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PII:	\$0020-1693(19)31154-5
DOI:	https://doi.org/10.1016/j.ica.2019.119168
Reference:	ICA 119168
To appear in:	Inorganica Chimica Acta
Received Date:	6 August 2019
Revised Date:	17 September 2019
Accepted Date:	22 September 2019



Please cite this article as: Y-Y. Hu, W. Luo, Y. Wang, B-H. Tong, M-K. Fung, Q-F. Zhang, Efficient yellow OLEDs based on bis-tridentate iridium(III) complexes with two C^N^N-coordinating ligands, *Inorganica Chimica Acta* (2019), doi: https://doi.org/10.1016/j.ica.2019.119168

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## Efficient yellow OLEDs based on bis-tridentate iridium(III) complexes with two C<sup>^</sup>N<sup>^</sup>N-coordinating ligands

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#### Abstract

Four bis-tridentate iridium(III) complexes with two different C<sup>N</sup>N<sup>-</sup>N-coordinating ligands have been synthesized and characterized. All complexes exhibited yellow/orange emission peaking at 580–604 nm with short lifetimes of 1.4–1.6  $\mu$ s and medium photoluminescence quantum yields (PLQYs) of 31%–53%. These complexes exhibit good thermal stability with decomposition temperature ( $T_d$ ) exceeding 310 °C. The luminescence efficiency and thermal stability of iridium complexes were improved by the *m*-substituted CF<sub>3</sub> groups. As a result, complex **2** exhibited the highest PLQYs of 0.53 and  $T_d$  of 348 °C. The OLEDs based on complex **2** showed good performances. The device at 2% doping concentration showed a maximum current efficiency of 36.4 cd A<sup>-1</sup>, power efficiency of 29.1 lm W<sup>-1</sup> and external quantum efficiency (EQE) of 14.4%. These results suggest that these complexes have potential for the application in high-efficiency OLEDs.

**Keywords:** Bis-tridentate iridium(III) complex, Cyclometalation,  $C^{\wedge}N^{\wedge}N$ -coordinating ligands, OLEDs

#### 1. Introduction

Cyclometalated iridium(III) complexes have attracted considerable attention due to their flexible color tenability, high luminescent efficiency and potential applications in organic light-emitting diodes (OLEDs).<sup>[11]</sup> The most common cyclometalated iridium(III) complexes have three bidentate ligands.<sup>[2]</sup> However, the multidentate ligands such as pincer tridentate ligand are potentially more robust against the metal-ligand dissociation compared with bidetate counterpart.<sup>[3,4]</sup> Meanwhile, due to the enhanced rigidity imposed by the tridentate ligand, these Ir(III) complexes usually possess higher luminescent efficiency.<sup>[5]</sup> For example, the bis-tridentate Ir(III) complexes have been proved to have higher thermal, photochemical stability and emission efficiency than the tri-bidentate reference.<sup>[6-8]</sup> The structural advantages with high symmetry are also beneficial to the functionalization of bis-tridentate Ir(III) complexes and the purification of products.<sup>[9]</sup>

The study of bis-tridentate Ir(III) complexes with monoanionic  $N^{\wedge}C^{\wedge}N$  ligands (i.e., 1, 3-di(2-pyridyl)benzene derivatives) was first carried out by Williams and coworkers.<sup>[10]</sup> They systematically studied the preparation and photophysical properties of these complexes, but their potential for OLED application has rarely been evaluated. Recently, the research of Chi and coworker advanced the OLED application of bis-tridentate Ir(III) complexes.<sup>[3,11]</sup> They designed and synthesized a series of novel charge-neutral bis-tridentate Ir(III) complexes with featured dianionic tridentate chelates of 2-pyrazolyl-6-phenyl pyridine derivatives. These complexes exhibited adequate stability and high electroluminescence efficiencies. Classically, the more desirable strategy for the synthesis of charge-neutral bis-tridentate Ir(III) complexes include the collocation of one monoanionic tridentate ligand and another dianionic tridentate ligand. For the monoanionic tridentate ligand, the N  $^{\wedge}$  C  $^{\wedge}$  N-coordinating ligands, such as the aforementioned 1, 3-di(2-pyridyl)benzene derivatives are often used in the preparation of tridentate Ir(III) complexes.<sup>[10,10]</sup>

