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# Novel yellow phosphorescent iridium complexes with dibenzothiophene-S, S-dioxide-based cyclometalated ligand for white polymer light-emitting diodes



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# ABSTRACT

We have designed and synthesized two novel yellow phosphorescent iridium complexes using dibenzothiophene-S,S-dioxide-based cyclometalated ligand for the first time, which are capable of producing highly efficient yellow and white polymer light-emitting devices (PLEDs). The resulted iridium complexes display good thermal stability and high photoluminescence quantum yields. Both yellow and white PLEDs are fabricated with an identical single-emission-layer configuration of ITO/PEDOT:PSS/emission layer (EML)/CsF/Al. For the yellow phosphorescent PLEDs based on (*p*-CzFSOPy)<sub>2</sub>IrPic, the best device performances with a peak luminous efficiency (LE) of 13.3 cd/A and a peak external quantum efficiency (EQE) of 5.3% are achieved. More importantly, the two-element WPLEDs containing iridium (III)bis (2-(4,6-difluorophenyl)-pyridinato-N,C<sup>2'</sup>) picolinate (FIrpic) as blue and (*p*-CzFSOPy)<sub>2</sub>IrPic as yellow phosphors doped into a PVK:OXD-7 matrix at an appropriate ratio exhibited a maximum LE of 19.2 cd/A, a maximum EQE of 9.6%, an extremely high luminance of 18717 cd/m<sup>2</sup> and Commission Internationale de L'Eclairage (CIE) coordinate of (0.317, 0.448). Moreover, at a luminance for practical application of 1000 cd/m<sup>2</sup>, the LE still remains as high as 19.0 cd/A, with a very slight decrease.

efficiency (PE), luminous efficiency (LE).

for the fabrication of the low-cost devices because of its greater ease of processing and large-area manufacturability [7,16–19]. However,

WPLEDs display much poorer device performance in terms of power

is most effective due to its demonstrated potential for achieving nearly

100% internal quantum efficiency by harvesting both singlet and triplet

excitons [5,20,21]. Compared to other phosphorescent emitters, cyclometalated iridium complexes are of paramount importance in the

field because of their short lifetime in excited states and high phos-

phorescent efficiencies for highly efficient OLEDs [22-24]. Up to date,

most of the high-performance WPLEDs ever reported are based on so-

lution-processed dye-doped systems, in which iridium complexes are

In order to obtain high-efficiency WPLEDs, electrophosphorescence

# 1. Introduction

White organic light-emitting devices (WOLEDs) have become of considerable commercialization interest in recent years for their potential applications in next-generation full color displays, back lighting of flat-panel displays and solid-state lighting [1–10]. In order to generate the desired white-light emission based on polymers and small molecules, the hybrids of three primary colors (red, green and blue) or two complementary colors, for example, blue and yellow, are typically required, and several methods and technologies are adopted towards realizing WOLEDs [6,11–15]. Compared to the WOLEDs fabricated by vacuum-deposition technologies, white polymer light-emitting devices (WPLEDs) fabricated by solution-processing technique, is more feasible

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doped into polymer (for example poly (N-vinylcarbazole) (PVK)) as emissive materials [11,25-27]. As a result, the WPLEDs with a combination of efficient electrophosphorescent blue and yellow emitters will likely optimize the efficiencies and simplify the device fabrication process. Unfortunately, to our best knowledge, the highly efficient yellow emitting iridium complexes have been reported rarely in the spin-coated WPLEDs [18,28]. For example, Wu et al. reported WPLEDs with single emitting layers containing skyblue emitting iridium (III)bis (2-(4,6-difluorophenyl)-pyridinato-N,C<sup>2'</sup>)picolinate (FIrpic) and some yellow emitting fluorine-based iridium complexes doped into a PVK:OXD-7 matrix, which exhibited an extremely high luminous efficiency (LE) of 42.9 cd/A. However, the device displayed warm white light with the Commission Internationale de L'Eclairage (CIE) coordinates of (0.395, 0.452) [12]. We have synthesized several yellow phosphorescent iridium complexes with triphenylamine- and fluorenefunctionalized cyclometalating ligands. The WPLEDs based on the synthesized iridium complex and FIrpic exhibited the maximal LE of 14.7 cd/A with a CIE coordinates of (0.33, 0.42) [29]. The CIE coordinates are very close to the ideal pure white color, but the device performances are not very high. Thus, the design and synthesis of new functional organic ligands for the iridium metal core is highly desirable in order to improve the efficiency and color purity of the WPLEDs.

On another aspect, the charge balance of electrons and holes are also becoming an important issue for a new breakthrough in OLED research. Along this line, we and others are interested in developing some multi-component systems capable of performing separate functional roles in a single molecule [30-32]. As we know, the electrondeficient dibenzothiophene-S,S-dioxide moiety was demonstrated to be beneficial for increasing electron affinity and fluorescence efficiency, and improving the electron transporting properties of materials [33–35]. As it has two reaction sites, it can be easily substituted with various electron-donating moieties such as carbazoles and triarvlamines, and altered its intrinsic electronic characteristics [36,37]. On the other hand, carbazole has a rigid molecular frame and good holetransport properties. Carbazole have been extensively used as the holetransporting (HT) components in the construction of numerous photoand electroluminescent devices [38,39]. However, there has been no report on the use of structures containing carbazole and dibenzothiophene-S,S-dioxide moieties in iridium complexes and their corresponding PLEDs.

In this paper, we have coupled carbazolyl and pyridinyl units to the dibenzothiophene-S,S-dioxide rings as the cyclometalated ligand of iridium complexes for the first time. Based on that, two novel yellow phosphorescent iridium complexes are synthesized. The photophysical, electrochemical and thermal properties, as well as electroluminescent properties of the resulting iridium complexes were discussed. We also have successfully fabricated a highly efficient WPLED based on (*p*-CzFSOPy)<sub>2</sub>IrPic in combination with the blue phosphor FIrpic to produce a white light source with CIE coordinate of (0.317, 0.448). The maximum LE of the WPLEDs can reach 19.2 cd/A.

