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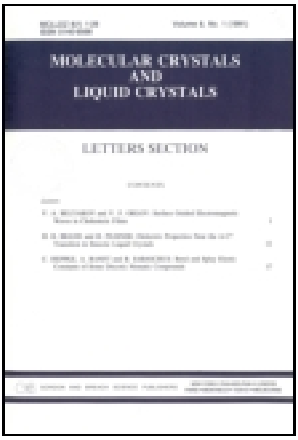

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Homoleptic vs. Heteroleptic Orange Light-Emitting Iridium Complexes Chelated with Benzothiazole Derivatives

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Homoleptic vs. Heteroleptic Orange Light-Emitting Iridium Complexes Chelated with Benzothiazole Derivatives

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The homoleptic and heteroleptic iridium(III) complexes exhibiting orange phosphorescence were investigated to compare their emission colors, luminance efficiency, and stability. The homoleptic iridium complexes, Ir(pbt-R)$_3$, were prepared from the reaction of the iridium(III) precursor and phenylbenzothiazole derivatives. The heteroleptic ones containing the anions of 4-methyl-2,3-diphenylquinoline (4-Me-dpq) and 2-phenylbenzothiazole (pbt) as ligands, Ir(pbt-OMe)$_2$(4-Me-2,3-dpq) and Ir(4-Me-2,3-dpq)$_2$(pbt-OMe), were synthesized via the chloro-bridged iridium dimer. We investigated photoabsorption and photoluminescence (PL) properties of the iridium complexes and studied their bandgaps with cyclic voltammetry (CV). Orange phosphorescence with the PL maxima of 530–620 nm 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. The electro-luminescence (EL) study of these complexes was not possible due to lack of sublimability. The light-emitting mechanisms regarding the phosphorescence colors were discussed.

Keywords Heteroleptic iridium complexes; homoleptic iridium complexes; phenylbenzothiazole derivatives; phosphorescence; orange emission

Introduction

For the past decade, organic light-emitting diodes (OLEDs) based on phosphorescence materials have drawn great interest due to their applications in low cost, more efficient flat-panel displays and solid-state lighting [1–2]. In particular, cyclometalated iridium complexes, which have relatively short excited-state lifetime, high phosphorescence efficiency and flexible color tunability, are regarded as the most promising phosphors in organic light-emitting devices [3–5]. Recently, the orange light-emitting iridium complexes beside the three primary color emitting materials have drawing attention since they can be used in combination with blue emitters to fabricate two-component white OLEDs, which has definitely become one of the most important directions of OLED studies [6–8].

Herein, our interest is to design and synthesis orange phosphorescent iridium complexes having high luminescence yields and excellent device performance for white OLED applications. For such purpose, we introduced 2-phenylbenzothiazole (pbt) derivatives as

