Blue Emitting Cationic Iridium Complexes Containing Two Substituted 2-Phenylpyridine and One 2,2'-Biimidazole for Solution-Processed Organic Light-Emitting Diodes (OLEDs)

Seong-Jae Yun,[†] Hoe-Joo Seo, Myungkwan Song,[†] Sung-Ho Jin,[†] and Young Inn Kim^{†,*}

Department of Chemistry, Pusan National University, Pusan 609-735, Korea [†]Department of Chemistry Education and Interdisciplinary Program of Advanced Information and Display Materials, Pusan National University, Pusan 609-735, Korea. ^{*}E-mail: yikim@pusan.ac.kr Received July 27, 2012, Accepted August 9, 2012

Two new blue emitting cationic iridium(III) complexes with two substituted 2-phenlypyridine ligands as main ligands and one 2,2'-biimidazole as an ancillary ligand, $[(L1)_2Ir(biim)]Cl(1)$ and $[(L2)_2Ir(biim)]Cl(2)$, where L1 = 2-(2',4'-difluorophenyl)-4-methylpyridine, L2 = 2-(2',4'-difluoro-3'-trifluoromethylphenyl)-4-methylpyridine and biim = 2,2'-biimidazole, were synthesized for applications in phosphorescent organic light-emitting diodes (PhOLEDs). Their photophysical, electrochemical and electroluminescent (EL) device performances were examined. The photoluminescent (PL) spectra revealed blue phosphorescence in the 450 to 485 nm range with a quantum yield of more than 10%. The iridium(III) compounds studied showed good solubility in organic solvents with no solvatochromism dependent on the solvent polarity. The solution-processed OLEDs were prepared with the configuration, ITO/PEDOT:PSS (40 nm)/mCP:Ir(III) (70 nm)/OXD-7 (20 nm)/LiF (1 nm)/Al (100 nm), by spin coating the emitting layer containing the mCP host doped with the iridium phosphors. The best performance of the fabricated OLEDs based on compound 1 showed an external quantum efficiency of 4.5%, luminance efficiency of 8.52 cd A⁻¹ and blue emission with the CIE coordinates (x,y) of (0.16, 0.33).

Key Words : Cationic iridium compound, Solution-processed, OLEDs, Blue phosphorescence

Introduction

Phosphorescent cyclometalated iridium(III) complexes have attracting increasing attention due to their applications in organic light-emitting diodes (OLEDs),¹ light-emitting electrochemical cells (LECs),² chemosensors,³ and luminescent biological-labeling reagents.⁴ These iridium(III) complexes can be divided into two classes. The first class is neutral iridium(III) complexes containing cyclometalated ligands and an anionic ligand.⁵ This class of neutral Ir(III) complex has high quantum yield and the emission wavelength and excited-state lifetime can be tuned by changing the cyclometalated ligands. For example, $(dfppy)_2 Ir(acac) (dfppy = 2-$ (2',4'-difluorophenyl)pyridine, acac = acethylacetonate)⁶ and $(dfppy)_2 Ir(pic)$ (pic = picolinate)⁷ exhibited an emission color at 482 nm and 468 nm with quantum yields of 62% and 42%, respectively. The other class is cationic iridium(III) complexes containing bidentate ligands, such as bipyridine.⁸ The synthesis of cationic iridium(III) complexes can be carried out under mild conditions.⁹ Cationic iridium(III) complexes have rich photophysical properties, ionic characteristics, and good solubility in polar solvents, even in an aqueous media. $[(piq)_2 Ir(bpy)]^+ PF_6^-$ (piq = 1-phenylisoquinoline, bpy = bipyridine), $[(piq)_2 Ir(phen)]^+ PF_6^-$ (phen = phenanthroline) and $[(piq)_2Ir(bqu)]^+PF_6^-$ (bqu = 2,2'-biquinoline) showed good solubility in polar solvents, whereas their photoluminescence was not dependent on the solvent polarity.¹⁰ This prompted us to use the cationic iridium complexes for solution-processed OLEDs. Solution-based manufacturing processes, such as spin coating or inkjet printing, provide a low cost alternative to vacuum deposition processing for the manufacture of OLEDs for large and/or flexible displays.

