Homoleptic tris-cyclometalated iridium(III) complexes with phenylimidazole ligands for highly efficient sky-blue OLEDs

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Homoleptic tris-cyclometalated iridium(III) complexes with phenylimidazole ligands for highly efficient sky-blue OLEDs

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Abstract

As an extension of our previous study, three sky-blue homoleptic iridium(III) complexes **1-3** with fluorine-free phenylimidazole ligands were synthesized and their photophysical, electrochemical and thermal properties were studied. All the complexes showed high photoluminescence quantum yields ranging from 0.50 to 0.53. The introduction of bulky isopropyl at the 2,6-position of the *N*-phenyl of the phenylimidazole ligands increases the quantum yield and the decomposition temperature of the iridium(III) complexes. As the conjugated system of the ligand becomes larger, a very small bathochromic-shift of 1 nm was observed in complex **3** (475 nm) compared with that of complex **1** (474 nm) and **2** (474 nm). All the OLED devices showed high current efficiencies of over 20 cd A^{-1} at the luminance of 1000 cd m^{-2}. Devices incorporating with complexes **1-3** all showed longer lifetime in comparison with that of FIrpic-based device.

Keywords: Homoleptic; Phenylimidazole ligand; Iridium(III) complex; Sky-blue; OLED.

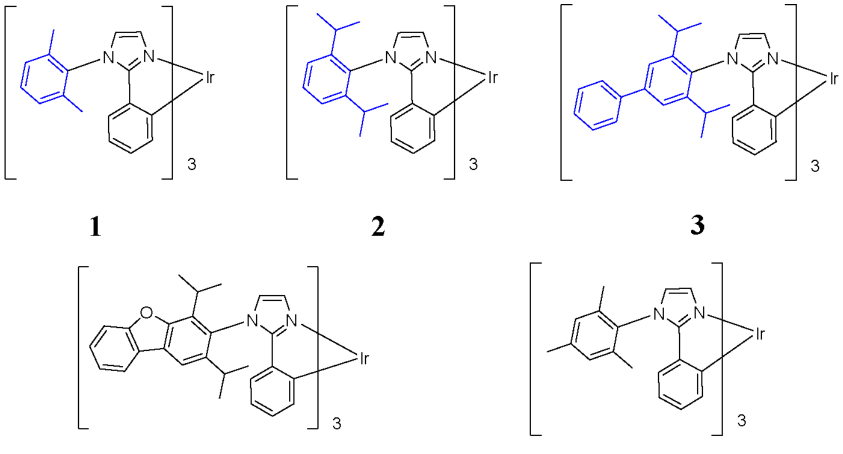
Introduction

Organic light-emitting diodes (OLEDs) have been successfully used in display and solid state lighting since the pioneering work of Tang and VanSlyke in 1987.[1]

Compared with fluorescent OLEDs, phosphorescent OLEDs using transition metal complexes as emitters can harvest both singlet and triplet excitons, which can achieve an internal quantum efficiency as high as 100%.[2-4] Thus, great efforts have been made on the development of the transition metal complexes, such as Ir(III),[5-13] Os(II),[14-17] Ru(II),[18-21] Pt(II),[22-25] Re(I)[26-29] or Cu(I).[30-33] Among these phosphorescent emitters, Ir(III) complexes have attracted most attention due to their efficient emission, excellent thermal stability and broadly tunable emission colors at both the molecular and device levels. The emission properties could be attributed to efficient intersystem crossing between the singlet and triplet excited state caused by the strong spin-orbit coupling of the Ir(III) metal ion.[34] These features of Ir(III) complexes also make them very attractive in the fields of sensing[35, 36], biolabeling[37, 38] and catalyzing.[39] In comparison with the large number of red and green emitters so far discovered and developed, the choices of blue emitting systems used in the OLED research have been based almost solely on bis[(4,6-difluorophenyl)-pyridinate-N,$C^{2\prime}$]picolinate (FIrpic).[40-44] Although a few categories of other materials have been investigated, either the efficiency or lifetime is not satisfied.[7, 24, 45-52] Usually, the research of the blue iridium(III) complexes is focused on the use of the electron-withdrawing fluorine atom or groups, like F and -CF_3, which increase the triplet energy and lead the blue shift. In addition, the strong electronegativity of the fluorine atom is believed to destabilize the molecule and shorten the device lifetime.[50, 53, 54] Therefore, the search for the fluorine-free blue emitters is very important and imperative. As a benchmark material in research work, its poor stability has been recently associated with its ancillary ligand, picolinate, which presumably decomposes in devices following an acid-induced degradation[55] similar to that of acetylacetonate complexes.[56] Generally, homoleptic triscyclometalated iridium(III) complexes have higher chemical stability and longer lifetime than their heteroleptic biscyclometalated counterparts with a labile or vulnerable ancillary ligand, such as picolinate in FIrpic.