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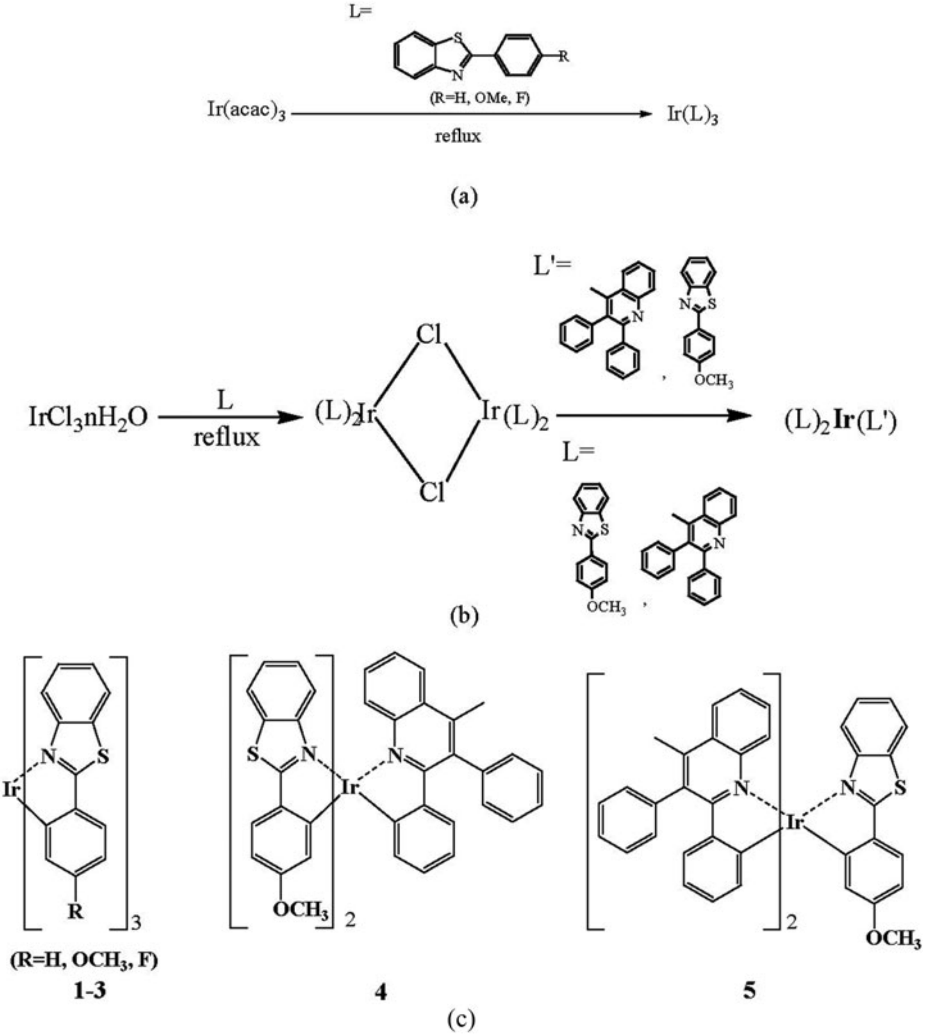

Scheme 1.

main ligands in the iridium complexes. The *para*-position of the phenyl moiety in the ligands in the complexes was substituted with the functional groups having different electronegativities. Thus, we synthesized the homoleptic iridium complexes of pbt-R (R = H, OMe, F), **1–3** (Scheme 1) and also prepared the heteroleptic complexes, **4-5**, with the anions of pbt-OMe and 4-methyl-2,3-diphenylquinoline (4-Me-dpq) as the ligands. The photophysical and electrochemical properties of the homoleptic and heteropleptic iridium complexes were investigated and compared.

Experimental

Synthesis of Ligands

2-(4-fluorophenyl)benzothiazole (pbt-F). 2-(4-fluorophenyl)-benzothiazole were synthesized according to the literature method [9]. Yield: 76 %

4-Methyl-2,3-diphenylquinoline (4-Me-2,3-dpq). 4-methyl-2,3-diphenylquinoline was obtained according to Friedlander reaction with the corresponding precursors, 2-aminoacetophenone (1.35 g, 10.0 mmol) and deoxybenzoin (1.96 g, 10.0 mmol)] [10–11]. Yield: 75 %

Synthesis of Iridium Complexes

Ir(pbt-R)$_3$(R=H, OMe, F). (1–3). Each complex was prepared from the reaction of Ir(acac)$_3$ with the respective pbt-R ligand according to the reported procedure [12]. Ir(acac)$_3$ (1.22 g, 2.5 mmol) and pbt-R (2.07 g, 10 mmol) were dissolved in 50 ml of ethylene glycol and the mixture was refluxed for 24 hr. After cooling, 1N HCl solution was added and the resulting precipitate was filtered off. The residue was purified by silica gel chromatography by using CH_2Cl_2.

Ir(pbt)$_3$: An orange powder (Yield: 49 %). ^{1}H NMR (400MHz, DMSO): δ 8.17–7.45 (m, 24H, aromatic C—H).

Ir(pbt-OMe)$_3$: An orange powder (Yield: 49 %). ^{1}H NMR (400MHz, DMSO): δ 8.12–6.51 (m, 24H, aromatic C—H) 3.51 (s, 6H).

Ir(pbt-F)$_3$: An orange powder (Yield: 49 %). ^{1}H NMR (400MHz, DMSO): δ 8.26–6.04 (m, 21H, aromatic C—H).