Recently we reported heteroleptic cationic iridium complexes containing two substituted 2-phenylquinoxaline and one 2,2-biimidazole.11 These complexes exhibited phosphorescence in the spectral range of 580 to 620 nm with high quantum efficiency of 58-78% depending on the cyclometalated main ligands. The color tuning of iridium complexes was elucidated based on the relative energy levels of the main and ancillary ligands. This paper reports the synthesis of blue-emitting heteroleptic cationic iridium(III) complexes with 2-(2',4'-difluorophenyl)-4-methylpyridine (L1) and 2-(2',4'-difluoro-3'-trifluoromethylphenyl)-4-methylpyridine (L2) as the main ligands, and 2,2'-biimidazole as the ancillary ligand. The introduction of electron-withdrawing -CF₃ substituents at the 3-position of the phenyl ring in L2 is expected to increase the energy gap between the HOMO and LUMO energy level leading a hypsochromic shift compared to the parent iridium(III) complexes. The performances of the solution-processed OLEDs, which were fabricated by spin coating the emitting layer based on the prepared iridium compounds, were examined.

Experimental Section

Materials and Synthesis. Unless otherwise noted, all chemicals were purchased from Sigma-Aldrich Chemicals and used as received. IrCl₃3H₂O was obtained commercially from Alfa Aesar. All solvents were purified and distilled prior to use according to literature procedures. 2-(2',4'-Difluorophenyl)-4-methylpyridine (L1), 2-(2',4'-difluoro-3'trifluoromethylphenyl)-4-methylpyridine (L2) and 2,2'biimidazole (biim) were prepared using the reported procedures.¹² 2-(2',4'-Difluorophenyl)-4-methylpyridine (L1) was prepared via a Suzuki coupling reaction with 2,4-difluorophenylboronic acid and 2-bromo-4-methylpyridine in 83% yield. The 2-(2',4'-difluoro-3'-trifluoromethylphenyl)-4methylpyridine (L2) was obtained in 39% yield by a treatment with (trifluoromethyl)trimethylsilane in the presence of CuI and KF after iodination of L1. 2,2'-Biimidazole (biim) is an intriguing biaryl molecule that was prepared from glyoxal and ammonium acetate.12c

 $[(L1)_2Ir(biim)]Cl (1)$. The cyclometalated iridium(III) μ chloride-bridged dimer, $[(L1)_2Ir(\mu-CI)]_2$, D1 is prepared using a slight modification of the method reported by Nonoyama.¹³ The iridium(III) trichloride hydrate (2.1 g, 6 mmol) and 2-(2',4'-difluorophenyl)-4-methylpyridine, L1 (3.7 g, 18 mmol) were dissolved in a mixture of 2-ethoxyethanol/water (50 mL; 3:1 v/v). After heating the mixture at 130 °C for 24 h, the reaction mixture was cooled to room temperature and the precipitates were collected. The dimer D1 was washed with ethanol and hexane, and dried in a vacuum (4.66 g, 61%). The dimer D1 (1.27 g, 1 mmol) and 2,2'-biimidazole (0.40 g, 3 mmol) were dissolved in methanol/dichloromethane (30 mL; 2:3 v/v). The mixture was heated under reflux for 8 h and the solvent was evaporated. The crude product was subjected to flash column chromatography (methanol:dichloromethane = 1:20) to give compound 1 as a yellow solid. Elemental analyses were performed at the Korean Basic Science Center. Yield: 74%. (270 mg). ¹H NMR (300 MHz, CDCl₃) δ 8.06 (s, 2H), 7.47 (d, 2H, J = 6.0Hz), 7.10 (s, 2H), 6.83 (d, 2H, J = 5.7 Hz), 6.49-6.42 (m, 4H), 5.79 (d, 2H, J = 8.7 Hz), 2.53 (s, 6H). Anal. Calcd for C₃₀H₂₂F₄IrN₆Cl: C, 46.78; H, 2.88; N, 10.91. Found: C, 46.09; H, 3.01; N, 9.51.