# 2. Experimentals

### 2.1. Materials

9-butyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-carbazole was prepared according to the reported procedures [40]. All reactions were performed under nitrogen. All solvents were carefully dried and distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated.

## 2.1.1. Synthesis of dibenzothiophene S,S-dioxide (1) [41]

A mixture of dibenzothiophene (3.7 g, 20 mmol), hydroperoxide (33%, 8.0 mL) and glacier acetic acid (50 mL) was refluxed for 3 h. The reaction mixture was poured into a large amount of water, filtered, and

the solid was collected. The crude product was recrystallized with chloroform to afford a white solid (4.1 g, 95%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.96 (d, J = 8.6 Hz, 2H), 7.65 (d, J = 9.8 Hz, 2H), 7.39–7.33 (m, 4H).

# 2.1.2. Synthesis of 3,7-dibromodibenzothiophene S,S-dioxide (2) [42]

At 0 °C, 3.89 g (18.0 mmol) of dibenzothiophene S,S-dioxide dissolved in 120 mL of H<sub>2</sub>SO<sub>4</sub>, and then 8.0 g (45 mmol) of NBS was added to the mixture and stirred for 10 h. The reaction was quenched by addition of water (40 mL) and extracted by dichloromethane (3 × 20 mL). The organic layer was dried with anhydride Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed in vacuo. The residue was purified by flash column chromatography to afford 5.86 g of white powder with a yield of 87%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.93 (s, 2H), 7.78–7.76 (d, *J* = 10 Hz, 2H), 7.64–7.62 (d, *J* = 8.4 Hz, 2H).

#### 2.1.3. Synthesis of 2,8-dibromodibenzothiophene (3) [43]

To a solution of dibenzothiophene (9.2 g, 50.0 mmol) in chloroform (100 mL), bromine (7.7 mL, 150 mmol) was dropwise added at 0 °C by stirring. Under nitrogen atmosphere the reaction mixture was stirred and kept overnight at room temperature. Saturated NaHSO<sub>3</sub> aqueous solution was added to the mixture. Then, the crude product was filtered off and washed with methanol to isolate 2,8-dibromodibenzothiophene (**3**). The product was obtained as a white powder in 67% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$ ppm: 8.22 (s, 2H), 7.71–7.69 (d, *J* = 8.4 Hz, 2H), 7.58–7.56 (dd, *J* = 10.4 Hz, 2H).

#### 2.1.4. Synthesis of 2,8-dibromodibenzothiophene S,S-dioxide (4)

A mixture of **3** (6.8 g, 20 mmol), hydroperoxide (33%, 15.0 mL), THF (120 mL) and glacier acetic acid (150 mL) was refluxed for 6 h. The reaction mixture was poured into a large amount of water, filtered, and the solid was collected. The crude product was recrystallized with chloroform to afford a white solid (6.1 g, 81%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 7.93 (s, 2H), 7.71 (s, 4H).

# 2.1.5. Synthesis of 3-bromo-7-(9-butyl- carbazol -3-yl) dibenzothiophene S,S-dioxide (5)

A mixture of  $Pd(PPh_3)_4$  (578 mg, 0.5 mmol), 3.7-dibromodibenzothiophene dioxide (2.17 g, 5.8 mmol), 9-butyl-3-(4,4,5,5tetramethyl-1,3,2-dioxaborolan-2-yl)-carbazole (1.02 g, 2.92 mmol), THF (150 mL) and 2.0 MK<sub>2</sub>CO<sub>3</sub> solution (20 mL) was degassed and heated to 90 °C with vigorously stirring for 24 h under N2 flow protection. After cooled to room temperature, the mixture was poured into water. The organic phase was separated and the aqueous phase was extracted with diethyl ether (3  $\times$  30 mL). The combined organic layers were dried over MgSO4 and evaporated to remove the solvents under vacuum. The residue was purified by column chromatography (petroleum ether/dichloromethane = 18/1) to provide 5 (1.04 g) as white solid in 69% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 8.34 (s, 1H), 8.16–8.14 (d, J = 8.0 Hz, 2H), 7.98–7.96 (dd, J = 8.0 Hz, 2H), 7.82–7.80 (d, J = 8.0 Hz, 1H), 7.76–7.70 (m, 2H), 7.67–7.65 (d, J = 8.0 Hz, 1H), 7.53–7.43 (m, 3H), 7.30–7.28 (t, J = 7.4 Hz, 1H), 4.35-4.31 (t, J = 7.0 Hz, 2H), 1.92-1.85 (m, 2H), 1.48-1.38 (m, 2H), 0.98-0.95 (t, J = 7.4 Hz, 3H).

# 2.1.6. Synthesis of 2-bromo-8-(9-butyl- carbazol -3-yl) dibenzothiophene S,S-dioxide (6)

The compound 6 was prepared similarly to 5 from 2,8-dibromodibenzothiophene dioxide (1.58 g, 4.28 mmol) and 9-butyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-carbazole (0.75 g, 2.14 mmol). Yield: 0.68 g, 62%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 8.36 (s, 1H), 8.20–8.18 (d, J = 8.0 Hz, 1H), 8.06–8.04 (d, J = 8.4 Hz, 2H), 7.91–7.86 (q, 2H), 7.74–7.66 (m, 3H), 7.54–7.45 (m, 3H), 7.31–7.28 (t, J = 7.4 Hz, 1H), 4.38–4.34 (t, J = 7.2 Hz, 2H), 1.94–1.86 (m, 2H), 1.46–1.40 (m, 2H), 0.99–0.96 (t, J = 7.4 Hz, 3H).

