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Graphical abstract



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Sky-blue phosphorescent iridium(III) complexes with two substituted 2-phenylpyridine derivatives and one picolinic acid for organic light-emitting diodes

Two sky-blue phosphorescent iridium(III) complexes, $[(dfpmpyCF_3)_2Ir(pic)]$ (1) and $[(dfpmpyhCz)_2Ir(pic)]$ (2), were synthesized for, and their electrochemical and photopysical properties were characterized along with a single crystal structure of complex 1 for the fabrication of OLEDs. The $-CF_3$ substituted on the phenylpyridine-based ligand caused a hypsochromic shift in complex 1, and there is an energy transfer from the carbazolyl moieties to the iridium(III) core resulting in high external quantum efficiency in complex 2.

Sky-blue phosphorescent iridium(III) complexes with two substituted 2-phenylpyridine derivatives and one picolinic acid for organic light-emitting diodes

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Abstract

Two sky-blue phosphorescent heteroleptic cyclometalated iridium(III) complexes, bis(2-(2',4'-difluoro-3'-trifluoromethylphenyl)-4-methylpyridinato-N,C^{2'})iridium(picolinate) bis(2-(2',4'-difluoro-3'-hexylcarbazolephenyl)-4- $[(dfpmpvCF_3)_2Ir(pic)]$ (1) and methylpyridinato-N,C^{2'})iridium(picolinate) [(dfpmpyhCz)₂Ir(pic)] (2), were synthesized and characterized. Energy transfer from the carbazol moiety to the iridium core in compound 2 resulted in higher quantum efficiency than with compound 1. The electronegative effect of the $-CF_3$ group on the phenyl ring in the phenylpyridine main ligand resulted in a hypsochromic shift of the emitting spectra in compound 1. In contrast, the sky-blue emission without a red shift in compound 2 indicated a negligible inductive effect of the long chain hexylcarbazole unit on the electronic state of the phenyl ring. The single crystal X-ray structural analysis showed that compound 1 adopts a distorted octahedral geometry around the iridium metal exhibiting *cis*-C,C' and *trans*-N,N' chelate disposition. An electroluminescent devices using the iridium complexes as a dopant in the emitting layer has been fabricated. The best device performance based on compound 1 demonstrated a maximum luminance (L), external quantum efficiency (EQE), luminance efficiency (LE) and power efficiency (PE) of 5750 cd/m², 7.53 %, 16.86 cd/A and 5.88 lm/W, respectively with Commission Internationale de L'Eclairage (CIE) coordinates of (0.17,0.40).

Keywords: Phosphorescent iridium(III) complex; Sky-blue phosphorescent emitting materials, Organic light-emitting diodes (OLEDs)

1. Introduction

Electroluminescent heavy-metal materials, such as iridium, platinum, ruthenium, and osmium complexes, have attracted considerable attention due to their potential applications in full-color flat panel displays and solid-state lighting [1-6]. Among phosphorescent emitters, the best performing phosphorescent materials were those based on iridium(III) complexes because of the relatively short triple lifetime, potential high device efficiency and emission wavelengths from blue to deep red. Iridium(III)-based phosphorescent cyclometalated complexes are used as efficient dopants for applications in the area of phosphorescent organic light-emitting diodes (PhOLEDs) [7-12], light-emitting electrochemical cells (LECs) [13-16] as well as chemosensors [17-18]. The properties of iridium(III) complexes, such as efficiency, brightness and emission wavelength, depend strongly on the structure of the cyclometalated ligand. The emission wavelength of the iridium(III) complexes can normally be tuned by changing the electronic nature or position of the substituents on the ligands. For example, the emission wavelength of the iridium(III) complexes covered the entire visible region by a modification or variation of cyclometalated 2-arylpyridine ligands [19]. Therefore, the design of cyclometalated ligands for iridium(III) complexes is important for achieving high efficiency and color purity for PhOLEDs.

In PhOLEDs, carbazole derivatives are used as host materials for both small-molecule PhOLEDs, such as 4,4'-bis(9-carbazolyl)-2,2'-biphenyl (CBP), and polymer OLEDs, such as poly(*N*-vinylcarbazole) (PVK), because of their high triplet energy and good hole-transporting ability [20-22]. Many iridium(III) complexes with phenylpyridine modified by introducing a carbazole unit have been reported. (2-CzPy)₂Ir(acac) [2-CzPy: 2-[3-(N-phenylcarbazolyl)]pyridine] and (3-PyC)₂Ir(acac) [3-PyC: 9-decyl-3-(pyridin-3-yl)-9H-carbazole] are examples exhibiting high luminance efficiency of 7.7 and 18.77 cd/A, respectively, and the emission colors of these complexes ranged from orange (515 nm) to red (594 nm) because of the large electron density of iridium (III) complexes by introducing a carbazole unit in the main ligand [23-25]. Therefore, iridium(III) complexes containing a carbazole unit that emits a blue color without a red shift are of interest.