[(L2)₂Ir(biim)]Cl (2). This compound was prepared using the same synthetic procedure used for compound 1 except that 2-(2',4'-difluoro-3'-trifluoromethylphenyl)-4-methylpyridine L2 was used instead of L1. Yield: 82% (375 mg). ¹H NMR (300 MHz, CDCl₃) δ 8.16 (s, 2H), 7.55 (d, 2H, J =5.7 Hz), 7.12 (s, 2H), 6.88 (d, 2H, J = 5.7 Hz), 6.49 (s, 2H), 5.79 (d, 2H, J = 10.5 Hz), 2.53 (s, 6H). Anal. Calcd for C₃₂H₂₀F₁₀IrN₆Cl: C, 42.41; H, 2.22; N, 9.27. Found: C, 41.76; H, 2.98; N, 8.92.

Characterization. The ¹H NMR spectra were recorded on Varian Mercury 300 MHz spectrometer, and CDCl₃ was used as the solvent. Chemical shifts were reported in parts per million (ppm) relative to the residual CDCl₃ at 7.26 ppm. Thermal analyses were carried out on a Metter Toledo TGA/ SDTA 851e analyzer under a nitrogen atmosphere at a heating rate of 10 °C min⁻¹. The UV-visible spectra were recorded on a Jasco V-570 spectrophotometer. The photoluminescence spectra were measured using a Hitachi F-4500 fluorescence spectrophotometer. The equation, $\Phi_s = \Phi_r$ $(\eta_s^2 A_r I_s / \eta_r^2 A_s I_r)$, was used to calculate the quantum yield, where the notations denote the usual meanings.¹⁴ Cyclic voltammetry (CV) was carried out using a Bioanalytical Systems CV-50W voltametric analyzer at potential scan rate of 50-100 mV s⁻¹ in a 0.1 M solution of tetra(n-butyl)ammonium tetrafluoroborate (Bu₄NBF₄) in anhydrous dichloromethane. An Ag/AgNO3 (0.1 M) electrode was used as the reference electrode and a Pt wire was used as the counter electrode. The working electrode was a Pt disc electrode (0.2 cm^2) . The potentials were reported relative to a ferrocene/ferrocenium (Cp2Fe/Cp2Fe⁺) redox couple as an internal reference (0.45 V vs SCE).¹⁵ The electrochemical experiments were performed under a nitrogen atmosphere at room temperature.

OLED Fabrication. Organic light-emitting devices were fabricated using iridium(III) complexes 1 and 2 as blue dopants in the emitting layer. The ITO (indium tin oxide)coated glass substrates were precleaned and UV-ozone treated for 20 min. The surface of the ITO substrate was modified by spin-coating using poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS, 40 nm), following by baking at 120 °C for 10 min under a nitrogen atmosphere. A 70 nm-thick emitting layer was prepared by spincoating in a chlorobenzene solution at 10 wt % of iridium(III) complexes doped into N,N-dicarbazolyl-3,5-benzene (mCP). 1,3-Bis[5-(4-tert-butylphenyl)-1,3,4-oxadiazole-2-yl]benzene (OXD-7) layer of 20 nm-thick was spin-coated on the emitting layer and annealed at 80 °C for 60 min. Successively, LiF and Al were evaporated at a base pressure of 5×10^{-8} Torr. The film thickness was determined using an α -Step IQ surface profiler (KLA Tencor, San Jose, CA, USA). The electroluminescence (EL) spectra and CIE coordinates were measured using a PR650 spectra colorimeter. The current density-voltage-luminescence (J-V-L) changes were measured using a current/voltage source meter (Keithley 238) and an optical power meter (CS-1000, LS-100). All processes and measurements were carried out in air at room temperature.