# 2.1.7. Synthesis of 3-(pyridin-2-yl)-7-(9- butyl-carbazol-3-yl) dibenzothiophene S,S-dioxide (p-CzFSOPy) [44]

2-(tributylstannyl)pyridine (0.46 g, 1.24 mmol) and 5 (0.64 g, 1.24 mmol) were mixed in dry toluene (50 mL) and  $Pd(PPh_3)_4$  (71.6 mg, 0.06 mmol) was then added to the solution to carry out the Stille-type coupling. The resulting mixture was stirred at 110 °C for 24 h. After cooling to room temperature, the reaction mixture was poured into a separating funnel and CH<sub>2</sub>Cl<sub>2</sub> (100 mL) was added followed by washing with water (3  $\times$  50 mL). The organic phase was dried over MgSO<sub>4</sub>. Then the solvent was removed and the crude product was purified by column chromatography eluting with petroleum ether/dichloromethane = 3/2. The title product was obtained as a white solid (0.48 g, 75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 8.75–8.74 (d. J = 4.4 Hz, 1H), 8.48 (s, 1H), 8.41–8.39 (d, J = 8.0 Hz, 1H), 8.37 (s, 1H), 8.19–8.16 (d, J = 11.6 Hz, 2H), 8.00–7.98 (dd, J = 8.0 Hz, 1H), 7.93-7.89 (m, 2H), 7.83-7.82 (m, 2H), 7.76-7.73 (dd, J = 10.4 Hz, 1H), 7.53–7.44 (m, 3H), 7.34–7.27 (m, 2H), 4.37–4.33 (t, J = 7.2 Hz, 2H), 1.93–1.86 (m, 2H), 1.46–1.40 (m, 2H), 0.99–0.95 (t, J = 7.4 Hz, 3H).

# 2.1.8. Synthesis of 2-(pyridin-2-yl)-8-(9- butyl-carbazol -3-yl) dibenzothiophene S,S-dioxide (m-CzFSOPy)

The compound *m*-CzFSOPy was prepared similarly to *p*-CzFSOPy from 2-(tributylstannyl)pyridine (0.32 g, 0.87 mmol) and 6 (0.45 g, 0.87 mmol). Yield: 0.34 g, 77%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  (ppm): 8.82–8.81 (d, *J* = 4.8 Hz, 1H), 8.73 (s, 1H), 8.41–8.39 (d, *J* = 9.2 Hz, 1H), 8.28 (s, 1H), 8.22–8.20 (d, *J* = 7.6 Hz, 1H), 8.11–8.09 (d, *J* = 8.0 Hz, 1H), 7.96–7.86 (m, 3H), 7.78–7.76 (dd, *J* = 8.4 Hz, 1H), 7.71–7.69 (m, 1H), 7.53–7.49 (m, 3H), 7.44–7.40 (m, 2H), 7.30–7.27 (m, 1H), 4.38–4.34 (t, *J* = 7.0 Hz, 2H), 1.94–1.88 (m, 2H), 1.70–1.65 (m, 2H), 0.99–0.96 (t, *J* = 7.2 Hz, 3H).

## 2.1.9. Synthesis of (p-CzFSOPy)<sub>2</sub>IrPic

To a mixture of iridium trichloride hydrate (120 mg, 0.34 mmol) and water (15 mL) was added *p*-CzFSOPy (386 mg, 0.75 mmol) and 2-ethoxyethanol (45 mL). The mixture was heated to reflux under an inert gas atmosphere for 20 h. After cooled to temperature, the colored precipitate was filtered off and washed respectively with water, ethanol and petroleum ether. The resulting dimer was obtained as a yellow solid (420 mg). The dimer was directly used in the following procedure.

A mixture of the foregoing dimer (420 mg, 0.17 mmol), picolinic acid (62 mg, 0.51 mmol) and Na<sub>2</sub>CO<sub>3</sub> (540 mg) was heated under reflux under an inert gas atmosphere in 2-ethoxyethanol (40 mL) for 16 h. After cooled to room temperature, the mixture was extracted with dichloromethane and the combined organic layer was dried over anhydrous magnesium sulfate. The crude product was purified by dry flash silica gel column (dichloromethane/ethyl acetate = 3/1 as eluent) to gain the target product (902 mg) as yellow solid in 65% yeild. <sup>1</sup>H NMR (400 MHz, DMSO, TMS)  $\delta$  (ppm): 8.73–8.69 (m, 6H), 8.63 (s, 1H), 8.34 (s, 1H), 8.31 (s, 1H), 8.29-8.26 (dd, J = 12.0 Hz, 2H), 8.21-8.19 (m, 4H), 8.07–8.04 (t, J = 6.0 Hz, 2H), 7.88–7.83 (t, J = 9.2 Hz, 3H), 7.76 (s, 1H), 7.66–7.63 (m, 4H), 7.59–7.57 (d, J = 8.4 Hz, 2H), 7.54–7.52 (d, J = 8.0 Hz, 1H), 7.48–7.42 (m, 4H), 7.24–7.20 (t, J = 7.4 Hz, 2H), 6.92 (s, 1H), 6.66 (s, 1H), 4.40–4.36 (t, J = 6.8 Hz, 4H), 1.75–1.71 (m, 4H), 1.29–1.22 (m, 4H), 0.86–0.82 (t, J = 8.6 Hz, 6H). <sup>13</sup>C NMR (DMSO, 100 MHz) δ (ppm): 172.12, 165.88, 165.29, 160.15, 158.14, 150.75, 149.30, 147.56, 146.96, 143.90, 141.03, 140.68, 140.64, 139.77, 132.36, 131.27, 130.50, 130.10, 128.82, 128.34, 126.57, 124.98, 122.75, 121.20, 119.37, 117.97, 110.32, 109.98, 42.62, 31.16, 20.23, 14.14. Anal. Calcd. for C70H50IrN5O6S2: C, 64.01; H, 3.84; N, 5.33; Found: C, 63.95; H, 3.65; N, 5.45. MALDI-TOF (*m*/*z*): calcd for [M]<sup>+</sup> 1313.2832, found  $[M + Na]^+$  1336.2686.