Recently, an iridium(III) complex containing a long-chain carbazole moiety in a phenylpyridine-based ligand was designed to prevent the interaction between carbazole and the main ligand. Blue iridium(III) complexes containing two 2-(2',4'-difluoro-3'-

hexylcarbazolephenyl)-4-methylpyridine (dfpmpyhCz) and one ancillary ligand, such as acetylacetone, picolinic acid N-oxide and biimidazole, and exhibiting energy transfer from the carbazole moieties to the iridium(III) cores were reported [26]. The reported complexes showed emission in the blue region with enhanced luminescent efficiency without a red shift. Furthermore, in a trial involving the synthesis of blue emitting iridium(III) materials, we reported the (dfpmpyCF₃)₂Ir(picolinic-N-oxide) complex, where dfpmpyCF₃ is 2-(2',4'-difluoro-3'-trifluoromethylphenyl)-4-methylpyridine, which showed bright deep-blue emission with the CIE coordinates of (0.147,0.210) and high external quantum efficiency of 23.3 % [27]. In this compound, the –CF₃ group in the 3-position of the phenyl ring played an important role in tuning the electronic state of the phenylpyridine ligand leading a blue shift in emission.

As a part of an ongoing study on blue emitting materials, this paper reports the synthesis and characterization of two iridium(III) complexes $(dfpmpyCF_3)_2Ir(pic)$ (1) and $(dfpmpyhCz)_2Ir(pic)$ (2), where pic is picolinic acid. Picolinic acid is a commonly used ancillary ligand that exhibits stable blue emission color. The emission properties of the synthesized iridium(III) complexes were studied and the device performance was examined for applications to OLEDs based on these complexes.

2. Experimental

2.1. Synthesis

The chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise noted. IrCl₃·3H₂O was obtained commercially from Alfa Aesar. All solvents were purified and distilled freshly prior to use according to the literature procedures. Scheme 1 shows the synthetic procedures.

2.1.1. Synthesis of 2-(2',4'-difluoro-3'-hexylcarbazolephenyl)-4-methylpyridine (dfpmpyhCz)
(4)

2-(2',4'-Difluorophenyl)-4-methylpyridine (**3**) was prepared using a Suzuki coupling reaction between 2,4-difluorophenylboronic acid and 2-bromo-4-methylpyridine. 2-(2',4'-Difluoro-3'-hexylcarbazolephenyl)-4-methylpyridine (**4**) was prepared employing a method reported elsewhere [26]. 2-(2',4'-Difluorophenyl)-4-methylpyridine (4.1 g, 20 mmol) was

dissolved in 50 mL of THF and cooled to -78 °C. Lithium diisopropylamide (2.0 g, 20 mmol) was added to the mixture. The mixed solution was stirred for 1h, and 9-(6-bromohexyl)carbazole (6.6 g, 20 mmol) was added to the solution. After stirring the solution for 1h at room temperature, the mixture was extracted with ethyl acetate (80 mL × 3 times) and dried over anhydrous MgSO₄. The crude product was subjected to flash column chromatography (ethyl acetate : *n*-hexane = 1 : 8) to afford compound **4** as a yellow oil (3.45 g, 38 %). ¹H NMR (300 MHz, CDCl₃) δ 8.56 (d, 1H, *J* = 5.1Hz), 8.11 (d, 2H, *J* = 6.6Hz), 7.77-7.69 (m, 1H), 7.52-7.38 (m, 4H), 7.23 (t, 2H, *J* = 7.8Hz), 7.08 (d, 1H, *J* = 4.5Hz), 6.95 (t, 1H, *J* = 7.2Hz), 4.31 (t, 2H, *J* = 7.2Hz), 2.72 (t, 2H, *J* = 7.5Hz), 2.41 (s, 3H), 1.89 (t, 2H, *J* = 7.2Hz), 1.61 (t, 2H, *J* = 6.9Hz), 1.44 (t, 4H, *J* = 3.9Hz). ¹³C NMR (CDCl₃) δ 172.70, 165.48, 163.98, 163.28, 161.23, 160.02, 159.69, 157.72, 156.67, 151.75, 149.73, 148.11, 147.95, 147.22, 146.41, 145.71, 140.32, 137.85, 128.28, 128.04, 125.52, 123.16, 122.71, 120.26, 118.71, 114.22, 113.38, 110. 47, 108.49, 42.90, 29.31, 29.01, 28.79, 26.93, 21.47. MALDI-TOF MS: *m/z* 454.32.

2.1.2. Synthesis of 2-(2',4'-difluoro-3'-trifluoromethylphenyl)-4-methylpyridine (dfpmpyCF₃) (5)

2-(2',4'-Difluoro-3'-trifluoromethylphenyl)-4-methylpyridine (**5**) was prepared using a previously published procedure [27]. A mixture of copper(I) iodide (6.00 g, 31.5 mmol) and anhydrous potassium fluoride (1.10 g,19.0 mmol) was heated under reduced pressure until the color changed to yellow. 2-(2',4'-Difluoro-3'-iodophenyl)-4-methylpyridine (4.18 g, 12.6 mmol), 1-methyl-2-pyrrolidone (30 mL) and (trifluoromethyl)trimethylsilane (4 mL) were then added to the mixture. The resulting mixture was then stirred vigorously for 24 h at room temperature. The mixture was poured into an aqueous ammonia solution (14%, 100 mL) and extracted with dichloromethane (50 mL × 3 times) to give an organic phase. This phase was washed with water (50 mL) and brine (50 mL), dried over anhydrous MgSO₄ and concentrated under vacuum. The crude product was subjected to flash column chromatography (ethyl acetate : *n*-hexane = 1 : 8) to give compound **5** (1.39 g, 39%). ¹H NMR (300 MHz, CDCl3, ppm): 8.59 (d, 1H, J = 5.1 Hz), 7.98 (td, 1H, J = 6.3, 9 Hz), 7.60 (s,