Ir(pbt-OMe)$_2$(4-Me-2,3-dpq). (4). The cyclometalated Ir(III) μ-chloro-bridged dimer, (4-Me-2,3-dpq)$_2$Ir(μ-Cl)$_2$Ir(4-Me-2,3-dpq)$_2$ (1.9 mmol), was first prepared according to the Nonoyama method. [13] In the second step, the resulting dimer and 4-Me-2,3-dpq ligands (6.5 mmol) were mixed with Na_2CO_3 (500 mg) in 2-ethoxyethanol (30 mL). The mixture was refluxed for 2 h and the red solid was filtered after cooling. Ir(4-Me-2,3-dpq)$_2$(pbt-OMe) were purified by chromatography on silica gel column with dichloromethane and recrystallization. An orange powder was obtained. (Yield: 49 %) FAB-MS: calculated 967; found 673 (M$^+$-4-Me-2,3-dpq). ^{1}H NMR (400MHz, DMSO): δ 8.35–6.20 (m, 27H, aromatic C-H) 3.52 (s, 6H) 2.50 (s, 3H).

Ir(4-Me-2,3-dpq)$_2$(pbt-OMe). (5). The complexes were prepared from the reaction of 4-Me-2,3-dpq with $IrCl_3\cdot H_2O$ and then treated with the pbt-OMe (2-phenylbeonzothiazole derivative), similar to the procedure described above. A red powder was obtained. (Yield 65 %) FAB-MS: calculated 1021; found 781(M$^+$-pbt-OMe). ^{1}H NMR(DMSO) (δ, ppm): 8.35∼6.00 (m, aromatic C-H, 33H); 3.48 (s, 3H); 2.50 (s, 6H).

Measurements

UV-Vis absorption spectra were measured on a Hewlett Packard 8425A spectrometer. PL spectra were measured on an Aminco-Bowman Series 2 luminescence. The UV-Vis and PL spectra of the iridium complexes were measured in 10^{-4} M dilute CH_2Cl_2 solution. Cyclic voltammograms were obtained at scan rate of 100 mV/s with Electrochemical Analyzer of CH Instruments, and tetrabutylammonium hexafluorophosphate was added as an electrolyte in CH_2Cl_2 solution.

Results and Discussion

The synthesis of the ligands, F-pbt and 4-Me-2,3-dpq, was straightforward, according to the procedures reported previously [9–11]. The other ligands were purchased and used

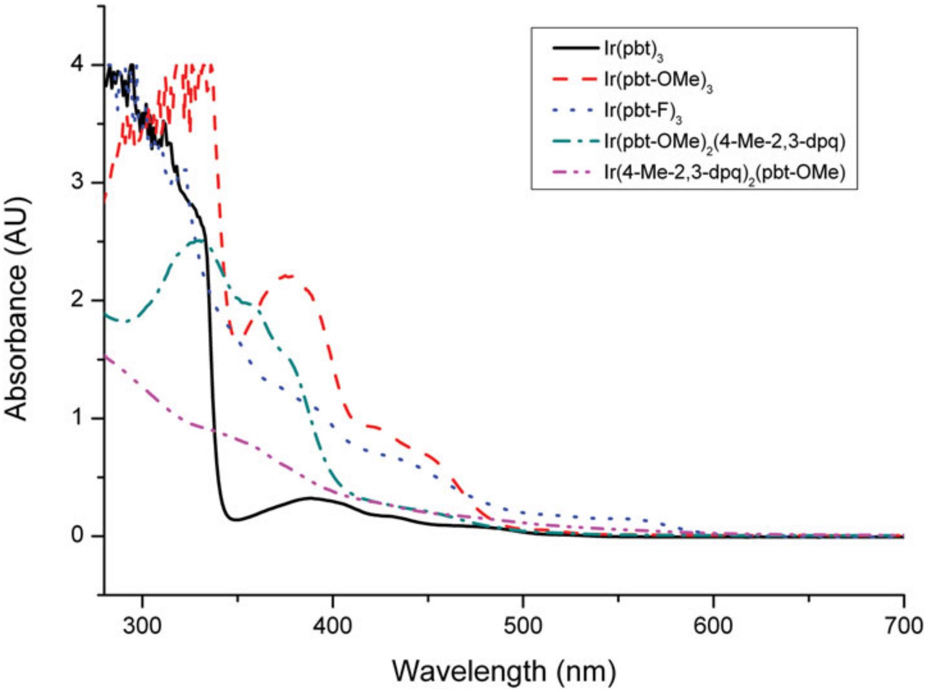

Figure 1. UV-Vis absorption spectra of iridium complexes in a 10^{-4} M CH_2Cl_2 solution.

directly. The homoleptic iridium complexes, Ir(pbt-R)$_3$, were prepared from the one-pot reaction of the corresponding main ligand with Ir(acac)$_3$ [12]. The heteroleptic iridium complexes were synthesized via two steps, as reported by Nonoyama [13]. The overall synthetic schemes are illustrated in Scheme 1.