# 2.1.10. Synthesis of (m-CzFSOPy)<sub>2</sub>IrPic

The compound (*m*-CzFSOPy)<sub>2</sub>IrPic was prepared similarly to (*p*-CzFSOPy)<sub>2</sub>IrPic from *m*-CzFSOPy (296 mg, 0.58 mmol) and iridium

trichloride hydrate (92 mg, 0.26 mmol). Yield: 258 mg, 68%. <sup>1</sup>H NMR (400 MHz, DMSO, TMS)  $\delta$  (ppm): 9.00 (s, 1H), 8.96 (s, 1H), 8.74–8.68 (m, 7H), 8.32–8.18 (m, 6H), 7.96–7.90 (m, 6H), 7.84–7.81 (t, J = 5.8 Hz, 2H), 7.78–7.76 (dd, J = 12.8 Hz, 2H), 7.69–7.64 (m, 4H), 7.54–7.48 (q, 3H), 7.29–7.25 (t, J = 7.4 Hz, 2H), 6.60 (s, 1H), 6.41 (s, 1H), 4.47–4.44 (t, J = 6.2 Hz, 4H), 1.80–1.77 (m, 4H), 1.33–1.28 (m, 4H), 0.90–0.86 (t, J = 7.4 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm): 172.03, 165.83, 165.24, 154.03, 152.04, 150.86, 149.81, 149.06, 148.56, 147.82, 141.20, 140.79, 140.00, 139.87, 138.43, 137.83, 133.35, 130.18, 129.71, 128.07, 126.11, 125.54, 122.67, 121.11, 119.55, 118.82, 110.34, 110.12, 42.67, 31.21, 20.26, 14.20. Anal. Calcd. for C<sub>70</sub>H<sub>50</sub>IrN<sub>5</sub>O<sub>6</sub>S<sub>2</sub>: C, 64.01; H, 3.84; N, 5.33; Found: C, 64.36; H, 3.78; N, 5.39. MALDI-TOF (*m*/*z*): calcd for [M] <sup>+</sup> 1313.2832, found [M + Na] <sup>+</sup> 1336.2709.

# 2.2. Measurements and characterization

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer operating respectively at 400 and 100 MHz at room temperature. Chemical shifts were reported as  $\delta$  values (ppm) relative to an internal tetramethylsilane (TMS) standard. Time-of-flight mass spectrometry (TOF-MS) was performed in the positive ion mode with a matrix of dithranol using a Bruker-autoflex III smartbeam. Thermogravimetric analysis (TGA) was measured on a Diamond TG/ DTA instrument under nitrogen atmosphere at a heating rate of 20 °C  $min^{-1}$  and  $T_d$  was reported as the temperatures at 5% weight losses. UV-vis absorption spectra were measured on a Hitachi U-3310 spectrophotometer. PL spectra were recorded on an LS55 luminescence spectrometer (PerkinElmer, UK). Emission life times were obtained on a FLS 980 (Edinburgh Instruments Ltd.) combined fluorescence lifetime and steady state spectrometer in CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature. The absolute photoluminescence quantum yield ( $\Phi_P$ ) was measured with a Hamamatsu absolute PL quantum yield spectrometer equipped with an integrating sphere (Quantaurus-QY, C11347). Cyclic voltammetry was carried out on a CHI660A electrochemical workstation in a solution of tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) (0.1 M) in acetonitrile at a scan rate of 50 mV/s at room temperature under the protection of argon. A platinum electrode was used as the working electrode. A Pt wire was used as the counter electrode, and a calomel electrode was used as the reference electrode.

#### 2.3. Theoretical calculations

The geometries of both iridium complexes  $(p-CzFSOPy)_2$ IrPic and  $(m-CzFSOPy)_2$ IrPic at the gas phase were fully optimized by the density functional theory (DFT) method at the 6-31G\* basis set with B3LYP functional [45,46] without any symmetry constraints by using the Gaussian 09 software package [47].

# 2.4. PLEDs fabrication and measurements

The ITO-coated glass substrates were ultrasonically cleaned with deionized water, acetone, detergent, deionized water, and isopropyl alcohol. Then a layer of 40 nm thick poly (3,4-ethylenedioxythiophene): poly (styrene sulfonic acid) (PEDOT:PSS) (H.C.Stack, 4083) was spin-coated onto the pre-cleaned and O<sub>2</sub>-plasma-treated ITO substrates. After that, the PEDOT:PSS layer was baked at 150 °C for 20 min to remove residual water, and then the devices were moved into a glove box under the argon-protected environment. A mixture of the iridium complex with PVK + PBD or OXD-7 (30%) (30 mg mL<sup>-1</sup> in *o* DCB) were spin-coated onto PEDOT:PSS at the speed of 2000 rpm to yield 90 nm thickness light emitting layers. The samples were transferred into a chamber and kept under vacuum ( $3.0 \times 10^{-4}$  Pa) for 2 h. Then caesium fluoride (CsF) with a thickness of 2.5 nm and aluminium with a thickness of 100 nm were subsequently deposited on top of the EML to form the cathode. The current density (*J*) and brightness (*L*)



Scheme 1. Synthetic routes to (*p*-CzFSOPy)<sub>2</sub>IrPic and (*m*-CzFSOPy)<sub>2</sub>IrPic.

versus voltage (*V*) data were collected using a Keithley 236 source meter and silicon photodiode. After typical encapsulation with UV epoxy and cover glass, the devices were taken out from the dry box and the luminance was calibrated by a PR-705 SpectraScan Spectrophotometer (Photo Research) with simultaneous acquisitions of the EL spectra.