1H), 7.17 (d, 1H, J = 4.8 Hz), 7.01–7.07 (m, 1H), 2.46 (s, 3H). ¹³C NMR (CDCl₃) δ 161.42, 159.29, 157.99, 155.78, 150.97, 149.57, 147.84, 146.98, 135.42, 125.26, 123.94, 112.94, 20.93.

2.1.3. Synthesis of $(dfpmpyCF_3)_2Ir(pic)$ (1)

The cyclometalated iridium(III) chloride-bridged dimer, $[(dfpmpyCF_3)_2Ir(\mu-Cl)]_2$ (6) was prepared using a modification of the method reported by Nonoyama [28]. The iridium(III) trichloride hydrate (2.1 g, 6 mmol) and dfpmpyCF₃($\mathbf{5}$) (9.54 g, 21 mmol) were dissolved in a solution of 2-ethoxyethanol/water (20 mL; 3:1 v/v). After heating the mixture to 130 °C for 24 h, the reaction mixture was cooled to room temperature, and the precipitate was collected. The dimer complex $\mathbf{6}$ was washed with ethanol and hexane and dried under vacuum (2.96 g, 64%). The dimer complex **6** (1.06 g, 0.5 mmol), sodium carbonate (0.5 g, 5 mmol) and picolinic acid (0.18 g, 1.5 mmol) was dissolved in 2-ethoxyethanol (30 mL). The mixture was heated under reflux for 24 h. The mixture was extracted with dichloromethane (50 mL \times 3 times) and dried over anhydrous MgSO₄. The crude product was subjected to flash column chromatography (methanol : dichloromethane = 1 : 20) to give compound **1**. Yellow solid. Yield: 0.24 g (66%). ¹H NMR (300 MHz, CDCl₃) δ 8.57 (d, 2H, J = 6.0Hz), 8.34 (d, 1H, J = 6.9Hz), 8.15 (s, 2H), 7.99-7.83 (m, 2H), 7.48 (t, 1H, J = 6.5Hz), 7.25 (s, 1H), 7.10 (d, 1H, J = 4.2Hz), 6.89 (d, 1H, J = 6.0Hz), 5.97 (d, 1H, J = 10.5Hz), 5.97 (d, 1H, J = 10.5Hz), 5.69 (d, 1H, J = 10.5Hz), 2.48 (s, 6H). ¹³C NMR (CDCl₃) δ 177.63, 167.91, 154.61, 153.27, 151.38, 150.62, 142.53, 133.70, 131.86, 130.57, 128.29, 127.73, 126.82, 119.92, 108.04, 34.62, 25.69, 24.38, 17.15. Elementaal analyses were performed at the Korean Basic Science Center. Anal. calcd. for C₃₂H₁₈F₁₀IrN₃O₂: C, 44.76; H, 2.11; N, 4.89. Found: C, 44.53; H, 2.38; N, 4.71.

2.1.4. Synthesis of $(dfpmpyhCz)_2Ir(pic)$ (2)

The iridium(III) complex (2) was prepared using a similar method to that employed for complex (1) using 2-(2',4'-difluoro-3'-hexylcarbazolephenyl)-4-methylpyridine (4). Yellow solid. Yield : 0.46 g (76 %). ¹H NMR (300 MHz, CDCl₃) δ 8.54 (d, 1H, *J* = 6.0Hz), 8.30 (d, 1H, *J* = 7.2Hz), 8.10 (d, 4H, *J* = 6.6Hz), 8.04 (s, 2H), 7.87 (t, 2H, *J* = 7.8Hz), 7.71 (d, 2H, *J* = 4.5Hz), 7.46-7.37 (m, 4H), 7.28-7.22 (m, 4H), 6.96 (d, 1H, *J* = 6.0Hz), 6.74 (d, 1H, *J* = 6.0Hz), 5.82 (d, 1H, *J* = 9.3Hz), 5.57 (d, 1H, *J* = 9.3Hz), 4.27 (t, 4H, *J* = 6.9Hz), 2.53 (s, 6H), 1.86-1.84 (m, 6H), 1.49-1.35 (m, 14H). ¹³C NMR (CDCl₃) δ 172.97, 168.38, 165.76, 164.16,

163.28, 161.67, 160.25, 158.31, 157.72, 156.67, 154.41, 152.05, 150.04, 148.45, 148.23, 147.49, 146.78, 140.61, 138.12, 128.56, 128.11, 125.80, 124.09, 123.82, 123.02, 120.58, 118.93, 114.39, 13.38, 111.39, 111.20, 108.92, 107.09, 42.95, 32.78, 31.39, 29.62, 29.29, 29.06, 27.24, 22.49, 21.79. MALDI-TOF MS: m/z 1222.08. Anal. calcd. for $C_{32}H_{18}F_{10}IrN_3O_3$: C, 43.94; H, 2.07; N, 4.80. Found: C, 44.18; H, 2.35; N, 4.57.