Results and Discussion

Synthesis of Complexes. The syntheses of the ligands and the iridium complexes are shown in Scheme 1. The synthetic procedure used to prepare the iridium(III) complexes involved two steps.¹⁶ Cyclometalated iridium(III) μ -chloride-bridged dimers **D1** and **D2** were prepared using the methodology reported by Nonoyama.¹³ Compounds **1** and **2** were easily converted to the mononuclear iridium(III) complexes by replacing two bridging chlorides of **D1** and **D2** with bidentate 2,2'-biimidazole ligand under mild reaction conditions. The final iridium(III) complexes were obtained with yields of 74-82%. Compounds **1** and **2** contain the counter ion, Cl⁻, for charge balance, and were characterized by ¹H Blue Emitting Cationic Iridium Complexes

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biim



Scheme 1. Synthetic procedure of the ligands and compounds 1 and 2.

NMR and elemental analysis.

Photophysical and Electrochemical Properties. The thermal stability of compounds 1 and 2 were evaluated by thermogravimetric analysis (TGA) under a nitrogen atmosphere. Their 5% weight loss temperatures (ΔT_d) showed high thermal stability at 276 °C and 278 °C for compounds 1 and 2, respectively as shown in Table 1.

Figure 1 shows the absorption spectra of compounds 1 and 2 in a dilute solution ($\sim 10^{-5}$ M in dichloromethane) and Table 1 gives a summary of the results. Compounds 1 and 2 displayed strong absorption bands between 250-300 nm, which can be attributed to the spin-allowed ${}^{1}\pi$ - π * transition (${}^{1}LC$).¹⁷ In addition, the weaker absorption tails were observed at longer wavelengths than 360 nm¹⁶ which suggested the substantial mixing of the ligand-based ${}^{3}\pi$ - π * states, spin forbidden metal to ligand charge transfer (${}^{3}MLCT$) and higher-lying ${}^{1}MLCT$ transition induced by the spin-orbit coupling effect.¹⁸ Spin-orbit coupling was enhanced by the presence of closely-spaced π - π * and MLCT states and the heavy-atom effect of the iridium(III) center.¹⁹ The absorption and the spin-orbit coupling the spin



Figure 1. Absorption spectra of compounds 1 and 2 in solution $(1.0\times 10^{-5}~M$ in CH_2Cl_2).

tion intensity of compound **2** was larger than that of compound **1**, and the low absorption bands of compound **2** (369 and 393 nm) were blue-shifted compared to those of

Table 1. Photophysical properties of compounds 1 and 2^a

Compound	Absorption λ (nm)	Emission λ_{max} (nm)			Φ^c	T_d^d
Compound	$(\varepsilon, \times 10^3 \mathrm{M}^{-1} \mathrm{cm}^{-1})$	298 K	77 K	film^b	(%)	(°C)
1	281(19.8), 302(12.4), 338(5.6), 373(4.9), 406(0.7)	456, 484	459	464, 486	10.2	276
2	283(28.1), 306(16.1), 336(8.4), 369(3.7), 393(1.9)	450, 478	455	456, 478	14.9	278

^{*a*}All data were measured in CH₂Cl₂ solution (1×10^{-5} M). ^{*b*}PMMA film doped with 5 wt % of Ir(III) complex. ^{*c*}Excitation wavelengths were 380 nm. Ir(ppy)₃ (40.0%) was used as an external reference. ^{*d*}T_d is the temperature at 5% weight loss.



Figure 2. Photoluminescence spectra of compounds 1 and 2 in CH_2Cl_2 of 1.0×10^{-5} M (solid) and 5 wt % doped in PMMA film (dash).

compound **1** (373 and 406 nm).