#### 3. Results and discussion

## 3.1. Synthesis and characterization

The synthesis of iridium complexes (p-CzFSOPy)<sub>2</sub>IrPic and (m-CzFSOPy)<sub>2</sub>IrPic are shown in Scheme 1. Dibenzothiophene S,S-dioxide (1) was synthesized by oxidation of dibenzothiophene into S,S-dioxide derivative after refluxing for 3 h in a mixture of hydrogen peroxide and acetic acid (H<sub>2</sub>O<sub>2</sub>/HOAc), and then 3,7-dibromodibenzothiophene S,Sdioxide (2) was obtained with a bromination reaction using sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and N-bromosuccinimide (NBS) at 0 °C in 87% yield. Contrast to the synthesis of 2, 2,8-dibromodibenzothiophene S,S-dioxide (3) could be prepared by first bromination of dibenzothiophene with bromine and then oxidation of the resulting bromide with  $H_2O_2$ . Compound 5 was obtained by a Pd-catalyzed Suzuki coupling of compouned 2 with 0.5 equiv of 9-butyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-carbazole. Stille-type cross-coupling of 5 with 2-(tributylstannyl)pyridine in toluene, in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> afforded the cyclometalated ligand of p-CzFSOPy in 75% yield. The final iridium complex (p-CzFSOPy)<sub>2</sub>IrPic was prepared in a two-step procedure [48-50]: the first step is IrCl<sub>3</sub>·nH<sub>2</sub>O reacted with an excess of p-CzFSOPy to give a chloride-bridged iridium dimmer [(C^N)<sub>2</sub>IrCl]<sub>2</sub>; the second step is a chloride-cleavage of the iridium dimer with 3 equiv of picolinic acid. The iridium complex (m-CzFSOPy)<sub>2</sub>IrPic was synthesized by the similar procedure of (p-CzFSOPy)<sub>2</sub>IrPic. Purification of the mixtures by silica chromatography furnished (p-CzFSOPy)<sub>2</sub>IrPic and (m-CzFSOPy)<sub>2</sub>IrPic as an air-stable yellow powder in high purity. Both the desired iridium complexes were confirmed by <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy, elemental analysis (EA) and mass (MS) spectrometry.

#### 3.2. Photophysical properties

The photophysical properties of iridium complexes (*p*-CzFSOPy)<sub>2</sub>IrPic and (*m*-CzFSOPy)<sub>2</sub>IrPic in CH<sub>2</sub>Cl<sub>2</sub> solution were investigated. The absorption and photoluminescence (PL) spectra of (*p*-CzFSOPy)<sub>2</sub>IrPic and (*m*-CzFSOPy)<sub>2</sub>IrPic at room temperature are shown in Fig. 1 and relevant data are presented in Table 1. The intense peaks



**Fig. 1.** Normalized UV–vis absorption and PL spectra of (*p*-CzFSOPy)<sub>2</sub>IrPic and (*m*-CzFSOPy)<sub>2</sub>IrPic in CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature.

#### Table 1

Photophysical, electrochemical and therma	l data of	( <i>p</i> -CzFSOPy) <sub>2</sub> IrPic and	( <i>m</i> -CzFSOPy) <sub>2</sub> IrPic.
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Complexes	$\lambda_{abs}$ [a] (nm)	$\lambda_{PL}[a]$ (nm)	${\it \Phi}_{\rm p}$ (%)	$τ_{\rm p}$ (μs)	$E_{\rm ox}[b]$ (V)	HOMO (eV)	LUMO (eV)	$E_{\rm g}~({\rm eV})$	<i>T</i> <sub>d</sub> (°C)
(p-CzFSOPy) <sub>2</sub> IrPic	275, 322, 394, 456	558	45.6	0.62	0.78	- 5.58	- 3.00	2.58	443
(m-CzFSOPy) <sub>2</sub> IrPic	293, 338, 476	554	38.1	0.64	0.72	- 5.52	- 2.91	2.61	434

[a]Measured in CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature. [b] Measured in a solution of Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) in acetonitrile at a scan rate of 50 mV/s at room temperature.



Fig. 2. The electron density distributions of HOMO and LUMO orbitals of (*p*-CzFSOPy)<sub>2</sub>IrPic (left) and (*m*-CzFSOPy)<sub>2</sub>IrPic (right) complexes.

