-shifted emission by extensive ILET, leading to deep-red phosphorescence.

Conclusions

We reported the detailed synthesis and photophysical properties of the phosphorescent iridium complexes bearing 2-(2-hydroxyphenyl)benzoxazolate (BOX) or 2-(2-hydroxyphenyl)benzothiazolate (BTZ) as the main and ancillary ligands. The homoleptic and heteroleptic iridium complexes were prepared and their photophysical properties were investigated. $Ir(BOX)_3$, $Ir(BTZ)_3$, $Ir(4\text{-}Me\text{-}2,3\text{-}dpq)_2(BOX)$ and $Ir(4\text{-}Me\text{-}2,3\text{-}dpq)_2(BTZ)$, synthesized in this study exhibited the emission peaks at 491, 519, 618 and 656 nm respectively. $Ir(BOX)_3$ which has 6-membered metallacycles showed the most blue shift in photoemission. The homoleptic iridium complexes, $Ir(BOX)_3$ and $Ir(BTZ)_3$ exhibited the blueish green emission at 491 and 519 nm, compared to the heteroleptic iridium complexes which showed the red luminescence. In the case of heteroleptic complexes, Ir(4-Me-2,3-dpq)$_2$(BOX) showed the emission at the shorter wavelength and had the larger energy gap than Ir(4-Me-2,3-dpq)$_2$(BTZ). Considering that the iridium complexes of the main ligand, 4-Me-2,3 dpq, usually had emission peaks around 600 nm, the heteroleptic complexes in this study seemed to undergo ILET, leading to a red-shift in emission. Especially, Ir(4-Me-2,3-dpq)$_2$(BTZ) showed the deep red phosphorescence presumably due to extensive ILET.

Acknowledgment

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