The UV-Vis absorption spectra of the complexes in CH_2Cl_2 are shown in Fig. 1. The absorption spectra of iridium complexes have strong absorption bands appearing at the ultraviolet region of the spectrum between 280 and 330 nm. These bands were assigned to the spin-allowed $^1\pi \rightarrow \pi^*$ transitions of the ligands. The $^1\pi$-π^* bands are accompanied by weaker and lower energy features extending into the visible region from 350 to 500 nm. These absorption are 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 intensities of the MLCT and $^3\pi$-π^* transition bands are varied, depending on the chelating ligands. These intensities are generally attributed to mixing of the charge-transfer transitions with high lying spin-allowed transitions on the chelating ligand [14].

The PL spectra of the Ir complexes in CH_2Cl_2 solution are shown in Fig. 2. The homoleptic complexes, Ir(pbt)$_3$, Ir(pbt-OMe)$_3$ and Ir(pbt-F)$_3$, showed the PL peaks at 550, 534, and 528 nm, respectively. Ir(pbt-OMe)$_2$(4-Me-2,3-dpq) and Ir(4-Me-2,3-dpq)$_2$(pbt-OMe) exhibited the emission maxima at 554 and 627 nm, respectively. Unexpectedly, the PL spectra of the homoleptic iridium complexes were not influenced by the substituent characteristics of the chelating ligands since both electron-withdrawing F and electron-donating OMe substituents led the emission of their complexes to shorter wavelengths than those of the unsubstitued Ir(pbt-H)$_3$. On the other hand, the heteroleptic iridium complexes have drastic contrasts, depending on the species and number of the chelating

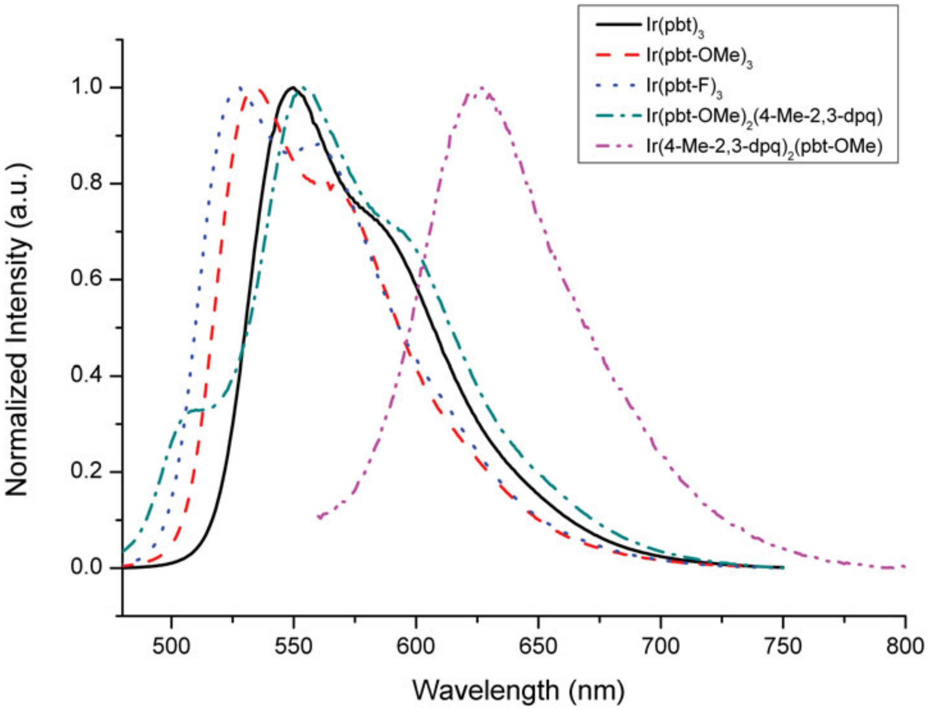

Figure 2. PL spectra of the iridium complexes in a 10^{-4} M CH_2Cl_2 solution.

