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# Iridium(III) complexes adopting thienylpyridine derivatives for yellow-todeep red OLEDs with low efficiency roll-off



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#### ABSTRACT

By introduction of trifluoromethyl and phenyl groups to 2-(2-thienyl)pyridine (thp), four new phosphorescent bis-cyclometalated iridium(III) complexes, (thp)<sub>2</sub>Ir(tpip), (cf<sub>3</sub>thp)<sub>2</sub>Ir(tpip), (cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) and (3-cf<sub>3</sub>btp)<sub>2</sub>Ir (tpip)  $(cf_3thp = 2-(thiophen-2-yl)-4-(trifluoromethyl)pyridine, cf_3btp = 2-(benzo[b]thiophen-2-yl)-4-(trifluoromethyl)pyridine, cf_3btp = 2-(benzo[b]thiophen$ 3-cf<sub>3</sub>btp = 2-(benzo[*b*]thiophen-3-yl)-4-(trifluoromethyl)pyridine, fluoromethyl)pyridine. tpip = tetraphenylimidodiphosphinate), were synthesized and fully characterized. The density functional theory and timedependent DFT calculations show that the frontier orbitals are mainly localized in the Ir(III) ion and the cyclometalated ligands. Thus, the photophysical properties were dominated by the cyclometalated C<sup>N</sup> ligand, attributed to <sup>3</sup>MLCT and <sup>3</sup>ILCT transition. These Ir(III) complexes emit in the yellow-to-deep red region with photoluminescence quantum yields in the range 40.5-86.4% in CH<sub>2</sub>Cl<sub>2</sub> solutions at 298 K. The organic lightemitting diodes (OLEDs) using (thp)<sub>2</sub>Ir(tpip), (cf<sub>3</sub>thp)<sub>2</sub>Ir(tpip) and (cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) as yellow, orange and deep red emitters display good electroluminescent performance with low efficiency roll-off. Notably, the device based on  $(cf_3thp)_2Ir(tpip)$  possesses very high EL efficiencies with the maximum luminance efficiency and external quantum efficiency (EQE) of 53.9 cd A<sup>-1</sup> and 17.9%, respectively. Furthermore, the EQE for this complex could be still retained as 15.4% at a luminance of 1000 cd m<sup>-2</sup>.

### 1. Introduction

Nowadays, phosphorescent iridium(III) complexes are regarded as the most promising phosphor materials for highly efficient organic light-emitting diodes (OLEDs) due to their relatively short phosphorescence lifetimes, high quantum efficiencies, tunable emission colors splendid electrochemical and thermal stability [1–3]. Many tris-cyclometalated Ir( $\hat{CN}$ )<sub>3</sub> and bis-cyclometalated Ir( $\hat{CN}$ )<sub>2</sub>(LX) Ir(III) complexes have been exploited for high-performance OLEDs, where  $\hat{CN}$  is a cyclometalated ligand and LX is an ancillary ligand. An attractive feature of these Ir(III) complexes is that their emission color can be controlled by different types of the  $\hat{CN}$  cyclometalated ligands. For instance, the green emissive complex Ir(ppy)<sub>3</sub> (ppy = 2-phenylpyridine) is a classic example of the homoleptic Ir( $\hat{CN}$ )<sub>3</sub> [4]. The sky-blue phosphorescent Ir(III) complex (dFppy)<sub>2</sub>Ir(acac) has been studied systematically by introducing electron-withdrawing F atoms on the 4,6positions of the phenyl ring of ppy (dFppy = 2-(2,4-difluorophenyl) pyridine, acac = acetylacetonate) [5]. As a traditional red-emitting Ir (III) complex (piq)<sub>2</sub>Ir(acac), the color of the complex is achieved by increasing the  $\pi$  system in the phenyl ring of ppy through the cyclometalated ligand (piq = 1-phenylisoquinoline) [6]. By designing appropriate ligands for Ir(III) complexes, certain emission colors have been readily obtained and used in OLEDs [7]. However, it is still a challenge for long-wavelength emitters, which are widely used as optoelectronic materials and as biological tags [8–10].

2-(2-Thienyl)pyridine (thp) is one typical ligand framework to construct Ir(III) complexes, in which the phenyl group of ppy ligand is replaced by a thiophene ring. The electron-rich nature of the thiophene ring compared to the benzene ring leads to red shifts in the emission energy of thp based complexes compared to those of ppy [11]. Here, based on the thp cyclometalated ligand, the other three thp derivatives (cf<sub>3</sub>thp, cf<sub>3</sub>btp and 3-cf<sub>3</sub>btp) by introducing trifluoromethyl and phenyl groups were systematically designed and synthesized, aiming to achieve high efficiency luminescent materials with long-wavelength

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Scheme 1. Synthetic routes of ligands and Ir(III) complexes (thp)<sub>2</sub>Ir(tpip), (cf<sub>3</sub>thp)<sub>2</sub>Ir(tpip), (cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) and (3-cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip).

(Scheme 1). Furthermore, the Ir(III) complexes using tpip (tetraphenylimidodiphosphinate) as the ancillary ligand always show good performances on the basis of our previous work. Hence in this paper, we synthesized four new bis-cyclometalated Ir(III) complexes based on thp derivatives with tpip as the ancillary ligand. The emission wavelengths of these Ir(III) complexes can be tuned from 571 to 652 nm, while keeping considerable photoluminescence quantum efficiencies ( $\Phi_{em}$ ) of 40.5–86.4% in degassed CH<sub>2</sub>Cl<sub>2</sub> solutions at room temperature. The phosphorescent OLEDs using Ir(III) emitters achieved good performance with the maximum current efficiency ( $\eta_{c,max}$ ) and external quantum efficiency (EQE<sub>max</sub>) of 53.9 cd A<sup>-1</sup> and 17.9%, respectively, with low efficiency roll-off.