Figure 2 shows the photoluminescence (PL) spectra of compounds **1** and **2** in a dilute solution ($\sim 10^{-5}$ M in dichloromethane) and thin film form. The film spectra were taken from the doped films in poly(methylmethacrylate) (PMMA) with a concentration of 5 wt %. Table 1 lists the resulting photophysical data. The PL quantum yield (Φ) was measured versus Ir(ppy)₃ (40%) as the standard material.²⁰

As depicted in Figure 2, compounds 1 and 2 exhibited blue emission (456 and 484 nm for compound 1, and 450 and 478 nm for compound 2) which were hypsochromic shifted by approximately 15-20 nm from FIrpic (470 and 494 nm).²¹ These values were similar to our reported blue emitting soft salt-based iridium(III) compound, $[(F_2CH_3$ $ppy)_2Ir(dppmp)]^+$,²² where dppmp = 2-[(diphenylphosphino)methyl]pyridine. Compound 2 exhibited ~6 nm blue-shift in emission compared to compound 1. This shows that the electron-withdrawing effect of the -CF₃ group at the 3position of the pyridyl ring in L2 reduced the HOMO energy level resulting in an increase in the HOMO-LUMO energy

Table 2. Photoluminescence properties of compounds 1 and 2 in different solvents^a

Compound	Emission λ_{max} (nm)						
Compound-	Toluene	C ₂ H ₅ OH	CH_2Cl_2	DMF	CH ₃ CN		
1	458	462	456	470	467		
2	452	457	450	464	460		
^{<i>a</i>} All data were measured at the same concentration $(1 \times 10^{-5} \text{ M})$.							

Table 4. Device performances for compounds 1 and 2

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Table 3. Electrochemical Properties of compounds 1 and 2^a

Compound	$E_{ox}(V)^{a}$	HOMO $(eV)^b$	LUMO (eV) ^c	$\Delta E_{gap} (eV)^d$
1	1.59	-6.25	-3.56	2.69
2	1.72	-6.39	-3.58	2.81

^{*a*}Potential values are reported *vs*. Fc/Fc⁺. ^{*b*}Determined from the onset oxidation potential. ^{*c*}HOMO + ΔE_{gap} = LUMO. ^{*d*} ΔE_{gap} collected in CH₂Cl₂ solution by UV-vis. spectrophotometer.

gap in compound **2**. The film PL spectra of compounds **1** and **2** were red-shifted by 6-8 nm compared to those of the solution spectra. This red shift can be understood by the increase in intermolecular interactions due to the decreased distances between the molecules in the film.²³ The emission spectra were investigated in a variety of solutions and the results are in Table 2. The results showed no solvatochromism dependent on the solvent polarity.^{10,22}

In order to evaluate charge injection and device performance, an energy band diagram was calculated. The energy band gap between HOMO and LUMO energy levels was determined from the absorption spectrum and a HOMO energy level was obtained from the electrochemical measurement. The electrochemical properties were investigated from cyclic voltammetry (CV) using a ferrocene/ferrocenium redox couple as the internal standard. The iridium(III) compounds 1 and 2 displayed quasi-reversible oxidations and no reduction processes were observed within the solvent cathodic potential limit. The HOMO energy levels were calculated by the formula of $E_{HOMO} = -(E_{ox} + 4.66)$ eV, where E_{ox} is the onset oxidation potential and 4.66 eV was obtained relative to Fc/Fc^+ couple. The LUMO energy levels were estimated from the HOMO values and values of optical band gaps (E_{gap}) by $E_{LUMO} = E_{HOMO} + E_{gap}$. The optical band gap was obtained from $E_{gap} = 1240 / \lambda_{edge}$ where λ_{edge} is the onset value of the absorption spectrum.²⁴ The summarized Eox, HOMO, LUMO and E_{gap} data of the iridium compounds 1 and 2 are shown in Table 3.