2.2. Instruments and device fabrications

2.2.1. Instruments

¹H and ¹³C nuclear magnetic resonance (NMR, Varian Mercury) spectra were recorded at 300 MHz using CDCl₃ as a solvent. The chemical shifts are reported in parts per million (ppm) relative to the residual CDCl₃ at 7.26 ppm (for ¹H NMR) and 77.0 ppm (for ¹³C NMR). 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 yields, where the symbols are the usual meanings [29]. Thermal analyses were carried out on a Metter Toledo TGA/SDTA 851e analyzer under a N₂ atmosphere at a heating rate of 10 °C min⁻¹. Cyclic voltammetry (CV, Bioanalytical Systems CV-50W) was carried out at a potential scan rate of 50-100 mV s⁻¹ in a 0.1 M solution of tetra(*n*-butyl)ammonium tetrafluoroborate in dichloromethane under a N₂ atmosphere at room temperature. An Ag/AgNO₃ (0.1 M) electrode and Pt wire was used as the reference and counter electrode, respectively. The working electrode was a Pt disc electrode (0.2 cm²). The potential was reported relative to a ferrocene/ferrocenium (Cp₂Fe/Cp₂Fe⁺) redox couple used as an internal reference (0.45 V vs SCE) [30].

X-ray intensity data was collected at room temperature on a Bruker SMART APEX-II CCD diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structure of complex **1** was solved by applying the direct method using a SHELXS-97 and refined by a full-matrix least-squares calculation on F^2 using SHELXL-97. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in the ideal positions on their respective carbon atoms ($B_{iso} = 1.2 B_{eq}$ and $1.5 B_{eq}$). Crystal data for compound **1**: $C_{30}H_{10}C_{16}F_{10}IrN_3O_2$, $M_w = 1097.43$, Triclinic, *P*-1, a = 11.280(2) Å, b = 12.010(2) Å, c = 16.030(3) Å, $\alpha = 93.95(3)$ °, $\beta = 105.94(3)$ °, $\gamma = 108.92(3)$ °, V = 1945.3(8) Å³, Z = 2, $D_{calc} = 1.874$ Mg m⁻³, $\mu = 3.928$ mm⁻¹, $\theta_{max} = 27.50$ °, 34894 reflections ($R_{int} = 0.0716$), 8918 unique

reflections, 505 parameters refined. GooF = 1.050, Final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.0560$, $\omega R_2 = 0.1416$, all data: $R_1 = 0.0786$, $\omega R_2 = 0.1575$.

2.2.2. Device fabrication

Organic light-emitting devices were fabricated based on iridium(III) complex 1 and 2 as blue dopants in the emitting layers. 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 a conducting PEDOT:PSS layer (CLEVIOS PH500) to a thickness of 40 nm followed by baking at 120 °C for 10 min under a N₂ atmosphere. A 50 nm-thick emitting layer was prepared by spin-coating in a chlorobenzene solution containing 12 wt% iridium(III) complexes doped into the host (PVK:OXD-7:UGH3), where PVK is poly(Nvinylcarbazole), OXD-7 is 1,3-bis(5-(4-tert-butylphenyl)-1,3,4-oxadiazol-2-yl)benzene and UGH3 is 1,3-bis(triphenylsilyl)benzene. A 20 nm-thick layer of TmPyPB [1,3,5-tri(m-pyrid-3-yl-phenyl)benzene)] was spin-coated on top of the emitting layer and annealed at 80 °C for 60 min. LiF and Al were then evaporated sequentially at a 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 EL spectra and CIE coordinates were measured using a PR650 spectra colorimeter. The current density-voltage-luminescence (J-V-L) changes were determined using a current/voltage source meter (Keithley 238) and optical power meter (CS-1000, LS-100). All processes and measurements described above were carried out in air at room temperature.

3. Results and discussion

3.1. Synthesis and structural characterization

Scheme 1 shows the synthetic method. The reaction of 2, 4-difluorophenylboronic acid with 2-bromo-4-methylpyridine yielded 2-(2,4-difluorophenyl)-4-methylpyridine (**3**). 2-(2', 4'-Difluoro-3'-hexylcarbazolephenyl)-4-methylpyridine (**4**) was obtained from a reaction of 9-(6-bromohexyl)carbazole with compound **3**. A reaction of compound **3** with (trifluoromethyl)trimethylsilane in the presence of CuI and KF gave 2-(2,4-difluoro-3-trifluoromethylphenyl)-4-methylpyridine (**5**). The cyclometalated iridium(III) μ -chloridebridged dimers **6** and **7** were synthesized from IrCl₃·3H₂O with an excess of compounds **4** and **5**, respectively. The dimer compounds **6** and **7** could be converted easily to the target

iridium(III) complex (dfpmpyCF₃)Ir(pic) (1) and (dfpmpyhCz)Ir(pic) (2) by replacing the bridged chlorides by bidentate monoanionic 2-picolinic acid. The final iridium(III) complexes were characterized by ¹H and ¹³C NMR, elemental analysis and single crystal X-ray analysis. Compounds 1 and 2 showed good solubility in chlorinated solvents as well as high thermal stability with 5 % weight loss at 346 and 398 °C, respectively, as determined by thermogravimetric analysis (TGA) under a nitrogen atmosphere.