# 2. Experimental section

## 2.1. General information

HRMS spectra were recorded on an Agilent 6540 UHD Accurate-Mass Q-TOF LC/MS instrument. X-ray diffraction data were collected using an Agilent Technologies Gemini An Ultra diffractometer equipped with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.7107$  Å) at room temperature. Data collection and reduction were processed with CrysAlisProsoftware [12]. All of the structures were solved using Superflip [13] and refined using SHELXL – 2014 [14] within Olex2 [15]. UV/Vis and photoluminescence spectra were measured on Hitachi U3900/3900H and Hitachi F7000 spectrophotometers in degassed CH<sub>2</sub>Cl<sub>2</sub> solutions at room temperature, respectively. Luminescence lifetime curves were measured on an Edinburgh Instruments FLS920P fluorescence spectrometer and the data were treated as one-order exponential fitting using OriginPro 8 software. The thermoanalytical analysis (TGA) was performed with a simultaneous NETZSCH STA 449C thermal analyzer. The elemental analyses were measured on a Vario EL Cube Analyzer system. All calculations were carried out with the Gaussian 09 software package [16]. Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculation were employed with no symmetry constraints to investigate the optimized geometries and

electron configurations with the Becke three-parameter Lee-Yang-Parr (B3LYP) hybrid density functional theory [17–19]. Cyclic voltammetry (CV) measurements were performed on a CHI 1210B electrochemical workstation, with a glassy carbon electrode as the working electrode, a platinum wire as the counter electrode, an Ag/Ag<sup>+</sup> electrode as the reference electrode, and 0.1 M n-Bu<sub>4</sub>NClO<sub>4</sub> as the supporting electrolyte.

### 2.2. Syntheses

Scheme 1 depicts the overall synthetic procedures of the ligands and Ir(III) complexes, and all reactions were performed under nitrogen atmosphere, and all reagents were purchased and used without further purification unless otherwise stated. 3-Bromobenzo[*b*]thiophene [20] and potassium tetraphenylimidodiphosphinate (Ktpip) [21] were prepared according to the previous reported methods. <sup>1</sup>H, <sup>19</sup>F and <sup>31</sup>P NMR were recorded on a Bruker AM 400 MHz instrument, and chemical shifts were reported in ppm relative to Me<sub>4</sub>Si as internal standard.

## 2.2.1. General syntheses of ligands

2.2.1.1. Synthesis of 2-(benzo[b]thiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2dioxaborolane (SM-4) intermediate. To a degassed solution of 3bromobenzo[b]thiophene (1.00 g, 4.69 mmol), *bis*(pinacolato)diboron (1.43 g, 5.63 mmol) and KOAc (921 mg, 9.39 mmol) in dry dioxane (15 mL), Pd(dppf)Cl<sub>2</sub> (200 mg) was added under stirring. After 3 h refluxing, the reaction solution was cooled and filtered through Celite. The solution was diluted with EtOAc (40 mL) and water (10 mL). The phases were separated, and the aqueous phase was extracted with EtOAc. The combined organic phase was washed with brine and concentrated. The residue was purified by column chromatography on silica gel, eluted with EtOAc/hexanes (1:200, v/v) to give SM-4 (0.86 mg, 70.9%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.36 (d, *J* = 7.9 Hz, 1H), 8.06 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.31–7.41 (m, 2H), 1.38 (s, 12H).

2.2.1.2. Synthesis of 2-(thiophen-2-yl)-4-(trifluoromethyl)pyridine

(cf<sub>3</sub>thp), 2-(benzo[b]thiophen-2-yl)-4-(trifluoromethyl) pyridine (cf<sub>3</sub>btp) and 2-(benzo[b]thiophen-3-yl)-4-(trifluoromethyl)pyridine (3-cf<sub>3</sub>btp). To a degassed solution of 2-bromo-4-(trifluoromethyl)pyridine (500 mg, 2.21 mmol) and the corresponding boric acid (1.2 equiv) or boric acid ester (SM-4, 1.2 equiv) in dry DMF (10 mL) were added Pd(dppf)Cl<sub>2</sub> (50 mg) and K<sub>3</sub>PO<sub>4</sub>·3H<sub>2</sub>O (1.18 g, 4.42 mmol). After 10 h heating at 100 °C, the reaction mixture was cooled to room temperature, diluted with EtOAc (50 mL) and filtered through a pad of Celite. The filtrate was washed with H<sub>2</sub>O and brine. After the solvent was removed, the residue was purified by column chromatography on silica gel, eluted with EtOAc/hexanes (1:50, v/v) to give corresponding cyclometalated ligands:

cf<sub>3</sub>thp: (0.48 mg, yield: 85.9%), white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.97 (d, J = 7.5 Hz, 1H), 7.66–7.69 (m, 2H), 7.44 (s, 1H), 7.31–7.34 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 154.00, 150.71, 143.53, 139.48, 137.21, 129.03, 128.44, 125.93, 117.30, 114.46. HRMS (*m*/*z*): calcd for C<sub>10</sub>H<sub>6</sub>F<sub>3</sub>NS requires [M+H] <sup>+</sup> 234.5690, found: 234.5678. Elemental anal. calcd. for C<sub>14</sub>H<sub>8</sub>F<sub>3</sub>NS: C, 52.40; H, 2.64; N, 6.11. Found: C, 52.34; H, 2.66; N, 6.12%.

cf<sub>3</sub>btp: (0.68 g, yield: 89.6%), white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.79 (d, J = 5.2 Hz, 1H), 7.98 (s, 1H), 7.93 (s, 1H), 7.87–7.90 (m, 1H), 7.82–7.85 (m, 1H), 7.38–7.42 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 154.00, 150.83, 143.36, 141.07, 140.33, 125.80, 124.92, 124.60, 122.79, 122.64, 118.01, 117.91, 115.24, 115.21. HRMS (*m*/*z*): calcd for C<sub>14</sub>H<sub>8</sub>F<sub>3</sub>NS requires [M+H] <sup>+</sup> 280.0330, found: 280.0404. Elemental anal. calcd. for C<sub>14</sub>H<sub>8</sub>F<sub>3</sub>NS: C, 60.21; H, 2.89; N, 5.02. Found: C, 60.22; H, 2.88; N, 5.01%.