in the short wavelength region below 420 nm are attributed to the spinallowed ligand-centered  ${}^{1}\pi$ - $\pi^{*}$  transition and the weaker absorption tails that appeared above 420 nm are assigned to an admixture of spinallowed singlet and spin-forbidden triplet metal-ligand-charge-transfer (<sup>1</sup>MLCT and <sup>3</sup>MLCT) excited states [48,50,51]. The admixture of <sup>1</sup>MLCT and <sup>3</sup>MLCT band was generated by the strong spin-orbital coupling which was induced by heavy-metal effect of Ir center between the singlet and triplet manifolds. Minor differences of PL profiles are observed for (p-CzFSOPy)2IrPic and (m-CzFSOPy)2IrPic in neat film. Both (p-CzFSOPy)<sub>2</sub>IrPic and (m-CzFSOPy)<sub>2</sub>IrPic displayed strong yellow phosphorescence emission and exhibited maximal emission at 558 and 554 nm, respectively, which are mainly characteristic of MLCT emission. Compared to (m-CzFSOPy)2IrPic, (p-CzFSOPy)2IrPic exhibited a little red-shifted emission with ca. 4 nm. This is owing to the longer conjugated  $\pi$  system in the cyclometalating ligand of (*p*-CzFSOPy)<sub>2</sub>IrPic than that of (m-CzFSOPy)<sub>2</sub>IrPic. The absolute photoluminescence quantum yields  $(\Phi_P)$  for (p-CzFSOPy)<sub>2</sub>IrPic and (m-CzFSOPy)<sub>2</sub>IrPic in CH<sub>2</sub>Cl<sub>2</sub> solution are measured by integrating sphere method (Table 1). The values of (p-CzFSOPy)2IrPic and (m-CzFSOPy)2IrPic were recorded to be 45.6 and 38.1%, respectively, suggesting they are evidently affected by the substituted positions of the pyridine- and carbazole-group at the aromatic ring of dibenzothiophene S,S-dioxide cores. The emission lifetimes (7p) in CH2Cl2 of (p-CzFSOPy)2IrPic and (m-CzFSO-Py)2IrPic were well fitted to a single-exponential decay at room temperature and measured as 0.62 µs and 0.64 µs, respectively (Fig. S1, ESI<sup>†</sup>). Accordingly, the radiative lifetimes ( $\tau_r$ ) of the triplet excited state were 1.36 µs for (p-CzFSOPy)<sub>2</sub>IrPic and 1.68 µs for (m-CzFSOPy)<sub>2</sub>IrPic, deduced from  $\tau_r = \tau_p/\Phi_p$ . The triplet radiative and non-radiative rate constant ( $k_{\rm r}$  and  $k_{\rm nr}$ ) are calculated from  $\Phi_{\rm p}$  and  $\tau_{\rm p}$ , using the expressions  $\Phi_{\rm p} = \Phi_{\rm ISC} [k_{\rm r}/(k_{\rm r} + k_{\rm nr})]$  and  $\tau_{\rm p} = (k_{\rm r} + k_{\rm nr})^{-1}$ , where the intersystem-crossing yield ( $\Phi_{\rm ISC}$ ) is safely assumed to be 1.0 for metal phosphors with strong heavy-atom effect. We obtained  $k_r$  and  $k_{nr}$  of  $7.35 \times 10^5$  and  $8.78 \times 10^5$  s<sup>-1</sup> for (*p*-CzFSOPy)<sub>2</sub>IrPic and  $5.95 \times 10^5$ and 9.68  $\times$  10<sup>5</sup> s<sup>-1</sup> for (*m*-CzFSOPy)<sub>2</sub>IrPic, respectively. Since the  $\tau_{\rm p}$  of (p-CzFSOPy)<sub>2</sub>IrPic and (m-CzFSOPy)<sub>2</sub>IrPic are very short, triplet-triplet annihilation could be avoided in the OLEDs at high brightness [52]. The PL emission spectra of hosts (PVK, PBD and OXD-7) show good overlap with the absorption spectrum of (p-CzFSOPy)<sub>2</sub>IrPic, which indicates that efficient Förster energy transfer from hosts to (p-CzFSOPy)2IrPic guest can be expected (Fig. S2, ESI<sup>†</sup>) [53,54]. Compared to (p $CzFSOPy)_2IrPic$ , the overlaps between hosts' emission and (*m*-CzFSO-Py)\_2IrPic absorption are much smaller, which means that the Förster energy transfer would be inefficient.

## 3.3. Electrochemical properties and theoretical calculations

The electrochemical behaviours of (p-CzFSOPy)<sub>2</sub>IrPic and (m-CzFSOPy)<sub>2</sub>IrPic were studied by cyclic voltammetry (CV) using ferrocene as the internal standard and the results are listed in Table 1. Both the iridium complexes show reversible anodic waves at 0.78 V and 0.72 V, respectively, recorded relative to the ferrocence/ferrocenium (Fe/Fe<sup>+</sup>) couple, due to the oxidation of the iridium center. On the basis of these onset oxidation potentials  $(E_{ox})$  and the formula of  $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.8) \text{ eV} [55]$ , the highest occupied molecular orbital energies ( $E_{HOMO}$ ) were calculated to be -5.58 eV for (*p*-CzFSOPy)<sub>2</sub>IrPic and -5.52eV for (*m*-CzFSOPy)<sub>2</sub>IrPic, respectively. Otherwise, duo to the reduction waves of the newly synthesized iridium complexes are quite poor, the lowest unoccupied molecular orbital energies ( $E_{LUMO}$ ) had to be calculated based on the equation of  $E_{LUMO} = E_{HOMO} + E_{g}$ , in which energy gap  $(E_g)$  was estimated from the edge of UV-vis absorption spectra. As a result, the  $E_{LUMO}$  are -3.00 eV for  $(p-CzFSOPy)_2$ IrPic and -2.91 eV for  $(m\text{-CzFSOPy})_2$ IrPic.

To get deep insights into the structure-property relationship of the iridium complexes at the molecular level, the geometrical and electronic structures of the complexes were performed using density functional theory (DFT). The electron density distributions of both HOMO and LUMO for complexes (p-CzFSOPy)2IrPic and (m-CzFSOPy)2IrPic are illustrated in Fig. 2. It is clear that the HOMO orbitals are mainly contributed by the carbazole group, while the LUMO orbitals are mainly delocalized on the dibenzothiophene S.S-dioxide moiety and the central Iridium atom. The calculated energies of HOMOs for (p-CzFSOPy)<sub>2</sub>IrPic and (*m*-CzFSOPy)<sub>2</sub>IrPic are -5.46 eV and -5.38 eV, respectively. And, the corresponding energies of LUMOs for (p-CzFSO-Py)<sub>2</sub>IrPic and (m-CzFSOPy)<sub>2</sub>IrPic are -2.42 eV and -2.24 eV, respectively. Based on the calculated HOMO and LUMO energies for both iridium complexes, we found that the calculated HOMO-LUMO energy gap of (p-CzFSOPy)<sub>2</sub>IrPic (ca. 3.04 eV) is smaller than that of (m-CzFSOPy)<sub>2</sub>IrPic (ca. 3.14 eV), which is qualitatively consistent with the experimental evidence from CV and absorption measurement.

# 3.4. Thermal properties

The thermal stabilities of these iridium complexes were evaluated by thermogravimetric analysis (TGA) under a stream of N<sub>2</sub> with a scanning rate of 20 °C min<sup>-1</sup>. Their TGA curves are shown in Fig. 3 and their degradation temperatures ( $T_d$ ) for 5% weight loss are listed in Table 1. The recorded  $T_d$  level is 443 °C for (*p*-CzFSOPy)<sub>2</sub>IrPic and 434 °C for (*m*-CzFSOPy)<sub>2</sub>IrPic, respectively. Compared to (*m*-CzFSO-Py)<sub>2</sub>IrPic, (*p*-CzFSOPy)<sub>2</sub>IrPic exhibits a higher decomposition temperature, which indicates the different substituted-situation of dibenzothiophene S,S-dioxide with pyridine and carbazole can distinctly affect the thermal stability of the resulting iridium complexes. The data indicate that these functionalized iridium complexes possess good thermal properties, which is very important for electroluminescent purpose.