The single crystal of compound **1** was obtained from a mixed solvent system (CHCl₃/hexane) and the structure was characterized by single crystal X-ray crystallography. Figure 1 shows the ORTEP diagram of compound **1** as well as the selected bond lengths and bond angles. As depicted in Figure 1, the iridium(III) ion adopts a distorted octahedral geometry being coordinated with three N atoms, two C atoms and one O atom of three bidentate ligands. The coordinated three ligands split the d-orbitals of the central iridium metal unequally and prefers the *cis*-C,C' and *trans*- N,N' chelate disposition [31]. The angles around the iridium atoms were in the range, 77.0(2) ~ 99.3(3)°. The Ir-O46 bond distance of 2.216(5) Å was longer than the mean Ir-O values of 2.088 Å reported in the Cambridge Crystallographic Database. This value can be understood by the large *trans* influence of the phenyl ring in 2-(2,4-difluoro-3-trifluoromethylphenyl)-4-methylpyridine. The Ir-N bond lengths were 2.075 and 2.039 Å, which are close to the reported values [32-33].

3.2. Optical and electrochemical properties

Figure 2 shows the absorption spectra of compounds **1** and **2** in a dichloromethane solution (~10⁻⁵ M) and the results are summarized in Table 1. By comparing the reported iridium(III) complexes [34-35], the intense peaks in the short wavelength region below 360 nm were assigned tentatively to the spin-allowed ${}^{1}\pi$ - π * transition (${}^{1}LC$) and the weaker absorption tails that appeared above 360 nm were attributed to the metal-to-ligand charge transfer (MLCT) transitions [36]. The absorption spectra revealed substantial mixing of ligand-based ${}^{3}\pi$ - π * states, spin forbidden metal to ligand charge transfer (${}^{3}MLCT$) and a higher-lying ${}^{1}MLCT$ transition induced by the spin-orbit coupling effect [37-38]. The photoluminescence (PL) spectra of compounds **1** and **2** excited at 300 nm were examined both in a dichloromethane solution (~10⁻⁵ M) and in film form. The film was fabricated by doping iridium(III) complexes in poly(methylmethacrylate) (PMMA) with a concentration of 5 wt %. The PL spectra are shown in Figure 3 and the results are listed in Table 1. The emissions of the

complexes showed vibronic fine structures with maximum PL peaks at 464 and 490 nm for compound **1**, and 475 and 501 nm for compound **2** in the solution state. Based on these observed vibronic fine structures, it is likely that the lowest exited triplet states are dominated by ligand-based ${}^{3}\pi$ - π * states.

The maximum peak of compound 1 was blue-shifted 6 nm from that of FIrpic (470 nm) [39]. The PL of compound 1 in the film state was red-shifted 11 nm compared to that in the solution state, whereas compound 2 showed a 9 nm blue shift compared to the solution state. Compound 2 in solution showed emission at approximately 355 nm, which is believed to be from a carbazole unit [27] and exhibited higher PL quantum efficiency of 18.4 % than that of compound 1 (10.2 %). This suggests that efficient energy transfer from the carbazole unit to iridium(III) cores in compound 2 was achieved. The emission peak at 355 nm was quenched in the films, suggesting that intermolecular energy transfer was also achieved due to aggregation resulting from the decreased distance between the molecules in films.

The optical band gaps (ΔE_g) of compounds **1** and **2**, which were deduced from the absorption edge of the absorption spectra, were 2.65 and 2.63 eV, respectively. The triplet energy levels (T₁), which were obtained from the PL spectra at 77K, was 2.67 eV (464 nm) for compound **1**, and 2.69 and 2.48 eV (461 and 500 nm) for compound **2**. The HOMO energy levels were obtained by cyclic voltammetry (CV) using ferrocene as a standard to evaluate the charge injection and device performance. Cyclic voltammetry exhibited a quasi-reversible oxidation potential (Eox) of 1.25 V for compound **1** and two quasi-reversible/reversible oxidation potentials of 0.74 and 1.27 V *vs*. Ag/AgNO₃ in a CH₂Cl₂ solution for compound **2**, as shown in Figure 4. The second oxidation potential of compound **2** was assigned to the carbazole unit of the main ligand [40-41], indicating that the carbazole unit did not affect the electrochemical properties of the cored-iridium(III) complexes significantly. The LUMO levels were estimated from the HOMO levels and optical band gaps using the formula, $E_{LUMO} = E_{HOMO} + \Delta E_g$. The resulting data is summarized in Table 1.