3-cf<sub>3</sub>btp: (0.71 g, yield: 89.8%), white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.93 (d, J = 5.2 Hz, 1H), 8.49 (d, J = 7.6 Hz, 1H), 7.92–7.94 (m, 3H), 7.41–7.51 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 156.00, 150.74, 141.04, 139.02, 136.93, 135.43, 127.99, 125.15, 125.07, 124.12, 122.97, 118.12, 117.48, 117.44. HRMS (*m*/*z*): calcd for C<sub>14</sub>H<sub>8</sub>F<sub>3</sub>NS requires [M+H]<sup>+</sup> 280.0330, found: 280.0409. Elemental anal. calcd. for C<sub>14</sub>H<sub>8</sub>F<sub>3</sub>NS: C, 60.21; H, 2.89; N, 5.02. Found: C, 60.23; H, 2.89; N, 5.03%.

# 2.2.2. General syntheses of Ir(III) complexes

The Ir(III) dichloro-bridged dimers,  $[(C^N)_2Ir(\mu-Cl)]_2$ , were synthesized by reaction of  $IrCl_3 \cdot 3H_2O$  and 2.2 equiv of corresponding cyclometalated ligands in a 3:1 mixture of 2-ethoxyethanol and deionized water according to a similar method reported by Nonoyama [22]. And the bis-cyclometalated Ir(III) complexes (thp)\_2Ir(tpip), (cf\_3thp)\_2Ir(tpip), (cf\_3btp)\_2Ir(tpip) and (3-cf\_3btp)\_2Ir(tpip) were obtained by the reaction of corresponding Ir(III) dichloro-bridged dimers with 2.5 equiv of potassium tetraphenylimidodiphosphinate (Ktpip) in anhydrous 2-ethoxyethanol at 110 °C for 2 h. The cooled reaction mixture was diluted with water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phase was washed with brine and concentrated, the residue was purified by flash column chromatography to give the products.

(thp)<sub>2</sub>Ir(tpip): (36 mg, yield: 45.8%), orange solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.83 (d, J = 5.6 Hz, 2H), 7.70–7.75 (m, 4H), 7.28–7.39 (m, 14H), 7.13–7.17 (m, 4H), 6.96–7.00 (m, 4H), 6.43–6.47 (m, 2H), 6.04 (d, J = 4.8 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 165.04, 149.72, 144.26, 139.59, 138.31, 136.97, 135.28, 131.31, 131.24, 131.13, 130.79, 130.68, 130.14, 129.68, 129.49, 128.04, 127.90, 127.64, 127.51, 127.23, 117.90, 116.42. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 24.17. HRMS (*m*/z): calcd for C<sub>42</sub>H<sub>32</sub>IrN<sub>3</sub>O<sub>2</sub>P<sub>2</sub>S<sub>2</sub> requires [M+H]<sup>+</sup> 930.1040, found: 930.1116. Elemental anal. calcd. for C<sub>42</sub>H<sub>32</sub>IrN<sub>3</sub>O<sub>2</sub>P<sub>2</sub>S<sub>2</sub>: C, 54.30; H, 3.47; N, 4.52. Found: C, 54.41; H, 3.40; N, 4.55%.

(cf<sub>3</sub>thp)<sub>2</sub>Ir(tpip): (43 mg, yield: 56.2%), red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.97 (d, J = 6.0 Hz, 2H), 7.73–7.78 (m, 4H), 7.66–7.68 (m, 2H), 7.32–7.39 (m, 10H), 7.24–7.26 (m, 2H), 7.17 (t, J = 6.8 Hz, 2H), 6.95–7.00 (m, 4H), 6.55–6.57 (m, 2H), 6.04 (d, J = 4.8 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 166.10, 150.29, 147.27, 139.61, 139.19, 138.85, 138.34, 134.51, 131.20, 131.04, 130.93, 130.60, 130.55, 130.49, 130.27, 129.57, 128.25, 128.12, 127.83, 127.70, 113.45, 113.42, 112.09, 112.05.  $^{19}{\rm F}$  NMR (377 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) -64.93.  $^{31}{\rm P}$  NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 24.71. HRMS (*m/z*): calcd for C<sub>44</sub>H<sub>30</sub>F<sub>6</sub>IrN<sub>3</sub>O<sub>2</sub>P<sub>2</sub>S<sub>2</sub> requires [M+H]  $^+$  1066.0788, found: 1066.0861. Elemental anal. calcd. for C<sub>44</sub>H<sub>30</sub>F<sub>6</sub>IrN<sub>3</sub>O<sub>2</sub>P<sub>2</sub>S<sub>2</sub>: C, 49.62; H, 2.84; N, 3.95. Found: C, 49.59; H, 2.81; N 3.96%.

(cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip): (47 mg, yield: 53.8%), dark red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 9.20 (d, J = 6.0 Hz, 2H), 7.67–7.75 (m, 6H), 7.55 (s, 2H), 7.30–7.40 (m, 10H), 7.22 (t, J = 7.6 Hz, 2H), 7.12 (t, J = 8.0 Hz, 2H), 7.01–7.06 (m, 4H), 6.80 (t, J = 7.6 Hz, 2H), 6.59 (dd,  $J_1 = 1.6$  Hz,  $J_2 = 6.0$  Hz, 2H), 6.06 (d, J = 8.0 Hz 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm) 167.27, 151.42, 146.10, 144.78, 142.52, 140.12, 139.78, 139.58, 138.29, 134.25, 130.85, 130.74, 130.55, 130.44, 128.30, 128.17, 127.95, 127.82, 125.80, 125.60, 124.07, 123.12, 113.60, 113.56, 113.37, 113.30. <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>): δ (ppm) – 64.63. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ (ppm) 24.10. HRMS (m/z): calcd for C<sub>52</sub>H<sub>34</sub>F<sub>6</sub>IrN<sub>3</sub>O<sub>2</sub>P<sub>2</sub>S<sub>2</sub> requires [M+H] <sup>+</sup> 1166.1101, found: 1166.1179. Elemental anal. calcd. for C<sub>52</sub>H<sub>34</sub>F<sub>6</sub>IrN<sub>3</sub>O<sub>2</sub>P<sub>2</sub>S<sub>2</sub>: C, 53.60; H, 2.94; N, 3.61. Found: C, 53.58; H, 2.92; N, 3.62%.