Fig. 3. TGA curves of (*p*-CzFSOPy)<sub>2</sub>IrPic and (*m*-CzFSOPy)<sub>2</sub>IrPic under nitrogen atmosphere.

#### 3.5. Electroluminescent devices

Monochromic yellow-light-emitting OLEDs with high efficiencies are indispensable for developing highly efficient WPLEDs. Hence, in order to investigate the electroluminescent performances of (p-CzFSOPy)<sub>2</sub>IrPic and (*m*-CzFSOPy)<sub>2</sub>IrPic as dopant emitters, two yellowemitting PLEDs with a configuration of ITO/PEDOT:PSS/ dopant + PVK:PBD/CsF/Al were fabricated. Poly (3,4-ethylenedioxvthiophene) poly (styrene sulfonate) (PEDOT:PSS) was used as a holeinjection layer. PVK was chosen as a host material due to its higherlying triplet state (3.0 eV), excellent film-forming properties, high glasstransition temperature ( $T_g \approx 160$  °C) and hole-transport characteristics [11]. In order to balance electron/hole injection in the emitting layer, 2-(4-biphenyl)-5-(4-tertbutylphenyl)-1,3,4-oxadiazole (PBD) was blended into PVK. The emitting layer consists of the dopants ((p-CzFSOPy)2IrPic or (m-CzFSOPy)2IrPic) and polymeric host matrix of PVK:PBD blend, in which the weight concentration of the dopant is 2 wt %, PBD weight ratio is 30 wt % in the PVK-PBD blend, respectively. A vacuum-deposited caesium fluoride (CsF) layer was used as an electroninjection layer.

Fig. 4 showed the electroluminescent (EL) spectra of the resulting iridium complexes. The EL spectra of  $(p-CzFSOPy)_2IrPic$  and  $(m-CzFSOPy)_2IrPic$  displayed yellow emission with a maximal phosphorescent peak at ca. 560 nm and 550 nm, respectively, which arose solely from the iridium complexes. Moreover, the EL spectrum of  $(p-CzFSO-Py)_2IrPic$  is identical to the corresponding PL emission. Nevertheless,



**Fig. 4.** EL spectra of the yellow-emitting PLEDs with (*p*-CzFSOPy)<sub>2</sub>IrPic and (*m*-CzFSOPy)<sub>2</sub>IrPic.



**Fig. 5.** (A) Current density (J) and brightness (L) versus voltage (V) characteristics (J–L–V); (b) The luminous efficiency–current density (LE–J) characteristics of the yellow-emitting PLEDs with (*p*-CzFSOPy)<sub>2</sub>IrPic and (*m*-CzFSOPy)<sub>2</sub>IrPic.

relative to PL spectrum, the presence of an additional emission peak at ca. 430 nm in the EL spectrum of (m-CzFSOPy)<sub>2</sub>IrPic indicates an incomplete energy transfer from the PVK:PBD host to iridium complex guest, which is consistent with results of photophysical measurement [56,57].

Fig. 5 shows the current density–voltage-brightness characteristics and the luminous efficiency (LE) versus current density for those devices from (*p*-CzFSOPy)<sub>2</sub>IrPic and (*m*-CzFSOPy)<sub>2</sub>IrPic, the relevant data are presented in Table 2. The devices based on (*p*-CzFSOPy)<sub>2</sub>IrPic and (*m*-CzFSOPy)<sub>2</sub>IrPic can be turned on at very low voltage (4.8 V for (*p*-CzFSOPy)<sub>2</sub>IrPic and 4.1 V for (*m*-CzFSOPy)<sub>2</sub>IrPic), and show maximum luminance ( $L_{max}$ ) with 9144 cd/m<sup>2</sup> and 2344 cd/m<sup>2</sup>, respectively. The device of (*p*-CzFSOPy)<sub>2</sub>IrPic shows a maximal LE of 13.3 cd/A with CIE coordinates of (0.486, 0.486) at a current density of 6.2 mA/cm<sup>2</sup>, while the peak LE of device of (*m*-CzFSOPy)<sub>2</sub>IrPic is 4.2 cd/A with CIE coordinates of (0.347, 0.392) at 12.4 mA/cm<sup>2</sup>. Compared to (*m*-CzFSO-Py)<sub>2</sub>IrPic, (*p*-CzFSOPy)<sub>2</sub>IrPic exhibits much better device performances, which may be attributed to that (*p*-CzFSOPy)<sub>2</sub>IrPic has higher  $\Phi_p$  than (*m*-CzFSOPy)<sub>2</sub>IrPic, and the energy transfer from PVK:PBD blend to (*p*-

Table 2		
The device performances of (p-	-CzFSOPy)2IrPic and (	(m-CzFSOPy)2IrPic.

Dopants	V <sub>on</sub> [a] (V)	V [b] (V)	<i>J</i> [b] (mA cm <sup>-2</sup> )	QE [b] (%)	$L_{\rm max}$ (cd m <sup>-2</sup> )	LE <sub>max</sub> (cd A <sup>-1</sup> )
(p-CzFSOPy) <sub>2</sub> IrPic	4.8	8.1	6.2	5.3	9144	13.3
(m-CzFSOPy) <sub>2</sub> IrPic	4.1	6.9	12.4	1.7	2344	4.2

[a] The turn-on voltage at which luminescence reach 1 cd m $^{-2}$ . [b] Device data at maximum LE.