<sup>12]</sup> Recently, we reported device based on bis-tridentate Ir(III) complexes with functional 1, 3-di(2-pyridyl)benzene tridentate ligands with a maximum EQE of 13.2% and luminance efficiency of 41.4 cd A<sup>-1</sup>.<sup>[13]</sup> Another common monoanionic ligand is C<sup>^</sup>N<sup>^</sup>N-coordinating ligands such as 6'-phenyl-2, 2'-bipyridine.<sup>[9, 14-19]</sup> In theory, these ligands will have fewer side coordination reactions than the N<sup>^</sup>C<sup>^</sup>N-coordinating ligands because of the guiding effect of central nitrogen atom. In fact, no side reactions were found in the cyclometallation reactions of 6-phenyl-2, 2'-bipyridine with other transition metal.<sup>[14]</sup> Mamo and coworkers even found the C<sup>^</sup>N<sup>^</sup>N-coordinating products from a reaction of IrCl<sub>3</sub> with an analogue of terpyridine.<sup>[18]</sup> Whittle and coworkers reported the synthesis of cationic bis-tridentate iridium(III) complexes with the reaction of [Ir(dpyx)Cl( $\mu$ -Cl)<sub>2</sub>] (dpyxH = 1,3-di(2-pyridyl)-4,6-dimethylbenzene) with 6-phenyl-2,2'-bipyridine (phbpyH) in refluxing ethylene glycol.<sup>[19]</sup> However the charge-neutral bis-tridentate Ir(III) complexes with C<sup>^</sup>N<sup>^</sup> N-coordinating monoanionic ligands were barely reported, and the associated chemistry and optoelectronic applications need to be explored.

As an extension of our research, four charge-neutral bis-tridentate Ir(III) complexes had been designed and synthesized in this paper. 4, 6-Diphenyl-2, 2'-bipyridine derivatives were employed as the monoanionic tridentate ligands, and the highly reactive 2-pyrazolyl-6-phenyl pyridine derivatives were used as the dianionic tridentate ligands. The effect of substituents on the photoelectric properties of complexes was studied. OLEDs were fabricated to evaluate their application prospects as efficient OLED emitters.

#### 2. Experimental

#### 2.1. Materials and characterization

All the commercially available reagents were used without further purification. All the reactions were conducted under a N<sub>2</sub> atmosphere. 6-Phenyl-4-(p-tolyl)-2, 2'-bipyridine (**L1H**) and 4-(4-bromophenyl)-6-phenyl-2, 2'-bipyridine (**L2H**) were purchased from Energy Chemical Company. 2-Phenyl-6-(3-(trifluoromethyl)-1H-pyrazol-5-yl) pyridine (**L3H**<sub>2</sub>) was prepared as previously described<sup>[13]</sup>. NMR spectra were measured with a Bruker AV400 spectrometer. High resolution mass spectra (HRMS) were recorded on a TOF 5600<sup>plus</sup> instrument. Cyclic voltammetry were investigated on a CHI1140B Electrochemical Analyzer. Thermogravimetric analysis (TGA) was carried out on a METTLER TGA 1 instrument. Photoluminescence (PL) spectra were measured with a PerkinElmer LS-55 fluorescence spectrophotometer. UV/Vis spectra were measured on a Purkinje General TU-1901 spectrophotometer. PL quantum efficiency and lifetime were measured with an Edinburgh FL920 instrument.