(3-cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip), (45 mg, yield: 51.6%), yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.96 (d, J = 6.0 Hz, 2H), 7.91–7.94 (m, 4H), 7.69–7.94 (m, 4H), 7.49 (d, J = 7.6 Hz, 2H), 7.26–7.30 (m, 12H), 7.11 (t, J = 7.2 Hz, 2H), 7.01 (t, J = 7.2 Hz, 2H), 6.86–6.90 (m, 4H), 6.59 (dd,  $J_1 = 1.6$  Hz,  $J_2 = 6.0$  Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm) 167.69, 162.74, 147.34, 143.26, 137.22, 135.35, 131.25, 131.20, 131.15, 130.68, 130.54, 130.49, 130.43, 128.19, 128.13, 128.06, 127.82, 127.75, 127.69, 124.64, 122.86, 121.39, 120.15, 119.81, 118.30, 116.41. <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>): δ (ppm) – 64.82. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ (ppm) 25.01. HRMS (m/z): calcd for C<sub>52</sub>H<sub>34</sub>F<sub>6</sub>IrN<sub>3</sub>O<sub>2</sub>P<sub>2</sub>S<sub>2</sub> requires [M+H]<sup>+</sup> 1166.1101, found: 1166.1164. Elemental anal. calcd. for C<sub>52</sub>H<sub>34</sub>F<sub>6</sub>IrN<sub>3</sub>O<sub>2</sub>P<sub>2</sub>S<sub>2</sub>: C, 53.60; H, 2.94; N, 3.61. Found: C, 53.61; H, 2.91; N, 3.65%.

# 3. Results and discussion

#### 3.1. Synthesis and characterization

The syntheses of the cyclometalated ligands and their corresponding Ir(III) complexes are showed in Scheme 1. The boric acid ester SM-4 for the cyclometalated ligand 3-cf<sub>3</sub>btp could be easily synthesized via the Miyaura Borylation reaction using Pd(dppf)Cl<sub>2</sub> catalyst, which used 3-bromobenzo[*b*]thiophene and bis(pinacolato)diboron (B<sub>2</sub>pin<sub>2</sub>) as raw materials. The cyclometalated ligands 3-cf<sub>3</sub>thp, cf<sub>3</sub>btp and 3-cf<sub>3</sub>btp were synthesized through the Suzuki coupling reaction in high yield over 85%. The Ir(III) complexes (thp)<sub>2</sub>Ir(tpip), (cf<sub>3</sub>thp)<sub>2</sub>Ir(tpip), (cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) and (3-cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) were prepared by the chloride-bridged dimer [(C<sup>^</sup>N)<sub>2</sub>Ir( $\mu$ -Cl)]<sub>2</sub> (1.0 equiv.) with Ktpip (2.5 equiv.) in anhydrous 2-ethoxyethanol. All the desired complexes were obtained in good yield and characterized by <sup>1</sup>H, <sup>19</sup>F, and <sup>31</sup>P NMR spectroscopy and mass spectrometry (supporting information).

The structures of bis-cyclometalated Ir(III) complexes  $(cf_3 thp)_2 Ir$ (tpip) and  $(cf_3 btp)_2 Ir(tpip)$  were further confirmed by X-ray diffraction crystallography and their ORTEP views are shown in Fig. 1. The corresponding crystallographic data and structure refinement details are listed in Table S1, and selected bond lengths and angles are listed in Table S2. Both Ir(III) complexes adopt distorted octahedral coordination geometry with *cis*-O,O, *cis*-C,C, and *trans*-N,N chelate disposition. The Ir–C and Ir–N bands are in the range  $1.92(2) \sim 2.011(15)$  Å and  $2.02(2) \sim 2.050(18)$  Å, respectively, which are consistent with values in previously reported Ir(III) complexes [23,24]. It is noteworthy that the bond lengths of the Ir–O for  $(cf_3 thp)_2 Ir(tpip)$  (2.207(13) and 2.234(14) Å) are longer than that of  $(cf_3 btp)_2 Ir(tpip)$  (2.181(3) and 2.195(3) Å), which is probably due to the strong *trans*-influence of the carbon donors [25]. In addition, the C–Ir–N, C–Ir–O and O–Ir–O bond angles between the iridium center are good agreement with the



**Fig. 1.** ORTEP views of  $(cf_3thp)_2Ir(tpip)$  (CCDC No. 1852094) and  $(cf_3btp)_2Ir$  (tpip) (CCDC No. 1852081) with the atom-numbering scheme at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

corresponding parameters described in similarly constituted Ir(III) complexes [13]. In the case of complex  $(cf_3thp)_2Ir(tpip)$ , the planar fused pyridyl ring (C1–C2–C3–C4–C5–N1) and the five-membered ring planar (C6–C7–C8–C9–S1) are almost coplanar with relatively small dihedral angle of 5.846°. While for complex  $(cf_3btp)_2Ir(tpip)$ , the relatively dihedral angle between pyridyl ring plane and the benzothiophenyl ring plane is 11.555°, which is slightly larger than that of the complex  $(cf_3tp)_2Ir(tpip)$ .

Furthermore, thermal properties of Ir(III) complexes are very important for efficient OLEDs. Thus, thermal stability of these new Ir(III) complexes were evaluated by thermogravimetric analysis (TGA) under a nitrogen steam with a heating rate of  $10 \,^{\circ}\mathrm{Cmin}^{-1}$  (Fig. 2). From the TGA curves of complexes (thp)<sub>2</sub>Ir(tpip), (cf<sub>3</sub>thp)<sub>2</sub>Ir(tpip), (cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) and (3-cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip), it can be seen that the decomposition temperatures (5% loss of weight) are 345 °C, 350 °C, 355 °C and 388 °C, respectively. Meanwhile, they all possess the decomposed temperatures higher than 270 °C. These results suggest that all complexes have good thermal stability and benefit their application in OLEDs.