**Fig. 6.** (a) EL spectra of the double-doped WPLEDs at different concentrations of (*p*-CzFSOPy)<sub>2</sub>IrPic:FIrpic; (b) EL spectra under different applied voltages when the concentration of (*p*-CzFSOPy)<sub>2</sub>IrPic:FIrpic is 1:20.

 $CzFSOPy)_2IrPic$  is more efficient than that from PVK:PBD blend to (*m*-CzFSOPy)\_2IrPic.

On the basis of these efficient monochromatic devices, a series of highly efficient WPLEDs with a configuration of ITO/PEDOT:PSS/ emitting layer/CsF/Al were fabricated by simultaneously doping blue emitter FIrpic and yellow phosphors (*p*-CzFSOPy)<sub>2</sub>IrPic into PVK:OXD-7 matrix. The emitting layer is PVK (63 wt%):OXD-7 (27 wt%):dopants (FIrpic and (*p*-CzFSOPy)<sub>2</sub>IrPic, 10 wt%). PVK was used as host, and OXD-7 was included into the host matrix to facilitate electron transport. We tuned the emission color by controlling the blending ratio of FIrpic/(*p*-CzFSOPy)<sub>2</sub>IrPic within the range of 10:1 to 30:1. Fig. 6(a) depicts the EL spectra of these WPLEDs at the current density of 5 mA/cm<sup>2</sup>. Two emission region of 440–530 nm and 530–700 nm were observed, which are assigned to the emission from FIrpic and (*p*-CzFSOPy)<sub>2</sub>IrPic, respectively. Moreover, there is a monotonous increase of the yellow emission as the doping concentration of (*p*-CzFSOPy)<sub>2</sub>IrPic:FIrpic increases from 1:30 to 1:10. As shown in Table 3, the CIE coordinates at



**Fig. 7.** (A) Current density (J) and brightness (L) versus voltage (V) characteristics (J–L–V); (b) The luminous efficiency–current density (LE–J) characteristics of double-doped WPLEDs at different concentrations of (*p*-CzFSOPy)<sub>2</sub>IrPic:FIrpic.

5 mA/cm<sup>2</sup> fluctuate from (0.283, 0.429) to (0.346, 0.450), all are within the white light-emission region. Of which, the CIE coordinate of (0.317, 0.448) is very close to the ideal CIE coordinate of (0.333, 0.333) for pure white color when the doping concentration of (p-CzFSO-Py)2IrPic:FIrpic is 1:20. In order to investigate the EL stability of WPLEDs, the EL spectra of devices was measured under different applied voltages when the mass ratio of (p-CzFSOPy)<sub>2</sub>IrPic:FIrpic is 1:20. As shown in Fig. 6(b), it can be seen that the EL CIE coordinates only shift from (0.334, 0.447) to (0.307, 0.439) with  $\Delta(x, y) = \pm (0.014, y)$ 0.004), while the driving voltages increasing from 6 V to 9 V. Therefore, the WPLEDs exhibited stable white emission under different driving voltages. As shown in Fig. 7, when the mass ratio of (p-CzFSO-Py)2IrPic:FIrpic is 1:20, the device exhibit best EL performances: the turn-on voltage ( $V_{on}$ ) is 5.3 V, the maximum luminance ( $L_{max}$ ) is 18717 cd/m<sup>2</sup>, the peak LE is 19.2 cd/A at 6.86 mA/cm<sup>2</sup>, and the corresponding EQE is 9.6%. At a high forward-view luminance of 1000 cd/  $m^2$ , the LE slightly decrease to 19.0 cd/A. Compared to the triphenylamine- and fluorene-functionalized iridium complexes which we have reported early, the iridium complex (p-CzFSOPy)<sub>2</sub>IrPic displayed better EL properties in WPLEDs [29]. As we know, most phosphorescent

Table	3
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Composition [a]	$V_{\rm on}$	Peak LE	Peak EQE	Peak PE	Peak L	Device performance at $1000 \text{ cd/m}^2$		CIE[b]	
	(V)	(cd/A)	(%)	(lm/W)	(cd/m <sup>2</sup> )	LE (cd/A)	EQE (%)	PE (lm/W)	(x, y)
10:1 20:1 30:1	5.5 5.3 4.6	16.9 19.2 9.1	8.4 9.6 4.6	7.43 8.44 3.26	17950 18717 13087	16.8 19.0 5.1	8.3 9.5 2.5	7.36 8.23 2.27	(0.346, 0.450) (0.317, 0.448) (0.283, 0.429)

[a]FIrpic: (p-CzFSOPy)<sub>2</sub>IrPic ratio. [b] Observe: 2 Degrees; obtained at 5 mA.

devices encountered a situation that the EL efficiency declines quickly as the current density increases [58,59]. Fortunately, the current efficiency of this device declines slowly with increasing the current density, the current efficiency remains 15.6 cd/A at  $50 \text{ mA/cm}^2$ , and still maintains 12.6 cd/A at  $100 \text{ mA/cm}^2$ , which indicates that the device possesses good stability.

# 4. Conclusions

In summary, we have synthesized and characterized two novel dibenzothiophene-S,S-dioxide-based iridium complexes that are yellow emitters and suitable for yellow and white electroluminescent devices. The newly synthesized iridium complexes possess good thermal stability and high photoluminescence quantum yields. Monochromic yellowemitting PLEDs using (*p*-CzFSOPy)<sub>2</sub>IrPic as emitter exhibit best device performance with peak LE of 13.3 cd/A at a current density of 6.2 mA/ cm<sup>2</sup>. More importantly, combination of the yellow phosphor (*p*-CzFSOPy)<sub>2</sub>IrPic with another blue phosphor FIrpic in a single-emissivelayer can lead to highly efficient WPLEDs. The WPLEDs show best performances with a maximal LE of 19.2 cd/A, a CIE coordinates of (0.317, 0.448) and an extremely high luminance of 18717 cd/m<sup>2</sup>. Work is still underway to improve the device efficiency and color purity of these all-phosphor WPLEDs.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.dyepig.2018.07.019.

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