#### 2.2. Preparation of ligands

*1-(6-(3-(Trifluoromethyl)phenyl)pyridin-2-yl)ethanone*: A mixture of 1-(6-bromopyridin-2-yl)ethanone (2.0 g, 10.0 mmol), 3-(trifluoromethyl)phenylboronic acid (1.9 g, 10.0 mmol), K<sub>2</sub>CO<sub>3</sub> (2.8 g, 20.0 mmol), PdCl<sub>2</sub>(dppf) (0.2 g, 0.3 mmol), THF (30 mL) and H<sub>2</sub>O (20 mL) was stirred at 100 °C for 12 h under N<sub>2</sub> atmosphere. After cooling to room temperature, the resulting mixture was poured into water and extracted with ethyl acetate. The ethyl acetate extract was washed with water, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated to yield a solid. Chromatography (V<sub>petroleum ether</sub>/V<sub>ethyl acetate</sub>, 7:1) afforded the 1-(6-(3-(trifluoromethyl)phenyl)pyridin-2-yl)ethanone as a white solid (1.5 g, 56%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.38 (s, 1H), 8.31 (d, *J* = 7.8 Hz, 1H), 8.06 (dd, *J* = 6.7, 2.1 Hz, 1H), 7.99 – 7.95 (m, 2H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.66 (t, *J* = 7.8 Hz, 1H), 2.85 (s, 3H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -62.70 (s). MS ((+)-ESI): m/z = 266.11 (calcd. 266.08 for [C<sub>14</sub>H<sub>11</sub>F<sub>3</sub>NO] [M+H]<sup>+</sup>).

2-(3-(Trifluoromethyl)-1H-pyrazol-5-yl)-6-(3-(trifluoromethyl)phenyl)pyridine (L4H2): A THF

solution of 1-(6-(3-(trifluoromethyl)phenyl)pyridin-2-yl)ethanone (2.7 g, 10.0 mmol) was added to a suspension of NaH (1.2 g, 50.0 mmol) in anhydrous THF (40 mL) in ice bath. After stirred for 30 min, ethyl trifluoroacetate (2.4 mL, 20.0 mmol) was injected and the mixture was refluxed overnight. After then, the mixture was neutralized with aqueous HCl. The organic solvent was removed in vacuo. The residue was extracted with ethyl acetate and washed with water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to yield the crude 1, 3-dione intermediate. Without further purification, this intermediate and N<sub>2</sub>H<sub>4</sub> (80%, 3 mL) was dissolved in ethanol (50 mL). After refluxing for 12 h, the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (V<sub>petroleum ether</sub>/V<sub>ethyl acetate</sub>, 3:1). The pure **L4H**<sub>2</sub> was obtained as a white solid in 33% yield (1.2 g).

<sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.05–8.00 (m, 2H), 7.95 (t, J = 7.9 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.57–7.48 (m, 3H), 7.03 (s, 1H). <sup>19</sup>FNMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -60.32 (s, 3F), -60.78 (s, 3F). MS ((+)-ESI): m/z = 358.13 (calcd. 358.08 for [C<sub>16</sub>H<sub>10</sub>F<sub>6</sub>N<sub>3</sub>] [M+H]<sup>+</sup>).

#### 2.3. Synthesis of Ir complexes

A mixture of the corresponding ligands (L1H or L2H, 1.8 mmol),  $IrCl_3 \cdot 3H_2O$  (0.6 g, 1.8 mmol), 2-ethoxyethanol (30 mL) and H<sub>2</sub>O (10 mL) was stirred at 120 °C for 12 h. After the solution was cooled to room temperature, the crude dimer intermediates were collected by filtration and washed successively with water and ethanol. Then the dimers were used in the subsequent reactions without further purification. A mixture of the respective dimers (0.1 mmol), 0.5 equivalents of L3H<sub>2</sub> or L4H<sub>2</sub>, and 10 equivalents of NaOAc in decalin (20 mL) was refluxed for 12 h. After cooling to room temperature, the mixture was purified by column chromatography on silica (petroleum ether, then petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> =1:1) to afford the respective products.