# 3.2. Photophysical property



The UV–Vis absorption spectra of complexes  $(thp)_2Ir(tpip)$ ,  $(cf_3thp)_2Ir(tpip)$ ,  $(cf_3btp)_2Ir(tpip)$  and  $(3-cf_3btp)_2Ir(tpip)$  in CH<sub>2</sub>Cl<sub>2</sub>

**Fig. 2.** TGA curves of complexes  $(thp)_2Ir(tpip)$ ,  $(cf_3thp)_2Ir(tpip)$ ,  $(cf_3btp)_2Ir(tpip)$  and  $(3-cf_3btp)_2Ir(tpip)$ .

solution are depicted in Fig. 3a, and the data are provided in Table 1. All complexes show intense bands in the UV region (< 320 nm), mostly ascribed to spin-allowed  $\pi$ - $\pi$ \* ligand-centered (<sup>1</sup>LC) transitions arising from the C^N cyclometalated ligands and tpip ligands. The shoulders observed in the region of 320–400 nm could be attributed to  $\pi$ - $\pi$ \* interligand (ILCT) transitions and spin-allowed <sup>1</sup>MLCT transitions [26,27]. The weaker absorption tail in the visible region (> 400 nm) is related to the mixed spin-forbidden <sup>3</sup>MLCT transitions and ligand-centered  ${}^{3}\pi$ - $\pi^{*}$  transition [28]. With respect to the pristine complex (thp)<sub>2</sub>Ir (tpip), the lowest-energy absorption band for (cf<sub>3</sub>thp)<sub>2</sub>Ir(tpip) with electron-withdrawing -CF<sub>3</sub> group display a red-shifted transition. Furthermore,  $(cf_3btp)_2Ir(tpip)$  with more extended  $\pi$  conjugation of the thp moiety shows more red-shifted transition than (cf<sub>3</sub>thp)<sub>2</sub>Ir(tpip) [29,30]. However, (3-cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) with different phenyl connection position on the thp-based cyclometalated ligand exhibit a tiny blue-shift when compared with  $(cf_3btp)_2Ir(tpip)$ . These experimental phenomena will be proved by DFT calculations discussed below.

The room-temperature emission spectra of complexes (thp)<sub>2</sub>Ir(tpip), (cf<sub>3</sub>thp)<sub>2</sub>Ir(tpip), (cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) and (3-cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) in degassed CH<sub>2</sub>Cl<sub>2</sub> solution are displayed in Fig. 3b, and the corresponding photophysical data (the emission wavelengths, lifetimes, quantum yields) are also summarized in Table 1. The complexes (cf<sub>3</sub>thp)<sub>2</sub>Ir(tpip) and (3cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) show a broad structureless emission, while complexes (thp)<sub>2</sub>Ir(tpip) and (cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) exhibit a structured emission band, despite the fact that complexes (cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) and (3-cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) are structural isomers. As expected, the emission maxima follow the  $(3-cf_3btp)_2Ir(tpip) < (thp)_2Ir(tpip) < (cf_3thp)_2Ir(tpip) < ($ order: cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip), in good agreement with those of the absorption spectra. This observation suggests that the electronic transitions of emissive excited states are the same with those of the lowest-energy absorption bands, which are a dominant <sup>3</sup>MLCT excited state and a weaker <sup>3</sup>LC contribution. To further prove the deduction, the emission lifetimes  $(\tau)$  of all complexes were measured in solution at room temperature. The relatively long lifetimes of 2.21–2.81  $\mu$ s indicate that the luminescence is derived from triplet excited states [31]. Furthermore, their photoluminescence quantum yields were determined based on the  $\Phi_{\rm em}$  value of the standard reference fac-Ir(ppy)<sub>3</sub> [32]. We found that the fluorine atoms in complexes (cf<sub>3</sub>thp)<sub>2</sub>Ir(tpip), (cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) and (3cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) play key role in the increasing of the phosphorescence quantum yield, which are similar with previously reported complexes in previous papers [33]. In particular, the quantum efficiency of complex  $(3-cf_3btp)_2Ir(tpip)$  (86.4%) is the highest one, possibly due to the steric hindrance of the C<sup>N</sup> cyclometalated ligand [34].

# 3.3. Theoretical calculations

To further investigate their electronic properties of complexes (thp)<sub>2</sub>Ir(tpip), (cf<sub>3</sub>thp)<sub>2</sub>Ir(tpip), (cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) and (3-cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip), density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed using the Gaussian 09 program. The most representative molecular frontier orbital diagrams for these complexes are presented in Fig. 4 and the compositions of the orbitals are listed in Table 2. The calculated spin-allowed electronic transitions are provided in Table S3, as well as the experimental absorption spectra data. For the investigated complexes, their HOMOs (highest occupied molecular orbital) are primarily composed of  $\pi$ -orbital of cyclometalated ligands (56.90–67.07%) with some contributions from  $d\pi$  orbital of the Ir(III) ion (29.96-39.26%). Meanwhile, their LUMOs (lowest unoccupied molecular orbital) are mostly located on  $\pi^*$ -orbital of cyclometalated ligands (83.47-89.41%). The LUMO-1 of (cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) has similar contribution with the LUMO, mainly comprised of  $\pi^*$  orbital of cyclometalated ligand (89.65%). Thus, the lowest-energy electronic transition of absorptions and the lowest-energy triplet excited state of emissions originating from HOMO→LUMO/LUMO+1 can be ascribed as MLCT and ILCT  $\pi \rightarrow \pi^*$  transition [35,36].

From Table 2 it can be seen that the HOMO energy levels of



Fig. 3. (a) Absorption spectra of complexes  $(thp)_2Ir(tpip)$ ,  $(cf_3thp)_2Ir(tpip)$ ,  $(cf_3btp)_2Ir(tpip)$  and  $(3-cf_3btp)_2Ir(tpip)$  in degassed  $CH_2Cl_2$  solution at 298 K  $(1.0 \times 10^{-5} \text{ mol L}^{-1})$  and (b) PL spectra of these iridium complexes in degassed  $CH_2Cl_2$  solution at 298 K.