Following the initial study of the phenylimidazole-based homoleptic iridium complexes in patent literature,[57-59] we reported highly efficient sky-blue emitting devices with sky-blue tris[1-(2,4-diisopropyldibenzo[b,d]furan-3-yl)-2-phenyl-1H-imidazole] iridium(III) complex (Ir(dbi)$_3$, Scheme 1) as the phosphorescent emitter .[10, 60] A maximum current efficiency and external quantum efficiency (EQE) of 61.5 cd A^{-1} and 23.1% were obtained, which were the highest among those ever reported for blue homoleptic iridium(III) complexes. High efficiencies of 53.5 cd A^{-1} and 20.1% EQE were achieved even at the luminance of 1000 cd m^{-2}. Very recently, Udagawa and coworkers reported OLED device with another phenylimidazole based iridium(III) complex as blue dopant (*fac*-Ir(mpim)$_3$ in Scheme 1). The blue device has a current efficiency of 75.6 lm W^{-1} and an EQE of 29.6% at 100 cd m^{-2}.[13]

In view of the demonstrated high potential of phenylimidazole based iridium(III) complex for practical blue OLED devices, we report here the synthesis and the physical properties of three structurally similar homoleptic iridium(III) complexes with phenylimidazole-based ligands of different substituents and conjugation degrees (Scheme 1). The OLED devices, with a simple architecture different from those reported before, were fabricated and compared.



1 **2** **3**

Ir(dbi)$_3$ *fac*-Ir(mpim)$_3$

Scheme 1. Chemical structure of the homoleptic iridium(III) complexes **1-3** in comparison with the reported materials Ir(dbi)$_3$ and *fac*-Ir(mpim)$_3$.

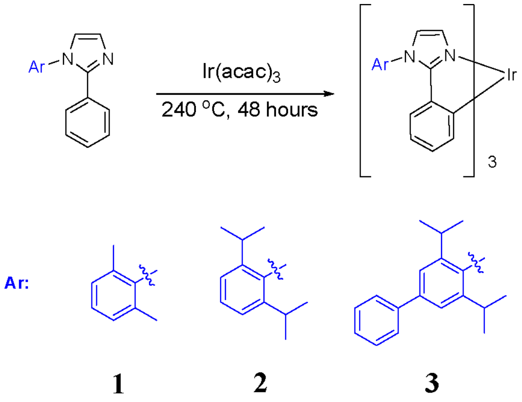
Experimental

General information

The phenylimidazole-based ligands (1-(2,6-dimethylphenyl)-2-phenyl-1H-imidazole, 1-(2,6-diisopropylphenyl)-2-phenyl-1H-imidazole, 1-(3,5-diisopropylbiphenyl-4-yl)-2-phenyl-1H-imidazole and tris(acetylacetonate)iridium (III) ($Ir(acac)_3$) were received from SunaTech Inc.. All reactants and solvents, unless otherwise stated, were purchased from commercial sources and used as received. ^1H NMR and ^{13}C NMR spectra were measured on a 400 MHz Varian NMR spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. UV-Vis absorption and photoluminescence (PL) spectra were recorded on a Perkin-Elemer Lambda 750 and a HITACHI F460 fluorescence spectrophotometer, respectively. The quantum efficiency measurements were carried out at room temperature in degassed acetonitrile solutions. Phosphorescence spectra were measured with an Edinburgh Instruments FLS920 spectrometer. Thermogravimetric analysis (TGA) was undertaken with a SII-EXSTAR 6000 TG/DTA 6200 thermobalance (SII Nano Technology Inc., Tokyo, Japan) under a nitrogen atmosphere by heating the samples from 25 to 750 °C at a heating rate of 10 °C min^{-1}. Elemental analysis was carried out using an EA1110 instrument (Carlo Erba Instruments, Italy) Cyclic voltammetry (CV) was carried out in a three-electrode electrochemical configuration with a platinum working electrode, a platinum auxiliary electrode and an Ag wire pseudo-reference electrode. The potential was referred to the internal standard ferrocene/ferrocenium (Fc/Fc^+) redox couple. The electrochemical cell was loaded with nitrogen-purged DMF and tetrabutylammonium hexafluorophosphate ($TBAPF_6$) supporting electrolyte in a nitrogen-filled glove box (oxygen and water contents < 0.1 ppm) at room temperature. A PARSTAT 2263-2 Advanced Electrochemical System with PowerSUITE software was used for electrochemical measurement and control. The purities of the iridium(III) complexes were determined by the high performance liquid chromatography (HPLC) was carried out using a HPLC from Agilent Instrument.

Synthesis

The synthesis of complex **1**-**3** followed the same synthetic approach as reported previously for Ir(dbi)$_3$ (Scheme 2). The ligand, Ir(acac)$_3$ and tridecane were mixed in a flask and reacted at 240 °C under nitrogen for 48 hours. The rude product was purified by silica gel column chromatography using hexane/DCM as eluent.