[Ir(L1)(L3)] (1), red solid, yield: 34%. <sup>1</sup>HNMR (400 MHz, DMSO-d<sub>6</sub>) δ 8.90 (d, J = 7.7 Hz, 2H), 8.66 (s, 1H), 8.23 (d, J = 7.5 Hz, 2H), 8.14–7.92 (m, 5H), 7.84 (d, J = 10.6 Hz, 2H), 7.74–7.63

(m, 2H), 7.40–7.32 (m, 1H), 7.13 (s, 1H), 6.77 (dt, J = 14.2, 7.4 Hz, 2H), 6.69–6.62 (m, 1H), 6.58 (dd, J = 11.4, 4.0 Hz, 1H), 5.94 (d, J = 6.9 Hz, 1H), 5.90 (d, J = 7.0 Hz, 1H), 1.20 (s, 3H). <sup>19</sup>FNMR (376 MHz, DMSO- $d_6$ )  $\delta$  -58.23 (s, 3F). HRMS ((+)-ESI): m/z = 802.1548 (calcd. 802.1770 for [C<sub>38</sub>H<sub>26</sub>N<sub>5</sub>F<sub>3</sub>Ir] [M+H]<sup>+</sup>).

[Ir(L1)(L4)] (2), red solid, yield: 23%. <sup>1</sup>HNMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.91 (s, 2H), 8.65 (s, 1H), 8.22 (dd, J = 26.1, 3.8 Hz, 3H), 8.03 (d, J = 16.6 Hz, 4H), 7.71 (d, J = 1.5 Hz, 1H), 7.47 (d, J = 7.1 Hz, 2H), 7.35 (s, 1H), 7.16 (s, 1H), 6.95 – 6.74 (m, 2H), 6.66 (d, J = 7.4 Hz, 1H), 6.18 (d, J = 7.6 Hz, 1H), 5.91 (d, J = 4.7 Hz, 1H), 5.73 (s, 1H), 1.20 (d, J = 0.5 Hz, 3H). <sup>19</sup>FNMR (376 MHz, DMSO-*d*<sub>6</sub>) δ -58.29 (s, 3F), -60.20 (s, 3F). HRMS ((+)-ESI): m/z = 870.1637 (calcd. 870.1643 for [C<sub>39</sub>H<sub>25</sub>N<sub>5</sub>F<sub>6</sub>Ir] [M+H]<sup>+</sup>).

[Ir(L2)(L3)] (3), red solid, yield: 28%. <sup>1</sup>HNMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.90 (d, J = 7.7 Hz, 2H), 8.66 (d, J = 2.3 Hz, 1H), 8.23 (d, J = 8.5 Hz, 2H), 8.08–7.93 (m, 5H), 7.86 (t, J = 7.3 Hz, 2H), 7.74–7.68 (m, 2H), 7.39–7.31 (m, 1H), 7.13 (s, 1H), 6.84–6.71 (m, 2H), 6.69–6.62 (m, 1H), 6.59–6.53 (m, 1H), 5.92 (dd, J = 17.0, 6.3 Hz, 2H). <sup>19</sup>FNMR (376 MHz, DMSO- $d_6$ )  $\delta$  -58.27 (s, 3F). HRMS ((+)-ESI): m/z = 866.0471 (calcd. 866.0718 for [C<sub>37</sub>H<sub>23</sub>N<sub>5</sub>BrF<sub>3</sub>Ir] [M+H]<sup>+</sup>).

[Ir(L2)(L4)] (4), red solid, yield: 29%. <sup>1</sup>HNMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.93 (d, J = 4.4 Hz, 1H), 8.89 (d, J = 8.4 Hz, 1H), 8.68 (s, 1H), 8.27–8.23 (m, 2H), 8.21 (s, 1H), 8.09 (d, J = 8.8 Hz, 1H), 8.06 (s, 1H), 8.04–8.01(m, 2H), 7.99 (d, J = 8.0 Hz, 1H), 7.83 (t, J = 6.7 Hz, 2H), 7.72 (d, J = 6.8 Hz, 1H), 7.40–7.31 (m, 1H), 7.17 (s, 1H), 6.87 (d, J = 7.4 Hz, 1H), 6.81 (t, J = 7.9 Hz, 1H), 6.67 (t, J = 7.1 Hz, 1H), 6.15 (d, J = 8.2 Hz, 1H), 5.91 (d, J = 7.6 Hz, 1H). <sup>19</sup>FNMR (376 MHz, DMSO- $d_6$ )  $\delta$  -58.48(s, 3F), -60.71 (s, 3F). HRMS ((+)-ESI): m/z = 934.0580 (calcd. 934.0592 for