3.3. Elecrtroluminescent properties

The light emitting devices based on compounds **1** and **2** were prepared and the OLED emission characteristics were examined. The device configuration was ITO/PEDOT:PSS (40 nm)/Host-Ir (50 nm)/TmPyPB (20 nm)/LiF (1 nm)/Al (100 nm), and Figure 5 shows their energy levels. The PVK:OXD-7:UGH3 was used as a host and 12 wt % of the iridium(III)

complexes were used as a dopant. The PVK:OXD-7 ratio was 1:1, and the UGH3 content in the host was varied to examine energy transfer from the host to guest because UGH3 has a higher triplet energy and wide band gap, which was used for both electron transfer and as a hole blocking layer. Devices I, II and III corresponding to 29, 22 and 17 wt % UGH3 in the host, respectively, were fabricated using compounds 1 and 2.

The EL spectra (Figure 6) showed two emission peaks, which resembled the PL spectra of the compounds. For compound 1, the emission peaks were red-shifted by ~10 nm compared to the PL spectra of the corresponding compounds, and the intensity of the second peak increased with increasing UGH3 content in the host. For example, the intensity of device I was stronger than that of device III, showing that the CIE coordinates (x,y) changed from (0.17, 0.40) for device 1-I to (0.16, 0.39) for device 1-III using compound 1. On the other hand, the devices using compound 2 gave almost completely superposed EL spectra. This suggests that the EL peaks and their CIE coordinates (x, y) were similarly independent of the UGH3 concentration in a host. This means that the carbazole unit in compound 2 might be attributed to the supplement of energy transfer between the host and guest.

Table 2 summarizes the device performance. Figure 7 shows the current density-voltageluminance (I-V-L) curves for all devices. Device I of compound **1** (device **1**-I) demonstrated a maximum luminance (L), external quantum efficiency (EQE), luminance efficiency (LE) and power efficiency (PE) of 5750 cd/m², 7.53 %, 16.86 cd/A and 5.88 lm/W, respectively. Device I showed the best performance compared to devices II and III using compounds **1** and **2**. The appropriate concentration of UGH3 in the host of device I may enhance energy transfer from the host to guest resulting in higher external quantum efficiency.

4. Conclusions

Two sky-blue phosphorescent iridium(III) complexes (dfpmpyCF₃)Ir(pic) (1) and (dfpmpyhCz)Ir(pic) (2) were synthesized using two electron density modulated phenylpyridine main ligands and one picolinic acid ancillary ligand for the fabrication of OLEDs. These complexes were thermally and electrochemically stable, and showed good photoluminescence efficiency (> 15%). The $-CF_3$ substituted on the phenylpyridine-based ligand caused a hypsochromic shift in the emitting spectra in compound 1, and hexylcarbazole substituted iridium(III) complex 2 exhibited energy transfer from the carbazolyl moieties to the iridium(III) core with high external quantum efficiency.

Supplementary Materials.

The crystallographic data for the structure of compound **1** was deposited in the Cambridge Crystallographic Data Center (Deposition No. CCDC-459401). The data can be obtained free of charge at <u>www.ccdc.cam.ac.uk/deposit</u> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-01223 336033; E-mail: <u>deposit@ccdc.cam.ac.uk</u>).

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References

- [1] C.W. Tang, S.A. Vanslyke, Appl. Phys. Lett. 51 (1987) 913.
- [2] M.A. Baldo, S. Lamansky, P.E. Burrows, M.E. Thompson, S.R. Forrest, Appl. Phys. Lett, 75 (1999) 4.
- [3] Y. Chi, P.-T. Chou, Chem. Soc. Rev. 36 (2007) 1421.
- [4] Y. Chi, P.-T. Chou, Chem. Soc. Rev. 39 (2010) 638.
- [5] G. Zhou, W.-Y. Wong, X. Yang, Chem. Asian J. 6 (2011) 1706.
- [6] P. Wang, S.-J. Liu, Z.-H. Lin, X.-C. Dong, Q. Zhao, W.-P. Lin, M.-D. Yi, S.-H. Ye, C.-X. Zhu, W. Huang, J. Mater. Chem. 22 (2012) 9576.
- [7] M. Ikai, S. Tokito, Y. Sakamoto, T. Suzuki, Y. Taga, Appl. Phys. Lett. 79 (2001) 156.
- [8] A. Kohler, J.S. Wilson, R.H. Friend, Adv. Mater. 14 (2002) 701.
- [9] A.B. Tamayo, B.D. Alleyne, P.I. Djurovich, S. Lamansky, I. Tsyba, N.N. Ho, R. Bau, M.E. Thompson, J. Am. Chem. Soc. 125 (2003) 7377.
- [10] L. Xiao, Z. Chen, B. Qu, J. Luo, S. Kong, Q. Gong, J. Kido, Adv. Mater. 23 (2011) 926.
- [11] Q. Zhao, S. Liu, M. Shi, C. Wang, M. Yu, L. Li, F. Li, T. Yi, C. Huang, Inorg. Chem. 45 (2006) 6152.
- [12] F. Zhang, L. Duan, J. Qiao, G. Dong, L. Wang, Y. Qiu, Organic Electronics 13 (2012)

1277.