ligands. The anion of 4-Me-2,3-dpq was reported to lead its iridium complexes to red phosphorescence around 600 nm [11]. Ir(4-Me-2,3-dpq)$_2$(pbt-OMe) which contains two 4-Me-2,3-dpq ligands showed a bathochromic shift, resulting in the emission at 627 nm, while Ir(pbt-OMe)$_2$(4-Me-2,3-dpq) which has only one 4-Me-2,3-dpq ligand exhibited the PL maxima at 554 nm near those of the homoleptic complexes. We attribute the red-shifted emission by Ir(4-Me-2,3-dpq)$_2$(pbt-OMe) to inter-ligand energy transfer (ILET) from pbt-OMe ligand to 4-Me-2,3-dpq ligands. The energy which the pbt-OMe ligand absorbs might be transferred and contributed to the emission by 4-Me-2,3-dpq ligands which have a smaller energy gap, resulting in a bathochromic shift in PL of their complex. ILET has been reported to occur between the ligands of the large and small energy gaps, according to the literatures recently published [3, 15].

We investigated the electrochemical properties of the Ir complexes by the cyclic voltammetry (CV) as shown in Table 1, which reveal their positions of the HOMO/LUMO [16–17]. The oxidation potentials which indicate the HOMOs of Ir(pbt)$_3$, Ir(pbt-OMe)$_3$, Ir(pbt-F)$_3$, Ir(pbt-OMe)$_2$(4-Me-2,3-dpq) and Ir(4-Me-2,3-dpq)$_2$(pbt-OMe) were reversible at 0.50–0.75 V relative to an internal ferrocenium/ferrocene reference (Fc^+/Fc), respectively. The LUMOs of the complexes were not observed within the electrochemical windows of the solvents and thus estimated from their respective absorption spectra. They were calculated to be between −0.76 and −2.37 eV, according to optical-edge estimation [17]. The resulting ΔEs ($E_{ox} - E_{red}$) of the complexes were well correlated with their tendencies of PL maxima.

The electroluminescence (EL) of these complexes prepared in this study was attempted, but the vacuum sublimation of the complexes to fabricate the light-emitting device was not

Table 1. Physical parameters for the complexes

Ir complex	λ_{em} /nm[a]	E_{ox} /V[b]	HOMO /eV[c]	LUMO / eV[d]	ΔE /eV[d]
$Ir(pbt)_3$	550	0.50	−4.30	−1.11	3.19
$Ir(pbt\text{-}OMe)_3$	534	0.52	−4.28	−1.01	3.27
$Ir(pbt\text{-}F)_3$	528	0.74	−4.06	−0.76	3.30
$Ir(pbt\text{-}OMe)_2(4\text{-}Me\text{-}2,3\text{-}dpq)$	554	0.75	−5.55	−2.37	3.18
$Ir(4\text{-}Me\text{-}2,3\text{-}dpq)_2(pbt\text{-}OMe)$	627	0.60	−4.20	−1.26	2.94

[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.

successful so far. We now try to fabricate devices of these orange phosphorescent complexes by the solution process to investigate the EL performance of the complexes.

Conclusions

We have synthesized and characterized the homoleptic and heteroleptic iridium complexes chelated with the anions of phenylbenzothiazoles having the substituents of different electronegativities. Surprisingly, the substituent, R, was found to have little influence on photoluminescence of the orange phosphorescent homoleptic complexes, $Ir(pbt\text{-}R)_3$. On the other hand, the heteroleptic iridium complexes, $Ir(OMe\text{-}pbt)_2(4\text{-}Me\text{-}2,3\text{-}dpq)$ and $Ir(4\text{-}Me\text{-}2,3\text{-}dpq)_2(OMe\text{-}pbt)$, exhibited quite contrasting luminescence properties. While $Ir(OMe\text{-}pbt)_2(4\text{-}Me\text{-}2,3\text{-}dpq)$ showed the emission maxima at 554 nm, similar to the homoleptic ones, $Ir(4\text{-}Me\text{-}2,3\text{-}dpq)_2(OMe\text{-}pbt)$ which contain two red-emitting 4-Me-2,3-dpq ligands underwent ILET to display red phosphorescence at 627 nm. The electrochemical measurement of these complexes supported their luminescence characteristics. The orange light-emitting iridium complexes developed in this study are now under investigation as candidates for the possible application to orange phosphors for white OLEDs.

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