Scheme 2. Synthetic route to complexes **1**-**3**

*1. Tris[1-(2,6-dimethyl phenyl)-2-phenyl-1H-imidazole] iridium(III) (**1**)*

1-(2,6-dimethylphenyl)-2-phenyl-1H-imidazole (18.30 g, 73.70 mmol), tris(acetylacetonate)iridium (III) (7.22 g, 14.74 mmol) and tridecane (4.5 mL) were mixed in a 250 mL three-neck oven-dried flask. The flask was purged 3 times with nitrogen, and the reaction mixture was then heated up to 240 °C under nitrogen for 48 hours. The crude product was purified by silica gel column chromatography using hexane/DCM as eluent to afford the target product. After roto-evaporation, the target product was dried *in vacuuo* (10.05 g, 73%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, δ): 7.29-7.22 (t, 3H), 7.18-7.12 (t, 6H), 6.72-6.61 (m, 9H), 6.52-6.46 (t, 3H), 6.34-6.28 (t, 3H), 6.12-6.06 (d, 3H), 2.05-1.98 (s, 9H), 1.83-1.78 (s, 9H); ^{13}C NMR (100 MHz, CD$_2$Cl$_2$, δ): 160.60, 156.94, 137.83, 137.10, 137.02, 136.83, 136.52, 129.85, 129.21, 129.12, 128.40, 126.46, 121.34, 120.22, 119.02, 18.16, 18.05. Anal. Calc′d for $C_{81}H_{75}IrN_6O_3$: C 70.87, H 5.51, N 6.12, found C 70.84, H 5.48, N 6.09.The purity of **1** was confirmed to be 99.3% by HPLC analysis and it was used in PHOLED fabrication without further purification by sublimation.

*2. Tris[1-(2,6-diisopropylphenyl)-2-phenyl-1H-imidazole] iridium(III) (**2**)*

1-(2,6-diisopropylphenyl)-2-phenyl-1H-imidazole (23.00 g, 75.56 mmol), tris(acetylacetonate)iridium (III) (7.40 g, 15.11 mmol) and tridecane (5 mL) were mixed in a 250 mL three-neck oven-dried flask. The flask was purged 3 times with nitrogen, and then the reaction mixture was heated up to 240 °C under nitrogen atmosphere for 48 hours. The crude product was purified by silica gel column chromatography using hexane/DCM as eluent to afford the target product. After roto-evaporation, the target product was died *in vacuuo* (11.99 g, 72%). ^{1}H NMR (400 MHz, CD_2Cl_2, δ): 7.59-7.50 (t, 3H), 7.40-7.31 (t, 6H), 6.89-6.78 (m, 6H), 6.74-6.66 (m, 3H), 6.62-6.54 (t. 3H), 6.44-6.36 (t, 3H), 6.21-6.13 (m, 3H), 2.80-2.64 (m, 3H), 2.41-2.25 (m, 3H), 1.26-1.18 (m, 9H), 1.07-0.89 (m, 27H); ^{13}C NMR (100 MHz, CD_2Cl_2, δ): 161.91, 159.87, 148.65, 148.00, 139.17, 137.94, 135.77, 131.87, 129.55, 127.45, 126.35, 126.07, 123.90, 123.32, 119.86, 104.99, 30.34, 30.02, 26.30, 26.05, 24.87, 24.74. The purity of **2** was confirmed to be 99.5% by HPLC analysis and it was used in PHOLED fabrication without further purification by sublimation.

*3. Tris[1-(3,5-diisopropylbiphenyl-4-yl)-2-phenyl-1H-imidazole] iridium(III) (**3**)*

1-(3,5-diisopropylbiphenyl-4-yl)-2-phenyl-1H-imidazole (27.30 g, 71.74 mmol), tris(acetylacetonate)iridium (III) (7.02 g, 14.35 mmol) and tridecane (5 mL) were mixed in a 250 mL three-neck oven-dried flask. The flask was purged 3 times with nitrogen, and then the reaction mixture was heated up to 240 °C under nitrogen atmosphere for 48 hours. The crude product was purified by silica gel column chromatography using hexane/DCM as eluent to afford the target product. After roto-evaporation, the target product was died *in vacuuo* (13.75 g, 72%). ^{1}H NMR (400 MHz, CD_2Cl_2, δ): 7.79-7.69 (d, 6H), 7.63-7.48 (m, 12H), 7.46-7.39 (t, 3H), 6.92-6.84 (d, 6H), 6.77-6.69 (d, 3H), 6.66-6.59 (t, 3H), 6.50-6.41 (t, 3H), 6.38-6.32 (d, 3H), 2.89-2.70 (m, 3H), 2.50-2.33 (m, 3H), 1.36-1.23 (d, 9H), 1.17-0.90 (m, 27); ^{13}C NMR (100 MHz, CD_2Cl_2, δ): 159.97, 149.02, 148.35, 144.60, 142.73, 139.28, 138.04, 135.15, 130.70, 129.59, 129.12, 127.59, 125.23, 124.95, 123.99, 123.50, 120.11, 30.54, 30.23, 26.36, 26.10, 24.93, 24.82. The purity of **3** was confirmed to be 99.2% by HPLC analysis and it was used in PHOLED fabrication without further purification by sublimation.