Table 1

Photophysical, electrochemical and theoretical data for complexes (thp)<sub>2</sub>Ir(tpip), (cf<sub>3</sub>thp)<sub>2</sub>Ir(tpip), (cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) and (3-cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip).

Complex	$T_d(^{\circ}C)^a$	Absorption <sup>b</sup>	Emission	Electroch	Electrochemical and Theoretical Data					
		λ <sub>abs</sub> (nm)	$\lambda_{em}(nm)^{b}$	$\tau \; (\mu s)^b$	$\Phi_{\rm em}$ (%) <sup>c</sup>	E <sub>ox</sub> (eV)	$E_{opt, g} (eV)^d$	HOMO/LUMO (eV) <sup>e</sup>	HOMO/LUMO (eV) <sup>f</sup>	
$(thp)_2Ir(tpip)$ $(cf_3thp)_2Ir(tpip)$ $(cf_3btp)_2Ir(tpip)$ $(3-cf_3btp)_2Ir(tpip)$	345 350 355 388	229, 289, 323, 416, 472 229, 296, 340, 386, 439, 509 227, 297, 301, 357, 450, 530 229, 294, 309, 352, 477	571 598 652 568	2.21 2.63 2.81 2.66	40.5 63.6 69.4 86.4	0.90 1.12 1.00 1.16	2.63 2.57 2.34 2.6	- 5.70/-3.07 - 5.92/-3.35 - 5.80/-3.46 - 5.96/-3.36	- 4.97/-1.35 - 5.17/-1.85 - 5.13/-2.04 - 5.26/-1.90	

<sup>a</sup>  $T_d$ : decomposition temperature.

<sup>b</sup> Data were collected from degassed CH<sub>2</sub>Cl<sub>2</sub> solutions at room temperature.

<sup>c</sup> fac-Ir(ppy)<sub>3</sub> as referenced standard (0.4) [32].

<sup>d</sup> Calculated from the UV–vis absorption edges.

<sup>e</sup> Deduced from the equation HOMO =  $-(E_{ox} + 4.8 \text{ eV})$  and LUMO = HOMO +  $E_{opt,g}$ , respectively.

<sup>f</sup> Obtained from theoretical calculations.



Fig. 4. The frontier molecular orbital diagrams of complexes (thp)<sub>2</sub>Ir(tpip), (cf<sub>3</sub>thp)<sub>2</sub>Ir(tpip), (cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) and (3-cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) from DFT calculations.

#### Table 2

Frontier orbital energy and	electron density distributed	tion for complexes	(thp) <sub>2</sub> Ir(tpip),	$(cf_3thp)_2Ir(tpip),$	(cf <sub>3</sub> btp) <sub>2</sub> Ir(tpip) a	nd (3-cf <sub>3</sub> btp) <sub>2</sub> Ir(tpip).
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Complex	Orbital	Energy (eV)	Ir(III)	Cyclometalated ligand	Ancillary ligand
(thp) <sub>2</sub> Ir(tpip)	LUMO	-1.35	6.45	83.47	10.08
	НОМО	- 4.97	39.26	56.90	3.84
(cf <sub>3</sub> thp) <sub>2</sub> Ir(tpip)	LUMO	-1.85	6.17	89.41	4.42
	НОМО	-5.17	38.85	57.23	3.92
(cf <sub>3</sub> btp) <sub>2</sub> Ir(tpip)	LUMO+1	-2.03	6.53	89.65	3.82
	LUMO	-2.04	7.41	89.41	3.17
	НОМО	-5.13	33.06	63.99	2.95
(3-cf <sub>3</sub> btp) <sub>2</sub> Ir(tpip)	LUMO	-1.90	6.42	88.77	4.81
	НОМО	-5.26	29.96	67.07	2.97

complexes (thp)<sub>2</sub>Ir(tpip), (cf<sub>3</sub>thp)<sub>2</sub>Ir(tpip), (cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) and (3-cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) are calculated as -4.97, -5.17, -5.13 and -5.26 eV, respectively. The HOMO energies of (cf<sub>3</sub>thp)<sub>2</sub>Ir(tpip), (cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) and (3-cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) are significantly higher than that of (thp)<sub>2</sub>Ir (tpip), because the  $\pi$ -orbitals of the cyclometalated ligands are stabilized by the electron-withdrawing  $-CF_3$  group. Similar results have also been obtained for their LUMO levels (-1.35 eV for (thp)<sub>2</sub>Ir(tpip), -1.85 eV for (cf<sub>3</sub>thp)<sub>2</sub>Ir(tpip), -2.04 eV for (cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) and -1.90 eV for (3-cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip). In addition, the energy bandgap of (cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) (3.10 eV, HOMO-LUMO + 1) is smaller than (cf<sub>3</sub>thp)<sub>2</sub>Ir(tpip) (3.35 eV, HOMO-LUMO) is larger, thereby leading to red-shifted and blue-shifted in spectra, respectively. From this it appears that the calculated results could well explain the photophysical properties discussed above.

#### 3.4. Electrochemical properties

The electronic properties of complexes  $(thp)_2Ir(tpip)$ ,  $(cf_3thp)_2Ir(tpip)$ ,  $(cf_3btp)_2Ir(tpip)$  and  $(3-cf_3btp)_2Ir(tpip)$  were investigated by cyclic voltammetry (CV) to obtain their HOMO and LUMO energy levels. The electrochemical waves are shown in Fig. 5 and all calculated data are listed in Table 1. On the basis of their oxidation potentials, the HOMO and LUMO energy levels are estimated and summarized in Table 1, as well as DFT-calculated values for comparison purposes. All complexes exhibit a quasi-reversible oxidation peak in the region of 0.90–1.16 V, which corresponds to the Ir(III)/Ir(IV) redox couple with contributions from the cyclometalated ligands fragments, as already confirmed by DFT calculations (Table 2). With respect to complex (thp)<sub>2</sub>Ir(tpip), the attachment of electron-withdrawing  $-CF_3$  substituents on the pyridyl ring of the cyclometalated ligands in complexes



**Fig. 5.** Cyclic voltammograms for complexes  $(thp)_2Ir(tpip)$ ,  $(cf_3thp)_2Ir(tpip)$ ,  $(cf_3btp)_2Ir(tpip)$  and  $(3-cf_3btp)_2Ir(tpip)$  in CH<sub>2</sub>Cl<sub>2</sub> solution containing *n*-Bu<sub>4</sub>NClO<sub>4</sub> (0.1 M) at a sweep rate of 100 mV/s.