Electroluminescent Devices. The electroluminescent properties of compounds **1** and **2** for OLEDs applications were evaluated with the configuration of ITO/PEDOT:PSS (40 nm)/mCP:Ir(III) (70 nm)/OXD-7 (20 nm)/LiF (1 nm)/Al (100 nm). The PEDOT:PSS was purchased from Bayer (AI 4083) or Baytron (CH8000) company and used as a hole transfer material. OXD-7 acted as an electron transport material. Iridium(III) compounds **1** and **2** were used as the doped emitters to fabricate the OLEDs using mCP as the host material. Devices I and II corresponding to PEDOT:

EML	Device	Turn-on (V)	L^a (cd m ⁻²)	QE ^a (%)	LE ^a (cd/A)	PE ^b (lm/W)	$CIE^b (x, y)$
1	I	14	1734	1.8	3.36	0.61	0.15, 0.32
	II	13	584	4.5	8.52	1.97	0.16, 0.33
2	I	14	153	1.5	2.44	0.45	0.15, 0.28
	II	15	63	1.3	2.37	0.48	0.16, 0.30

^aValues were maximum efficiency. ^bValues collected at a current density of 10 mA/cm²

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Figure 3. Energy levels of the materials in the EL study.

PSS using AI 4083, Bayer (type I) and CH8000, Baytron (type II) as hole transporting materials, respectively, were fabricated using iridium compounds 1 and 2. The resulted device performances are in Table 4.

Figure 3 shows the relative HOMO and LUMO energy levels of the materials used to fabricate the OLEDs. The energy level diagrams show that the LUMO and HOMO energy levels of compounds 1 and 2 are below those of the host indicating that iridium compounds 1 and 2 can trap both electrons and holes in the emitting layer. OXD-7 was introduced as a hole blocking and electron transport layer for an effective charge carrier balance within the emitting layer. Figure 4 shows the electroluminescent (EL) spectra of compounds 1 and 2 at a current of 10 mA/cm². The EL spectra showed two emission peaks (464 and 492 nm for



Figure 4. Electroluminescence spectra of compounds 1 and 2 at a current density of 10 mA cm^{-2} .



Figure 5. Quantum efficiency and luminance efficiency versus current density of the devices based on compounds 1 and 2.

compound 1 and 458 and 486 nm for compound 2), which were red-shifted by ~10 nm compared to those of the PL spectra. These differences between the EL and PL spectra were attributed to the optical effect caused by the change in recombination zone in the EL device. Figure 5 presents the current density-luminance and quantum efficiency characteristics. Device I using compounds 1 and 2 (1-I and 2-I) exhibited a very low roll-off at high current density, which is common in other OLEDs based on cationic iridium complexes.²⁵ This can be explained by the counter anions in the lattice separating the cations leading to reduced aggregation of dopants in the polar host resulting in reduced efficiency roll-off in the devices through the suppression of triple-triple annihilation.²⁶ In device type I, the maximum luminance (L), quantum efficiency (QE) and luminance efficiency (LE) were 1734 cd m⁻², 1.8% and 3.36 cd/A for compound 1, and 153 cd m^{-2} , 1.5% and 2.44 cd/A for compound 2, respectively. The device based on compound 1 exhibited superior electroluminescent properties to compound 2. This might be due to the HOMO energy level of compound 2 (-6.39 eV) being lower than that of compound 1 (-6.25 eV). The efficient hole blocking from the dopants to OXD-7 in compound 1 is anticipated. The EL spectra exhibited blue emission with color purity at CIE coordinates of (0.15, 0.32) and (0.15, 0.28) for compounds 1 and 2, respectively.

Conclusions

Two blue-emitting cationic iridium(III) compounds, $[(L1)_2$ -Ir(biim)]Cl (1) and $[(L2)_2$ Ir(biim)]Cl (2), were synthesized and the EL device performances based on compounds 1 and 2 were investigated. The cationic iridium(III) compounds studied exhibited good solubility in organic solvents as well as good film forming properties. Therefore, the solutionprocessed OLEDs were fabricated by spin coating the emitting layer doped in the mCP host. The compounds destabilized the LUMO energy levels resulting in blue emissions with CIE coordinates of (0.15, 0.32) and (0.15, 0.28) for compounds 1 and 2, respectively. The results suggest that iridium(III) compounds 1 and 2 are thermally stable and good candidates for blue phosphors in solution3650 Bull. Korean Chem. Soc. 2012, Vol. 33, No. 11

processed OLEDs.

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