6

#### $[C_{38}H_{22}N_5BrF_6Ir] \ [M{+}H]^+).$

#### 2.4. OLED fabrication and testing

OLEDs were fabricated by successively vacuum deposition of molecular materials on ITO glass which was treated by a standard process.<sup>[13]</sup> MoO<sub>3</sub> was served as the hole-injection material. Di-[4-(N, N-ditolyl-amino)-phenyl] cyclohexane (TAPC) acted as the hole-transport material and 1, 3-bis(N-carbazolyl)benzene (mCP) as the host material. N, N, N-tris(4-(9-carbazolyl)phenyl)amine (TCTA) acted as the electron-blocking material. 1, 3, 5-Tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB) acted as the electron-transporting materials and 8-hydroxyquinolinolato-lithium (Liq) as the electron-injection materials. Aluminum was used as the cathode. Inficon thickness monitor was used to monitor the film thickness. The electroluminescence (EL) spectra were measured using a Spectra Scan PR650. The current-voltage (I-V) and luminance-voltage (L-V) characteristics were measured using a Keithley 2400 Sourcemeter unit with a calibrated silicon diode.

#### 3. Results and Discussion

#### 3.1. Synthesis, characterization and thermal properties

In order to obtain good volatility of iridium(III) complexes, it is necessary for complexes to maintain charge neutrality. So, two kind of tridentate ligands, i.e. the monoanionic  $C^N^N$ -N-coordinating chelates and dianionic  $C^N^N$ -N-coordinating chelates, were used to balance the charge of trivalent iridium atoms. In view of the fact that some cyclometallated transition-metal complexes can be prepared by the directly reaction of the monoanionic  $C^N^N$ -N-coordinating chelates and transition metal salts (such as K<sub>2</sub>[PdCl<sub>4</sub>], K<sub>2</sub>[PtCl<sub>4</sub>], RhCl<sub>3</sub>)<sup>[14]</sup>, while the tridentate ligand already present in the coordination sphere of the Ir(III) atom may be inhibiting the 7

cyclometallation of the incoming monoanionic  $C^N^N$ -coordinating chelates<sup>[9]</sup>, the monoanionic  $C^N$ N<sup>A</sup>N-coordinating chelates reacted with iridium trichloride firstly to ensure the cyclometallation in our experiments. Then the further coordination will be smoothly carried out with the dianionic chelates with pyrazolyl fragments which have strong coordination ability. Therefore, the synthesis of the bis-tridentate Ir(III) complexes includes two steps (**Scheme 1**). In the first step, the monoanionic chelates (**L1H** or **L2H**) reacted with equivalent amounts of IrCl<sub>3</sub>-3H<sub>2</sub>O in 2-ethoxyethanol/H<sub>2</sub>O mixed solution by refluxing for 12 h, forming the red precipitates of cyclometalate Ir(III) dimer intermediates. Then, the crude intermediates reacted with equivalent amounts of dianionic chelates (**L3H<sub>2</sub>** or **L4H<sub>2</sub>**) in the presence of NaOAc and in high boiling solvent decalin by refluxing for 12 h, forming the desirable products in moderate yields. All complexes are quite stable under air and were fully characterized by proton NMR and HRMS.

Thermogravimetric analysis (TGA) showed that all these iridium(III) complexes have good thermal stability (**Table 1** and **Fig. 1**). The 5% weight loss temperature ( $T_d$ ) of complex **1** is 323 °C, The  $T_d$  of complexes **2** is the highest, reaching 348 °C. Complexes **3** and **4** have the relatively lower  $T_d$  of 312 and 314 °C, respectively. The excellent thermal stability of these complexes is conducive to sublimation and improvement of the service life of OLEDs based on them.