Device fabrication and measurement

OLED devices were fabricated by sequentially depositing organic layers and metal cathode layer using thermal evaporation in one run under high vacuum ($\sim 4.5 \times 10^{-4}$ Pa) onto an indium tin oxide (ITO) glass substrate. Prior to use, the substrate was degreased with solvents and cleaned in a UV-ozone chamber for 15 min before it was loaded into the evaporation system. The active device area for all the devices was 3×3 mm^2. The thickness of the deposited layer and the evaporation speed of the individual materials were monitored with quartz crystal microbalance monitors. Electrical testing and optical measurements were performed in the air without encapsulation except for the lifetime measurement. The devices for lifetime evaluation were encapsulated immediately after preparation by using epoxy and glass lids. The EL spectra were measured with a Spectra Scan PR655 spectrometer. The current-voltage (*I*-*V*) and luminance-voltage (*L*-*V*) relations were characterized with a computer controlled Keithley 2400 Sourcemeter.

Results and discussions

In order to systematically investigate the four iridium(III) complexes, i.e., **1-3,** we conducted studies on their photophysical, electrochemical and thermal properties. Based on these properties, we discuss the relationship between the structure and the properties of the complexes. Device performance including the lifetime are evaluated and compared.

Photophysical properties

The UV-Vis absorption and photoluminescence (PL) spectra of the four complexes are shown in Figure 1 and were recorded at the room temperature in acetonitrile (CH_3CN), the detailed data are summarized in Table 1. The absorption of all the four complexes has intense bands in the ultraviolet part of the spectrum ranging from 200 to 320 nm. These bands could be attributed to the spin-allowed $^1(\pi\text{-}\pi^*)$ of the phenylimidazole ligands.[34] At the long wavelength of the spectra, the bands from 320 to 450 nm are assigned to both the spin-allowed singlet-to-singlet metal-to-ligand charge-transfer (^{1}MLCT) and spin-forbidden singlet-to-triplet ^{3}MLCT transitions.[46] The high intensity of these MLCT bands could be attributed to the effective mixing of these charge transitions caused by the strong spin-orbit coupling of iridium ion. As demonstrated in Figure 1, the spectrum of complex **2** is almost the same as the complex **1**. Since both complex **1** and **2** shares the same backbone of the phenylimidazole based ligand, the similarity of the spectrum indicates the substituent of methyl and isopropyl on the ligand doesn't change the absorption largely. The absorption intensity of complex **3** is higher than complex **1** and **2** in the ultraviolet part of the spectrum between 200 and 320 nm. In comparison with complex **1** and **2**, the ligand **3** has one more phenyl group, so the conjugated system is larger. Therefore the high molar extinction coefficient of **3** is believed to be caused by the strong spin-allowed $^1(\pi\text{-}\pi^*)$ of the phenylimidazole ligands. The band gaps of the complexes calculated from the absorption edge are 2.77, 2.76 and 2.75 eV, respectively. Though the band gaps are very close, the changing trend is obvious. The detailed data are summarized in Table 1.

The photoluminescence emission quantum yields (Φ) of the three complexes were measured in deareated acetonitrile (CH_3CN) solution using *fac*-tris[2-phenylpyridinato]iridium(III) (Ir(ppy)$_3$, $\Phi = 0.4$) as a reference. The emission quantum yields in degassed solutions are very high, ranging from 0.50 to 0.53. As shown in Figure 1, the PL intensity of the complexes increases from complexes **1** to **3**. Since the absorption of **1** and **2** are very similar, the high emission quantum yield is expected for complex **2**. The emission quantum yield of complex **1** is 0.50, while complex **2** was measured to be as high as 0.53. For complex **3**, an emission quantum yield of 0.52 was obtained. As for the molecular structure, complex **1** and **2** differ only in the subsituent, i.e., methyl for complex **1** and isopropyl for complex **2**. Methyl and isopropyl group both belong to the electron donating group, but do not have much difference in the electron donating capability. The slightly higher quantum yield of complex **2** could be attributed to the larger steric hindrance of the substituted isopropyl group, which will limit the molecular vibrational and rotational motion. Complex **3** has the emission quantum yield of 0.52, which is close to the value of complex **2**. The increased PL intensity could be attributed to the stronger absorption of complex **3**.

Unlike the absorption, the emission spectra of the three complexes have almost the same feature, i.e., a main peak around 474 nm and a shoulder around 503 nm. The vibronic structure of the emission bands come from the mixing of the ligand centered and MLCT state.[51] The main peak and shoulder peak of complex **1** and **2** are exactly the same, which are 474 and 503 nm, respectively. The peak emission of the reported material *fac*-Ir(mpim)$_3$, which has a similar structure as complex **1** (Scheme 1), is also at 474 nm. A very small bathochromic-shift was observed as the ligand conjugation becomes larger. Both the main peak spectra of complex **3** and Ir(dbi)$_3$ are at 475 nm, which are 1 nm red-shift relative to complex **1** and **2**. Also, 1 nm red-shift was found in the shoulder peak for complex **3** and Ir(dbi)$_3$. Therefore, in order to obtain deep blue tris-cyclometalated iridium(III) emitters, the conjugated system of the ligand should be carefully designed.