- [13] T. Hu, L. Duan, J. Qiao, L. He, D. Zhang, R. Wang, L. Wang, Y. Qiu, Organic Electronics 13 (2012) 1948.
- [14] W.-J. Xu, S.-J. Liu, T.-C. Ma, Q. Zhao, A. Pertegás, D. Tordera, H.J. Bolink, S.-H. Ye, X.-M. Liu, S. Sun, W. Huang, J. Mater. Chem. 21 (2011) 13999.
- [15] B. Chen, Y. Li, W. Yang, W. Luo, H. Wu, Organic Electronics 12 (2011) 766.
- [16] F. Dumur, G. Nasr, G. Wantz, C.R. Mayer, E. Dumas, A. Guerlin, F. Miomandre, G. Clavier, D. Bertin, D. Gigmes, Organic Electronics 12 (2011) 1683.
- [17] W.-J. Xu, S.-J. Liu, X.-Y. Zhao, S. Sun, S. Cheng, T.-C. Ma, H.-B. Sun, Q. Zhao, W. Huang, Chem. Eur. J. 16 (2010) 7125.
- [18] Q. Zhao, F. Li, S. Liu, M. Yu, Z. Liu, T. Yi, C. Huang, Inorg. Chem. 47 (2008) 9256.
- [19] C. Yang, X. Zhang, H. You, L. Zhu, L. Chen, L. Zhu, Y. Tao, D. Ma, Z. Shuai, J. Qin, Adv. Funct. Mater. 17 (2007) 651.
- [20] S. Kappaun, S. Sax, S. Eder, K.C. Mo[°]ller, K. Waich, F. Niedermair, R. Saf, K. Mereiter, J. Jacob, K. Mu[°]llen, E.J.W. List, C. Slugovc, Chem. Mater. 19 (2007) 1209.
- [21] S.-J. Lee, J.S. Park, M. Song, K.-J. Yoon, Y.-I. Kim, S.-H. Jin, H.-J. Seo, Appl. Phys. Lett. 92 (2008) 193312.
- [22] N. Tian, A. Thiessen, R. Schiewek, O.J. Schmitz, D. Hertel, K. Meerholz, E. Holder, J. Org. Chem. 74 (2009) 2718.
- [23] C.-L. Ho, W.-Y. Wong, Q. Wang, D. Ma, L. Wang, Z. Lin, Adv. Funct. Mater. 18 (2008) 928.
- [24] X. Zhang, Z. Chen, C. Yang, Z. Li, K. Zhang, H. Yao, J. Qin, J. Chen, Y. Cao Chem. Phys. Lett. 422 (2006) 386.
- [25] W.-J. Xu, S.-J. Liu, T.-C. Ma, Q. Zhao, A. Pertegás, D. Tordera, H.J. Bolink, S.-H. Ye, X.-M. Liu, S. Sun, W. Huang, J. Mater. Chem. 21 (2011) 13999
- [26] H.-J. Seo, M. Song, S.-H. Jin, J. H. Choi, S.-J. Yun, Y.-I. Kim, RSC Adv. 1 (2011) 755.
- [27] H.-J. Seo, K.-M. Yoo, M. Song, J.S. Park, S.-H. Jin, Y.I. Kim, J.-J. Kim, Org. Electronics 11 (2010) 564.
- [28] M. Nonoyama, Bull. Chem. Soc. Jpn. 47 (1974) 767.
- [29] H.S. Joshi, R. Jamshidi, Y. Tor, Angew. Chem. Int. Ed. 38 (1999) 2722.
- [30] F.O. Graces, K.A. King, R.J. Watts, Inorg. Chem. 27 (1988) 3464.
- [31] L.-L. Wu, C.-H. Yang, I.-W. Sun, S.-Y. Chu, P.-C. Kao, H.-H. Huang, Organometallics

26 (2007) 2017.

- [32] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau, M.E. Thompson, Inorg. Chem. 40 (2001) 1704.
- [33] N. Sengottuvelan, S.-J. Yun, S.K. Kang, Y.-I. Kim, Bull. Korean Chem. Soc. 32 (2011) 4321.
- [34] C.L. Ho, W.Y. Wong, G.J. Zhou, Z. Xie, L. Wang, Adv. Funct. Mater. 17 (2007) 2925.
- [35] S.C. Lo, C.P. Shipley, R.N. Bera, R.E. Harding, A.R. Cowley, P.L. Burn, I.D.W. Samuel, Chem. Mater. 18 (2006) 5119.
- [36] P.J. Hay, J. Phys. Chem. A 106 (2002) 1634.
- [37] A.P. Wilde, K.A. King, R.J. Watts, J. Phys. Chem. 95 (1991) 629.
- [38] M.C. Columbo, A. Hauser, H.U.Güdel, Top. Curr. Chem. 171 (1994) 143.
- [39] C. Adachi, R.C. Kwong, P. Djurovich, V. Adamovich, M.A. Baldo, M.E. Thompson, S.R. Forrest, Appl. Phys. Lett. 79 (2001) 2082.
- [40] B.-L. Li, L. Wu, Y.-M. He, Q.-H. Fan, Dalton Trans. (2007) 2048.
- [41] S. Bettington, M. Tavasli, M.R. Bryce, A. Beeby, H. Al-Attar, A.P. Monkman, Chem. Eur. J. 13 (2007) 1423.