#### 3.2 UV-vis absorption and PL properties

The UV-vis absorption and PL spectra are exhibited in **Fig. 2**. All complexes exhibit similar absorption spectra. The two strong absorption bands ( $\varepsilon > 8 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>) below 310 nm are attributed to the  ${}^{1}\pi$ - $\pi^{*}$  transitions of two different tridentate ligands. The intense absorption bands ( $\varepsilon > 2 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>) around 380 nm are belong to the singlet metal-to-ligand charge transfer

(MLCT) transitions. The weak absorption from 460 nm extended to the visible region are likely due to a combination of triplet MLCT transitions and  ${}^{3}\pi$ - $\pi^{*}$  transitions.<sup>[13]</sup> Compared with complexes **1** and **3**, complexes **2** and **4** show a hypsochromic shift in absorption due to the introduction of the electron-withdrawing trifluoromethyl substituents.

As show in Fig. 2, all bis-tridentate Ir(III) complexes exhibit strong yellow-to-orange emission with maxiumum emitting wavelength between 580 nm and 604 nm in CH<sub>2</sub>Cl<sub>2</sub> at RT. Unlike our previously reported bis-tridentate Ir(III) complexes,<sup>[13]</sup> these complexes exhibit broad and featureless emission. It is suggested that their luminescence may mainly originate from the <sup>3</sup>MLCT and ligand -to-ligand charge transfer (LLCT) transitions.<sup>[19, 20]</sup> The yellow/orange phosphors are essential components to realizing high efficiency, economical two-color white OLEDs solid-state light sources.<sup>[2]</sup> Compared with the emission wavelength (567 nm) of homoleptic bis-tridentate Ir(III) complex of ligand L3,<sup>[13]</sup> the emission wavelengths of these titled complexes were red shifted by more than 13 nm, which confirms the dominance of ligands L1 and L2 in emission because of their more large conjugated system. Similarly, the electro-withdrawing trifluoromethyl substituents also cause a blue shift in the peak of the emission. For example, compared with complexes 1 and 3, the introduction of trifluoromethyl substituents in complexes 2 and 4 blue shifts the PL peaks from 604 and 601 nm to 586 and 580 nm, respectively. Meanwhile, compared with complexes 1 and 2, replacing the electron donating methyl substituent in L1 with the electron-withdrawing bromo substituent in L2, forming complexes 3 and 4, leads to a slightly blue shifts in PL peaks from 604 and 586 nm to 601 and 580 nm, respectively. To eliminate the interference of oxygen, the photoluminescence quantum yields (QYs) of these complexes doped in poly(methyl methacrylate) (PMMA) at a concentration of 1 wt% were determined. As shown in Table 1, complexes 1 and 3

had the lower QYs of 0.31 and 0.37, while complexes **2** and **4** had the higher QYs of 0.53 and 0.46. This might be because introducting of trifluoromethyl group on benzene unit of **L4** can effectively prevent molecular aggregation and concentration quenching is reduced. Indeed, the low vibrational frequency C-F bond can reduce the radiationless deactivation rate and the electron-withdrawing nature of trifluoromethyl group can also enhance the electron affinity and electron mobility of the iridium complexes.<sup>[13]</sup> The transient photoluminescence decay curves (**Fig. 3, Table 1**) displayed single exponential decay with fitting lifetimes between 1.4 and 1.7 µs for titled complexes, together with the oxygen sensitivity confirming their triplet-emitting nature.<sup>[7]</sup> Complexes **3** and **4** have shorter luminescence lifetimes than complexes **1** and **2**, due to the presence of heavy atoms of bromine, which introduced faster radiative decay rates ( $1.94 \times 10^5$  and  $3.12 \times 10^5$ s<sup>-1</sup> for **1** and **2**, 2.64  $\times 10^5$  and  $3.28 \times 10^5$  s<sup>-1</sup> for **3** and **4**, respectively ).