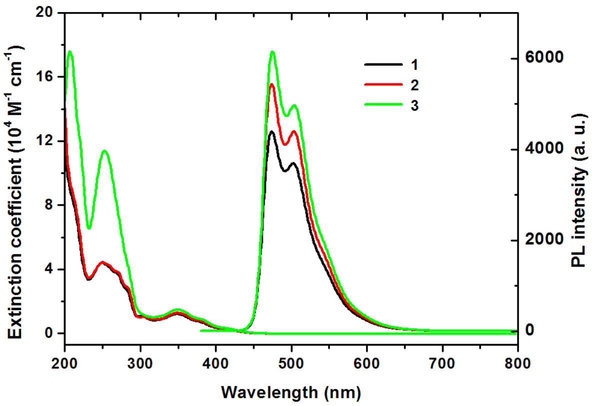


Figure 1. The UV-Vis absorption and PL spectra of **1**-**3** (each at 1 × 10^{-5} M in CH_3CN, excited at 357 nm) at room temperature.

Electrochemical properties

The electrochemical properties of the tris-cyclometalated iridium(III) complexes were investigated by cyclic voltammetry in DMF solutions containing 0.1 M *tetra*-butylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte. The voltammogramms are demonstrated in Figure 2, and the detailed numerical data are summarized in Table 1. As shown in Figure 2, all the complexes exhibited a reversible oxidation wave, with the potentials ranging from 0.10 V to 0.12 V.

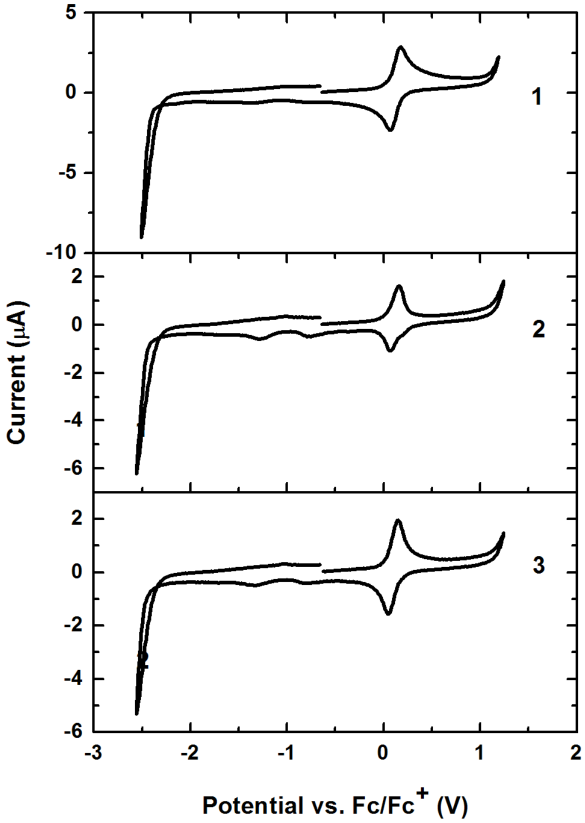


Figure 2. Cyclic voltammograms of **1**-**3** (2×10^{-3} M in DMF, 0.1 M of TBAPF$_6$, scan rate 100 mV s^{-1}).

Thermal properties

The thermal properties of the iridium(III) complexes were investigated by thermogravimetric analysis (TGA), which are displayed in Figure 3. The decomposition temperatures (T_d) of the complexes are in the range of 276 to 429 °C, defined as the temperature at that 5% weight loss occurs. In comparison with complex **1**, the T_d of complex **2** is much higher. As the alkyl substituents changing from methyl to isopropyl, the decomposition temperature of complex **2** increases by nearly 100 °C. The increased T_d value of complex **2** indicates that the size and steric hindrance of isopropyl is beneficial for thermal stability of the transition-metal complex. The ligand of complex **3** has one more benzene ring, so a higher decomposition temperature was expected compared with complex **2**. The detailed thermal data are summarized in Table 1.

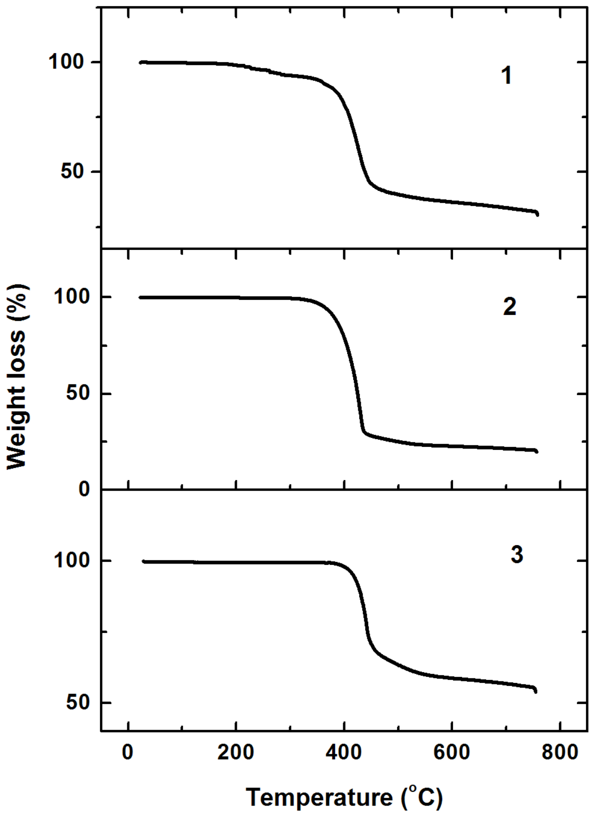


Figure 3. TGA of **1**-**3** (10 °C min^{-1} from 25 to 750 °C).