Scheme 1. Synthetic procedure of main ligands and iridium(III) compounds 1 and 2.

Figure Captions

Figure 1. ORTEP diagram of compound **1** (ellipsoids with 30% probability). Selected bond lengths (Å) and bond angles (°) for compound **1**; Ir-C(8) 1.992(8), Ir-C(27) 1.984(7), Ir-N(1) 2.075(6), Ir-N(20) 2.039(6), Ir-N(39) 2.134(6), Ir-O(46) 2.126(5), C(27)-Ir-C(8) 89.6(3), C(27)-Ir-N(20) 80.5(3), C(8)-Ir-N(20) 94.2(3), C(27)-Ir-N(1) 97.0(3), C(8)-Ir-N(1) 80.5(3), N(20)-Ir-N(1) 174.2(2), C(27)-Ir-O(46) 175.1(2), C(8)-Ir-O(46) 94.2(2), N(20)-Ir-O(46) 96.1(2), N(1)-Ir-O(46) 86.7(2), C(27)-Ir-N(39) 99.3(3), C(8)-Ir-N(39) 170.9(3), N(20)-Ir-N(39) 89.0(2), N(1)-Ir-N(39) 96.6(2), O(46)-Ir-N(39) 77.0(2).

Figure 2. Absorption spectra of compounds **1** and **2** in solution $(1.0 \times 10^{-5} \text{ M in CH}_2\text{Cl}_2)$.

Figure 3. Photoluminescence spectra of compounds 1 and 2 in solution $(1.0 \times 10^5 \text{ M in } \text{CH}_2\text{Cl}_2)$ and 5 wt % doped in PMMA film.

Figure 4. Cyclic voltammograms of compounds 1 and 2 at scan rate of 100 mV/S.

Figure 5. Energy levels and triplet energy of materials in an EL study.

Figure 6. Electroluminescence and photoluminescence spectra of compounds 1 (a) and 2 (b) at current density of 10 mA/cm^2 .

Figure 7. Electroluminescence characteristics: J-V-L curves of compounds 1 (a) and 2 (b); Luminance efficiency and power efficiency versus current density of compounds 1 (c) and 2 (d).















Fig. 5

1







Compound		PL		Φ^{c}	E _{ox} ^d	HOMO ^e	LUMO	$\mathbf{E_{g}}^{\mathbf{f}}$
	ŬV	MC ^a	film ^b	(%)	(V)	(eV)	(eV)	(eV)
1	258(0.74),283(0.62),				1.25	-5.75		
	304(0.48),329(0.31)	464,	475,	15 1			2 10	264
	,375(0.18),407(0.11),	490	494	15.1			-5.10	2.04
	442(0.03)							
2	263(0.54),282(0.78),		466,					
	294(0.62),314(0.38),	475,		10.4	0.74,	-5.24,	-2.61,	2.63
	334(0.31),347(0.26),	501	489	18.4	1.27	-5.77	-3.14	
	337(0.17),419(0.04)							
4	285(0.20),297(0.25),	255	-	-	1.36	-6.08	-2.63	3.44
	316(0.04),336(0.08),	355,						
	349(0.07)	369						

ligand 4^a

^aAll data were measured in a CH₂Cl₂ solution (concentration = 1×10^{-5} M).

^bPMMA film doped with 5 wt% of Ir(III) complex.

^cExcitation wavelengths were 380 nm using $Ir(ppy)_3$ (0.40) as an external reference.

^dPotential values were reported vs. Fc/Fc⁺.

^eDetermined from the onset oxidation potential.

^fCollected in CH₂Cl₂ solution using a UV-vis. spectrophotometer.

 Table 2. Device performance based on iridium(III) compounds 1 and 2

Compound	Device	Turn-on	EQE	LE	PE	L	EL	CIE
		voltage(V) ^a	(%) ^a	(cd/A) ^a	(lm/W) ^a	$(cd/m^2)^a$	$(\mathbf{nm})^{\mathbf{b}}$	(x , y) ^b
1	Ι	5	7.53	16.86	5.88	5750	472,	0.17,
						at 12 V	502	-0.40
	II	5	6.03	14.38	5.64	3682	473,	0.16,
						at 13 V	504	0.41
	III	5	4.80	10.96	3.82	2240	469,	0.16,
						at 15 V	493	0.39
2	I	5.5	7.44	19.48	8.74	5007	478,	0.19,
						at 13 V	502	0.46
	II	5.5	5.99	15.00	5.89	4353	478,	0.18,
						at 13 V	505	0.44
	III	5.5	4.12	10.53	3.32	2363	478,	0.18,
						at 17 V	502	0.44

^aMaximum efficiency.

^bValues collected at a current density of 10 mA/cm².

Highlights

- ▶ Two sky-blue phosphorescent iridium(III) complexes were developed.
- The energy transfer from carbazolyl moiety to iridium(III) core was observed.
- ▶ The devices showed that EQE increased with increasing UGH3 in the host.