#### 3.3 Electrochemical properties

Cyclic voltammetry measurement shows all these complexes exhibited reversible oxidation (Fig. 4). The oxidation potential of complex 2 was 645 mV, which was higher than that of complex 1 (545 mV) due to the influence by the electron-withdrawing trifluoromethyl substituent on benzene unit of L4 in complex 2. The oxidation potential of complex 4 (739 mV) was higher than that of complex 3 (573 mV) for the same reasons. Replacing the electron donating methyl substituent in L1 with the electron-withdrawing bromo substituent in L2 has also led to the increase of oxidation potential of complex 3 (or 4) was slightly higher than that of complex 1 (or 2). The reason for greater influence of trifluoromethyl substituent than that of bromo substituent can be attributed to the stronger electron pulling capability of the trifluoromethyl

group compared with bromine atom and their different substitution positions. The HOMO and LUMO levels were deduced from the CV data and UV absorption edges. The results showed the electron-withdrawing substituents have concurrently dragged down the HOMO and LUMO levels, but have a greater impact on the HOMO levels. The overall result is the widening of the energy gap, which is consistent with the change of PL wavelength.

#### 3.4 Electrophosphorescent properties

Because complex 2 exhibited the highest QY, its EL properties were studied with the device structure shown in Fig. 5. The EL characteristics of devices D1–D4 (complex 2, 2–8%) were displayed in Fig. 6 and Table 2. As displayed in the EL spectra (Fig. 6a), devices show strong yellow light emissions at 572–580 nm with a shoulder around 612 nm. The structured emission profiles suggest a neglectable contribution from the  $\pi$ - $\pi$ \* transitions under the electric excitation. With the increase of doping concentration, the EL peaks red shift, which can attributed to the aggregation of complex at high concentrations. The EL spectra reveal 6–14 nm blue shift compared with the PL spectra in CH<sub>2</sub>Cl<sub>2</sub>, which is probably due to the different media polarity and restricted molecular vibration in rigid medium. Except the EL emissions originate from complex 2, no other emission peak was observed, implying an efficient energy transfer from the host to phosphor. The Commission Internationale de L'Eclairage (CIE) coordinates were slightly changed from (0.54, 0.46) to (0.55, 0.44) from devices D1 to D4.

**Fig. 6b** shows the current density-voltage-luminance properties. They display turn-on voltages of 3.5–3.9 V. The maximum brightness of devices is between 6878 and 9472 cd m<sup>-2</sup>. The brightness decreases with increasing doping concentration, and is highest at 2% low doping concentration. As

shown in **Fig 6c** and **Fig 6d**, device **D1** (2%) exhibits a maximum current efficiency of 36.4 cd A<sup>-1</sup>, power efficiency of 29.1 lm W<sup>-1</sup> and external quantum efficiency (EQE) of 14.4%. With the increase of doping concentration, the device efficiency decreases. Especially when the doping concentration is exceed 4%, the efficiency decreases obviously, for example, the maximum EQE of device **D2** (4%) is 97% of **D1**, while the maximum EQEs of **D3** (6%) and **D4** (8%) reduce to 80% and 60% of **D1**, respectively, which indicates that the aggregation of complexes is serious under this condition. This is due to the large conjugate plane of tridentate ligands, which leads to the strong aggregation tendency of these bis-tridentate iridium(III) complexes.<sup>[3]</sup>

#### 4. Conclusions

Four novel bis-tridentate iridium(III) complexes with two different  $C^N^N$ -coordinating ligands have been successfully synthesized. The effects of different substituents on the photophysical properties of the bis-tridentate iridium(III) complexes were studied. These complexes exhibited good thermal stability with decomposition temperature ( $T_d$ ) exceeding 310 °C. These complexes exhibited bright yellow phosphorescence with PL quantum yields from 0.31 to 0.53 in PMMA films. The OLEDs based on complex **2** showed good performances. The device at 2% doping concentration showed a maximum current efficiency of 36.4 cd A<sup>-1</sup>, power efficiency of 29.1 lm W<sup>-1</sup> and external quantum efficiency (EQE) of 14.4%. Our results suggest these bis-tridentate iridium(III) complexes are promising for high-efficiency OLED applications.