Table 1 Comparison of iridium complexes **1**-**3** with $Ir(dbi)_3$ and *fac*-$Ir(mpim)_3$.

Complex	ε (M^{-1} cm^{-1}) @λ(nm)	λ_{em}@λ_{ex} (nm)	HOMO (eV)	LUMO (eV)	E_{ox} (V)	E_g (eV) [a]	T_d (°C) [b]	Φ
1	44178@249, 12109@348	474, 503@357	4.92	2.15	0.12	2.77	276	0.50
2	44460@250, 12879@349	474, 503@357	4.91	2.15	0.11	2.76	363	0.53
3	113922@252, 14901@350	475, 504@357	4.90	2.15	0.10	2.75	416	0.52
$Ir(dbi)_3$[c]	103457@254, 95115@285, 16073@349	475, 504@357	4.95	2.21	0.15	2.74	429	0.52
fac-$Ir(mpim)_3$[d]		474@353					412	

[a] Calculated from the absorption edge of UV-vis absorption.

[b] T_d corresponding to 5% weight loss.

[c] The data of $Ir(dbi)_3$ are quoted from Ref. 10 for comparison.

[d] The data of *fac*-$Ir(mpim)_3$ are quoted from Ref. 13 for comparison.

OLED performance

The electroluminescent properties of these homoleptic triscyclometalated iridium(III) complexes were evaluated with fabricated OLED devices that have the following configuration: ITO/TAPC (30 nm)/iridium(III) complex: CTPO 10-15 wt.% (30 nm)/BCP (30 nm)/LiF (1 nm)/Al, where TAPC is 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane, CTPO is 9-(3-(5-(4-(diphenylphosphoryl)phenyl)-4-phenyl-4H-1,2,4-triazol-3-yl)phenyl)-9H-carbazole, BCP is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline. TAPC was used as the hole transport material, CTPO as the host material and BCP as the electron transport material. Device 1, 2 and 3 are corresponding to the devices based on complex **1**, **2** and **3**, respectively. Figure 4 shows the device architectures and the chemical structures of the used materials.

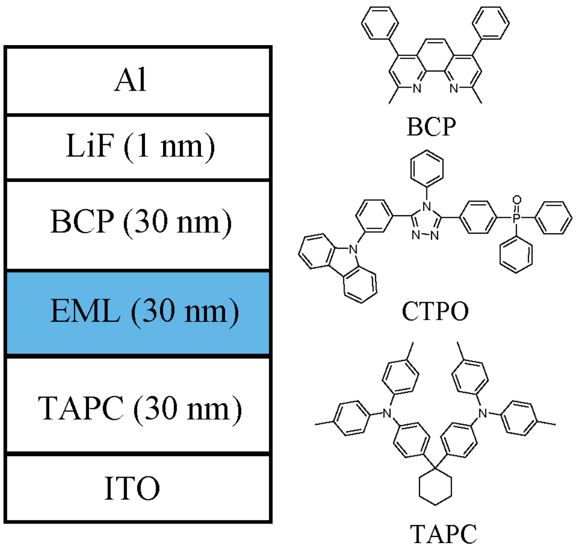


Figure 4. Structure of OLED devices and the materials used. EML: CTPO doped with **1**-**3**.

The current density-voltage-luminance (*J*-*V*-*L*) and the current efficiency-voltage-power efficiency (CE-*V*-PE) characteristics are illustrated in Figure 5. The EL spectra of all the devices are similar to the photoluminescence of the complexes in solution. Interestingly, the EL spectra peaks are all at 472 nm, which is the same as the devices using FIrpic as the emitter. All the device performances are summarized in Table 2. For each complex, the concentration was optimized and the doping concentrations are 12 wt%, 14 wt% and 10 wt%, respectively. Devices based on complex **1-3** showed peak current and power efficiency of 31.1 cd A^{-1} & 17.4 lm W^{-1}, 35.7 cd A^{-1} & 28.2 lm W^{-1}, 31.0 cd A^{-1} & 26.5 lm W^{-1}, respectively. The current efficiencies all remained higher than 20 cd A^{-1} even at the high luminance of 1000 cd m^{-2}, which are 21.6, 25.5, and 29.2 cd A^{-1}, respectively. The higher current and power efficiencies achieved for complex **3** (Φ = 0.53) could be attributed to its higher quantum yield compared with complex **1** (Φ = 0.50) and **2** (Φ = 0.52).