 $(cf_3thp)_2Ir(tpip)$ ,  $(cf_3btp)_2Ir(tpip)$  and  $(3-cf_3btp)_2Ir(tpip)$  gives rise to an anodic shift, the finding in accordance with the decreasing electron density around the Ir(III) center (Table 2) [37].

Furthermore, compared to (cf<sub>3</sub>thp)<sub>2</sub>Ir(tpip), the different extended conjugations in complexes (cf3btp)2Ir(tpip) and (3-cf3btp)2Ir(tpip) leads to different changes of oxidation potentials. As a result, the trend in oxidation potentials  $(E_{\rm ox})$ is  $(thp)_2 Ir(tpip) < (cf_3 btp)_2 Ir$  $(tpip) < (cf_3thp)_2Ir(tpip) < (3-cf_3btp)_2Ir(tpip)$ , while the order of the HOMO energy levels is  $(thp)_2Ir(tpip) > (cf_3btp)_2Ir(tpip) > (cf_3thp)_2Ir$  $(tpip) > (3-cf_3btp)_2Ir(tpip)$  (Table 1). Besides, the variation of the LUMO energy levels obtained from the HOMO and  $E_{opt,g}$  values is  $(thp)_2Ir(tpip) < (cf_3btp)_2Ir(tpip) < (cf_3thp)_2Ir(tpip) < (3-cf_3btp)_2Ir$ (tpip), in line with the theoretical findings. Notably, the HOMO/LUMO energy levels inferred from the CV data are systematically slightly lower than the DFT data (Table 1), which is consistent with the previous literature [38,39].

# 3.5. OLEDs performance

In order to investigate the electroluminescent (EL) properties, the monochrome OLED devices D1, D2 and D3 using complexes (thp)<sub>2</sub>Ir (tpip),  $(cf_3thp)_2Ir(tpip)$  and  $(cf_3btp)_2Ir(tpip)$  as the emitters were fabricated, respectively, with a simple architecture: ITO/MoO<sub>3</sub> (molybdenum oxide, 5 nm)/TAPC (30 nm)/2,6-DCzPPy: Ir(III) complex (2 wt%, 10 nm)/TmPyPB (40 nm)/LiF (1 nm)/Al (100 nm). The schematic energy levels diagram of phosphorescent OLEDs and the molecular structures of used materials are shown in Fig. 6. MoO<sub>3</sub> and LiF were used as hole-injection layer (HIL) and electron-injection layer (EIL), respectively. TAPC (4,4'-(cyclohexane-1,1-diyl)bis(N,N-di-p-tolylaniline)) was applied as hole transport/electron block layer (HTL/EBL) due to its good hole mobility  $(1.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$  and high LUMO level (-2.0 eV), while TmPyPB (1,3,5-tri[(3-pyridyl)-phen-3-yl] benzene) was used as electron transport/hole block layer (ETL/HBL) for its good electron mobility  $(1.0 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$  and low HOMO level (-6.7 eV). Meanwhile, the bipolar material 2,6-DCzPPy (2,6-bis (3-(9H-carbazol-9-yl)phenyl)pyridine) was employed as the host and buffer layer to achieve the cascade hole-injection from HTL to the emitting layer (EML) because its' nearly equal electron mobility ( $\mu_e$ ) and hole mobility ( $\mu_{\rm h}$ ) values (1-8 × 10<sup>-5</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at an electric field between  $6.0 \times 10^5$  and  $1.0 \times 10^6$  V cm<sup>-1</sup>), which benefits the electronhole balance in the EML [40-42].

The EL spectra, luminance (*L*) – voltage (V) – current density ( $C_d$ ), current efficiency ( $\eta_c$ ) – luminance (*L*) and external quantum efficiency (EQE) – luminance (*L*) characteristics of the OLEDs are displayed in Fig. 7, and the key EL data are summarized in Table 3. From Fig. 7a it should be noted that the EL emissions of the single EML device **D1** ~ **D3** were observed at 551, 575 and 654 nm, respectively. Compared with PL spectra of the corresponding Ir(III) complexes, the EL spectra are similar with the PL spectra of these complexes, which indicated the energy can be transferred from 2,6-DCzPPy host to the emitters. Obviously, the devices **D1** and **D3** display weak emission at 350–500 nm, which originates from the emission of 2,6-DCzPPy and means that the



Fig. 6. Energy level diagram of phosphorescent OLEDs and their molecular structures of used materials.



**Fig. 7.** Characteristics of devices **D1**, **D2** and **D3**: (a) normalized EL spectra at 8 V; (b) luminance (L) – voltage (V) – current density ( $C_d$ ); (c) current efficiency ( $\eta_c$ ) – luminance (L); (d) external quantum efficiency (EQE) – luminance (L).

#### Table 3 EL performance of single-EML devices D1 – D3.

Device	Emitter	V <sub>turn-on</sub> <sup>a</sup> (V)	$L_{max}^{b}$ (cd·m <sup>-2</sup> (V))	${\eta_c}^c \ (cd{\cdot}A^{-1})$	$\eta_p{}^c \text{ (lm-W^{-1})}$	EQE <sup>c</sup> (%)	$\lambda_{EL}^{d}$ (nm)	CIE <sup>e</sup> (x, y)
D1	(thp) <sub>2</sub> Ir(tpip)	3.9	15818(13.4)	38.3/33.6	17.5/13.8	11.3/10.0	551	(0.41, 0.49)
D2	(cf <sub>3</sub> thp) <sub>2</sub> Ir(tpip)	3.9	21934(13.6)	53.9/45.8	25.3/15.8	17.9/15.4	575	(0.53, 0.46)
D3	(cf <sub>3</sub> btp) <sub>2</sub> Ir(tpip)	4.0	6138(14.0)	9.1/6.1	6.1/2.0	10.8/7.3	654	(0.56, 0.28)

<sup>a</sup> Turn-on voltage recorded at a luminance of  $1 \text{ cd m}^{-2}$ .