#### Acknowledgements

This work is supported by the National Natural Science Foundation of China (21572001 and 61875144).

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Scheme 1 Synthetic routes of the iridium(III) complexes.



Fig. 1 Thermal gravimetric spectra of as-prepared iridium (III) complexes.



Fig. 2 UV-vis absorption (a) and photoluminescence spectra (b) of as-prepared iridium complexes in

CH<sub>2</sub>Cl<sub>2</sub> solution.



Fig. 3 Emission decay curves of as-prepared irdium(III) complexes in PMMA films at a conc. of 1 wt%.



Fig. 4 Cyclic voltammetry curves of as-prepared iridium (III) complexes in CH<sub>2</sub>Cl<sub>2</sub>.



Fig. 5 General structure for the devices and their energy level diagram.





**Fig. 6** (a) EL spectra of complex **2** under different doping level. (b) Current density-voltage-luminance (J-V-L) characteristics. (c) Power efficiencies/luminance efficiencies vs. luminance. (d) External quantum efficiency vs. luminance.

Table 1 Physical properties for the iridium(III) complexes									
complex	$\lambda_{max}^{a}$	$\eta^{ m b}$	$ au^{ m b}$	HOMO <sup>d</sup>	LUMO <sup>e</sup>	$E_g^{ m opt}$	$T_{d}{}^{\rm f}$		
	(nm)	(%)	(µs)	(eV)	(eV)	(eV)	(°C)		
1	604	31	1.6	-5.35	-3.29	2.06	323		
2	586	53	1.7	-5.45	-3.34	2.11	348		
3	601	37	1.4	-5.37	-3.30	2.07	312		
4	580	46	1.4	-5.54	-3.42	2.12	314		

[a] Photoluminescence spectra were recorded in  $CH_2Cl_2$  at a conc. of  $10^{-5}$  M. [b] Lifetime and quantum yields were recorded in PMMA at a conc. of 1 wt%. [c] HOMO =  $-4.8 - E_{1/2}^{ox}$ . [e] LUMO levels were calculated from HOMO and  $E_g^{opt}$ .  $E_g^{opt}$  was estimated from the absorption edge. [f] Temperature corresponding to 5% weight loss to the initial weight in TGA analyses.

device (concentration)	λ <sub>EL,max</sub> (nm)	turn-on votage	brightness (cd m <sup>-2</sup> )	current efficiency	Power efficiency	η <sub>EQE</sub> (%)	$CIE_{x, y}$ coordinates
		(V)		$(cd A^{-1})$	(lm W <sup>-1</sup> )		
D1 (2%)	572	3.9	9472	36.4	29.1	14.4	0.54, 0.46
D2 (4%)	576	3.9	9446	34.0	27.5	13.9	0.54, 0.46
D3 (6%)	580	3.7	8402	27.0	18.6	11.5	0.55, 0.45
D4 (8%)	580	3.5	6878	20.5	13.4	8.7	0.55, 0.44

 Table 2 Summary of device luminescence and efficiency data of complex 2

1, Unusual neutral Ir(III) complexes with two C^N^N ligands were synthesized.

- 2, The structure-property relationship in these complexes had been revealed.
- 3, The CF<sub>3</sub> substituted complex **2** exhibited the best PLQYs of 0.53 and  $T_d$  of 348 °C.
- 4, The yellow device based on 2 gave a peak external quantum efficiency of 14.4%.

19

For Table of Contents

# Efficient yellow OLEDs based on bis-tridentate iridium(III) complexes with two $C^N N^N$ -coordinating ligands

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#### Abstract

Complex 2 exhibited the highest PLQYs of 0.53,  $T_d$  of 348 °C and peak EQE 14.4%.



Conflict of interest statement

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled, "Efficient yellow OLEDs based on bis-tridentate iridium(III) complexes with two  $C^{\wedge}N^{\wedge}N$ -coordinating ligands"!