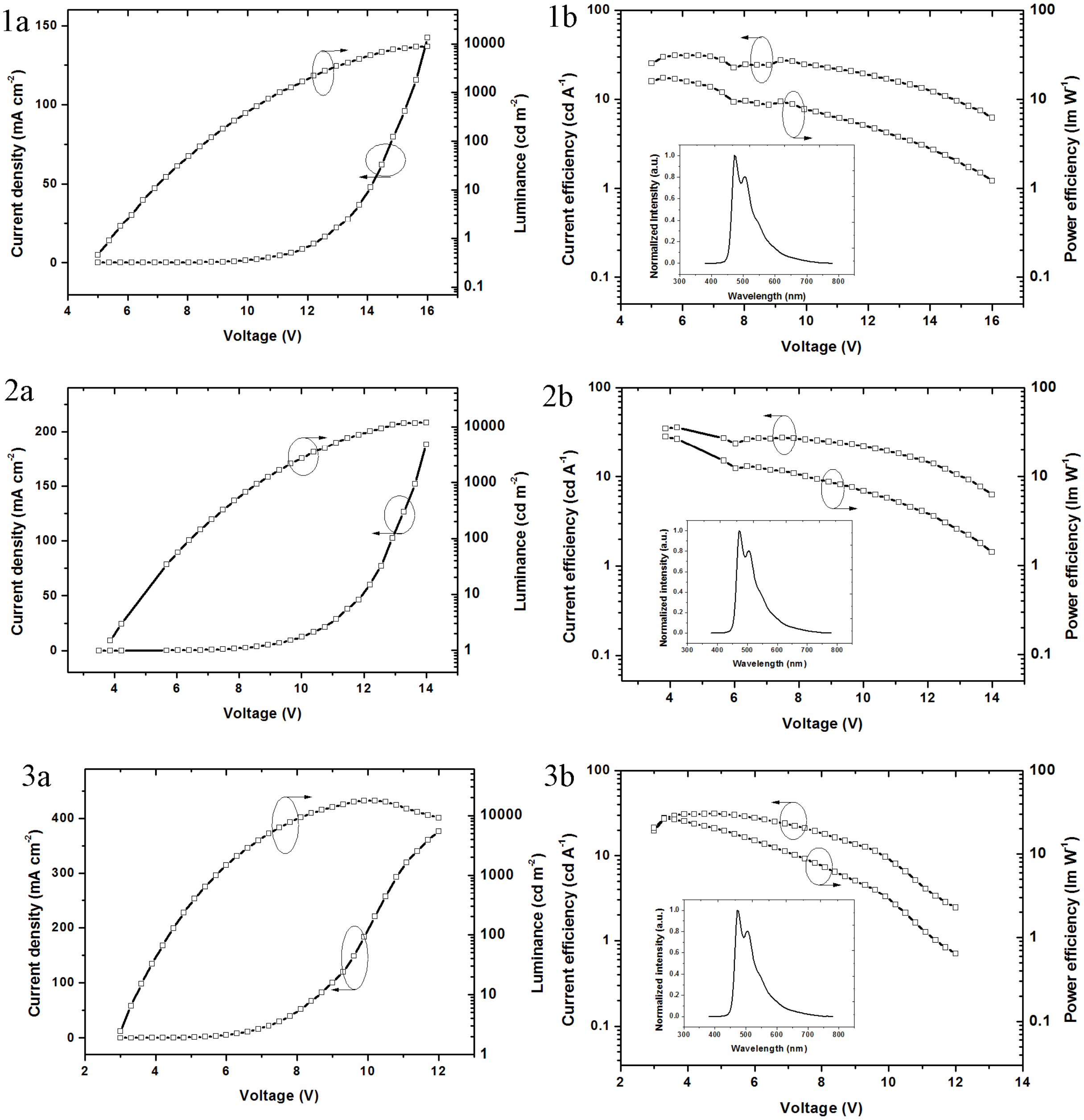


Figure 5. *J*-*V*-*L* and CE-*V*-PE characteristics of the devices based on iridium(III) complexes **1-3** . Inset in 1b, 2b and 3b: EL spectra of the device.

Table 2 EL data of devices based on iridium(III) complexes **1**-**3**.

Complex	100 cd m^{-2}			1000 cd m^{-2}			Maxium CE		Maxium PE		CIE (x, y)
	Voltage	CE	PE	Voltage	CE	PE	Voltage	CE	Voltage	PE	
1	8.6	24.3	8.8	11.0	21.6	6.1	6.5	31.1	5.4	17.4	0.19, 0.39
2	6.4	26.6	12.4	8.6	25.5	7.9	4.2	35.7	3.8	28.2	0.20, 0.38
3	4.3	30.7	27.4	5.6	29.2	21.3	4.8	31.0	3.3	26.5	0.19, 0.38

Voltage: V; CE: cd A^{-1}; PE: lmW^{-1}.

In order to investigate the charge transport ability of the complexes with different phenylimidazole-based ligands, devices with the structure of ITO/TAPC (30 nm)/iridium(III) complex: CTPO 10 wt% (30 nm)/BCP (30 nm)/LiF (1 nm)/Al were fabricated. As shown in Figure 6, Over the voltage range from 0 V to 14 V, the current densities are almost the same for the devices based on **1**-**3**, indicating that the differences of the ligands barely affect the charge transport ability of the iridium(III) complexes.