<sup>b</sup> Maximum luminance.

<sup>c</sup> Data at maximum and 1000 cd m<sup>-2</sup> for current efficiency ( $\eta$ c), power efficiency ( $\eta$ p), and EQE, respectively.

<sup>d</sup> Values were collected at 8 V.

<sup>e</sup> CIE (Commission Internationale de l'Eclairage) coordinates (CIE) at 8 V.

energy and/or charge transfer from the host to the phosphor is not complete upon electrical excitation, which is possibly due to the great difference between dopants and host. Their corresponding Commission Internationale de L'Eclairage (CIE) coordinates operated at 8 V are (0.41, 0.49), (0.53, 0.46) and (0.56, 0.28), respectively, which are corresponded to the yellow, orange and deep-red light.

Due to the similar molecular structures of these phosphorescent materials, their EL performance are mainly depend on their photophysical ( $\phi_{em}$  especially) and electrochemical properties [43]. For the device **D1**, a maximum current efficiency ( $\eta_{c,max}$ ) of 38.3 cd A<sup>-1</sup> with an external quantum efficiency (EQE<sub>max</sub>) of 11.3%, a maximum power efficiency  $(\eta_{p,max})$  of 17.5 lm·W<sup>-1</sup> and a maximum luminance  $(L_{max})$  of 15818 cd m<sup>-2</sup> were obtained, respectively. Compared with the device D1, the device D2 using  $(cf_3thp)_2Ir(tpip)$  as the emitter has better EL performance with the  $L_{\text{max}}$  of 21934 cd m<sup>-2</sup>, a  $\eta_{c,\text{max}}$  of 53.9 cd A<sup>-1</sup>, a  $\eta_{p,max}$  of 25.3 lm·W<sup>-1</sup> and an EQE<sub>max</sub> of 17.9%, respectively. Furthermore, the device **D2** still remains high efficiency even at relatively high luminance with a low efficiency roll-off. For instance, even at a luminance of 1000 cd m<sup>-2</sup>, the device **D2** still retains high EQE ( $\eta_c$ ,  $\eta_p$ ) of 15.4% (45.8 cd A<sup>-1</sup>, 15.8 lm W<sup>-1</sup>). The higher  $\Phi_{\rm em}$  value of the emitter  $(cf_3thp)_2Ir(tpip)$  ( $\Phi = 64.9\%$ ) than that of  $(thp)_2Ir(tpip)$  ( $\Phi = 40.5\%$ ) may be the main reason for the better EL performance of the device D2 than that of the device D1. The device D3 using the deep red light phosphorescent material  $(cf_3btp)_2Ir(tpip)$  ( $\Phi = 69.4\%$ ) also exhibited good performance with the  $L_{\text{max}}$ ,  $\eta_{\text{c,max}}$ ,  $\eta_{\text{p,max}}$  and EQE<sub>max</sub> of 6138 cd m<sup>-2</sup>, 9.1 cd A<sup>-1</sup>, 6.1 lm·W<sup>-1</sup> and 10.8%, respectively. It is noteworthy that the EL performances of the device D3 are obviously lower than **D2**, which may be attributed to the difference excited state lifetimes of (cf<sub>3</sub>thp)<sub>2</sub>Ir(tpip) (2.81 µs) and (cf<sub>3</sub>btp)<sub>2</sub>Ir(tpip) (2.63 µs). The longer lifetime will lead to exciton quenching through triplet-triplet annihilation (TTA) and triplet-polaron annihilation (TPA) effects, which would result in relatively poor EL performances. Furthermore, the emission band of D3 lasts to the near infrared (NIR) region, the efficiency measured with the normal photodetector is much lower than that in the yellow and orange regions. When the luminance rises to 1000 cd m<sup>-2</sup>, the EQE and the  $\eta_c$  of the device **D3** are remained as 7.3% and  $6.1 \text{ cd A}^{-1}$ . In general, the good device performance should be attributed to the application of tpip as the ancillary ligand, which would results in good electron mobility of Ir(III) complexes caused by the P=O bonds, and the emitters with good electron mobility will lead to a well-balanced charge carrier transport and efficient recombination.

# 4. Conclusion

In summary, four phosphorescent bis-cyclometalated 2-(2-thienyl) pyridine-based Ir(III) complexes:  $(thp)_2Ir(tpip)$ ,  $(cf_3thp)_2Ir(tpip)$ ,  $(cf_3btp)_2Ir(tpip)$  and  $(3-cf_3btp)_2Ir(tpip)$  were developed. By introducing  $-CF_3$  group, increasing  $\pi$ -conjugation system and/or changing phenyl connection position of the cyclometalated ligands, the emission colors of these Ir(III) complexes can be adjusted from yellow to deep red in CH<sub>2</sub>Cl<sub>2</sub> solution at 298 K. Due to the HOMOs and LUMOs are primarily located on the metal center and cyclometalated ligands, the variation of the cyclometalated ligands can affect their photophysical and

electrochemical properties. The phosphorescent OLEDs comprising  $(thp)_2Ir(tpip)$ ,  $(cf_3thp)_2Ir(tpip)$  and  $(cf_3btp)_2Ir(tpip)$  as yellow, orange, and deep red dopants realize state-of-art device performance with EQE<sub>max</sub> of 11.3%, 17.9% and 10.8% and low efficiency roll-off, which still remain high EQE of 10.0%, 15.4% and 7.3% at a luminance of 1000 cd m<sup>-2</sup>, respectively. These results suggest that the rational design of Ir(III) complexes based on 2-(2-thienyl)pyridine derivatives is an effective method for the development of high performance OLEDs.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2018.11.017.

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