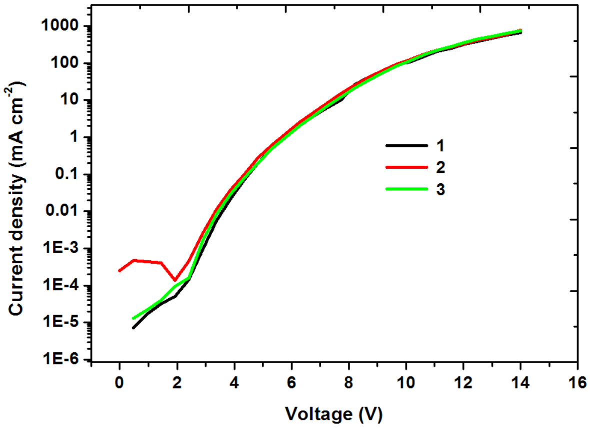


Figure 6. Current density-voltage characteristic of the devices based on **1**-**3**. Device based on **4** is given as a reference.

At the luminance of 100 and 1000 cd m^{-2}, the OLED devices based on different emitters have different working voltages. As shown in Figure 7, the the working voltage dropped quickly from **1** to **3**. Since complexes **1**-**3** have nearly the same charge transport ability, the difference in the working voltages could be attributed to radiative transition of the excitons.

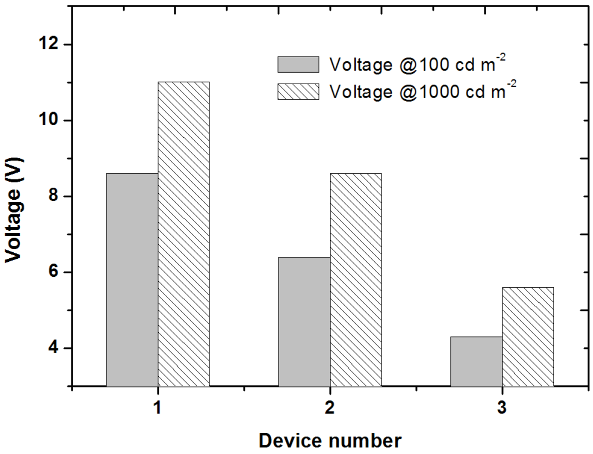


Figure 7. Operating voltage of the devices at the luminance of 100 and 1000 cd m^{-2}.

Lifetime measurement

The stability of complexes **1**-**3** at the device level is evaluated by measuring the lifetime T_{50} (in hour), which is defined as the time when the luminance of an OLED device is reduced to the half of its initial value during the test. As demonstrated in luminance-time profile in Figure 8, the luminance of devices based on **1**-**3** show almost the same decay bahavior. The T_{50} of complexes **1**-**3** based devices are 4.9, 5.2 and 4.6 hours, respectively. For comparison, the decay of the FIrpic-based device is also presented in Figure 8. Although the lifetimes were assessed under a simple encapsulation condition, the big difference in lifetime (~ 5 hrs for **1**-**3** based devices vs. ~ 0.1 hrs for FIrpic-based device) does indicate a much higher stability of the complexes **1**-**3** based devices relative to FIrpic-based device. There are a number of materials used in the construction of the OLED devices, but the excellent molecular stability of the homoleptical cyclometalated iridium(III) complexes is certainly the reason for the big difference in the device lifetimes..

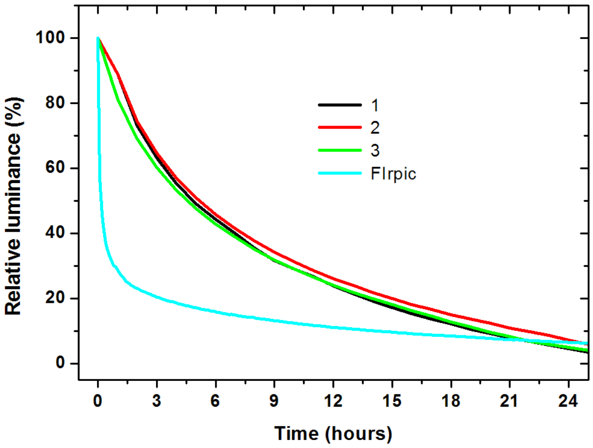


Figure 8. Luminance-time characteristics for the devices with an initial luminance of around 1000 cd m^{-2}.

Conclusions

In summary, we have synthesized four tris(phenylimidazole) cyclometalated iridium(III) complexes **1-3**. The photophysical, elcetrochemical and thermal properties as well as the OLED performance were characterized. The complexes with bulky substituents, like isopropyl group, have higher quantum yield than that of complexes with methyl groups. A red-shift was observed in PL spectra as the conjugated system of ligand become larger. Together with a number of the previous reports, this work prove that the materials properties and device performance are consistently linked to the conjugation degree of the phenylimidazole ligands and that the phenylimidazole based fluorine-free homoleptic iridium(III) complexes are very promising sky-blue emitters for phosphorescent OLEDs.

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