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# Effect of substituents on properties of diphenylphosphoryl-substituted bis-cyclometalated Ir(III) complexes with a picolinic acid as ancillary ligand

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#### ABSTRACT

A series of diphenylphosphoryl-substituted bis-cyclometalated Ir(III) complexes (**POFIrpic**, **4Me-POFIrpic**, **5Me-POFIrpic**, **5F-POFIrpic** and **5CF<sub>3</sub>-POFIrpic**) with a picolinic acid as the ancillary ligand have been synthesized and characterized. The influence of substituents (CH<sub>3</sub>, F, CF<sub>3</sub>) at the pyridyl moiety of the cyclometalating ligand POFdFppy (2-(2',4'-difluoro-3'-diphenylphosphoryl)phenylpyridine) on the photophysical and electrochemical properties of these Ir(III) complexes has been investigated. These Ir(III) complexes exhibit intense emission bands at 455–492 nm and high phosphorescence quantum yields ( $\Phi_{PL}$ ) in a range of 54–64% in CH<sub>2</sub>Cl<sub>2</sub>. The phosphorescence oxygen sensing properties of these complexes were studied in solution and in polymer film, and a fast response time and excellent operational stability were observed. Two-site model fitting indicates that **5Me-POFIrpic** is the most sensitive oxygen sensing material among the complexes, with a quenching constant  $K_{sv}^{app}$  of 0.00793 Torr<sup>-1</sup>. Photodegradation tests demonstrate that introduction of a CF<sub>3</sub> group into the cyclometalating ligand improves the photostability of the corresponding Ir(III) complex.

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# 1. Introduction

Oxygen detection techniques are applied in various fields, including chemical, clinical analysis, environmental monitoring, oceanography and life science [1–4]. Optical methods with excellent performances have attracted increasing interests for the determination of oxygen in recent years. An optical oxygen sensor relies on the quenching of the fluorescence or phosphorescence of an oxygen-sensitive probe (OSP) by molecular oxygen [5,6]. The essential demands for an efficient OSP, are high phosphorescence quantum yield ( $\Phi_{PL}$ ), long excited state lifetime and good photostability [7]. Cyclometalated Ir(III) complexes, in particular, are promising candidates as OSPs for oxygen sensing due to their lifetimes on the microsecond time-scale, generally high  $\Phi_{PL}$ , and unique color-tuning capability across the entire visible spectrum [8–11]. So far, cyclometalated Ir(III) complexes as the OSPs for oxygen sensing have been explored [12–16]. However, in contrast to

green and red phosphorescent complexes, the OSPs based on blue Ir(III) complexes are rarely reported [17]. It is attractive for developing blue OSPs with high sensitivity and  $\Phi_{PL}$ , which will provide a possibility for improving the efficiency of the sensors in the entire visible region. In addition, excellent blue OSPs could offer a chance to enhance the sensor performance when red emitters are present in the media or in order to perform colorimetric sensing and multifunctionalized optical measurements [17]. However, owing to the large emission energy gap and relatively low  $\Phi_{PL}$ , the development of blue emitting Ir(III) complexes as the OSPs with high performances remains a challenge [18–20].

The most investigated sky-blue emitting bis-cyclometalated Ir(III) complex is iridium(III) bis[(4,6-difluorophenyl)-pyridinato- $N,C^{2\prime}$ ] picolinate (FIrpic) [21]. Some popular strategies aiming to modify the structural frame of FIrpic are adopted to tune the emission to blue, among which the diphenylphosphoryl (Ph<sub>2</sub>PO) substituted Ir(III) complexes are good examples of the implementation of this strategy. In view of its electron-deficient feature, the diphenylphosphoryl group (Ph<sub>2</sub>PO) has been widely used to construct ambipolar host materials, for its ability to improve the electron-injecting and electron-transporting performance [22].







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Furthermore, this strong electron-withdrawing group can tune the emission of the corresponding Ir(III) complex toward a blue-shift. For example, introduction of a Ph<sub>2</sub>PO group at the 3-position of the phenyl unit for Ir(III) complexes POFIrpic [23] and Ir(dppfm)<sub>2</sub>-pic [24] tuned the emissions to the blue region, both of the complexes exhibited excellent performances in organic light-emitting diodes (OLEDs). Very recently, we reported several greenish-blue to blue phosphorescent diphenylphosphoryl-substituted cationic Ir(III) complexes with different N<sup>N</sup> ancillary ligands [25], and it was found that the ancillary ligand has profound effects on the properties of the corresponding Ir(III) complexes. Similarly, effect of the substituents at the pyridyl moiety of the diphenylphosphoryl-substituted cyclometalating ligands on the Ir(III) complexes is also of great interest for understanding the structure-property relationship.

In this paper, a series of bis-cyclometalated Ir(III) complexes with a diphenylphosphoryl group in the cyclometalating ligand and a picolinic acid (pic) as the ancillary ligand have been synthesized and characterized. The chemical structures of these Ir(III) complexes (**POFIrpic**, **4Me-POFIrpic**, **5Me-POFIrpic**, **5F-POFIrpic** and **5CF<sub>3</sub>-POFIrpic**), are illustrated in Scheme 1. The influence of substituents (CH<sub>3</sub>, F, CF<sub>3</sub>) at the pyridyl moiety of the cyclometalating ligand POFdFppy (2-(2',4'-difluoro-3'-diphenylphosphoryl)phenylpyridine) on the photophysical and electrochemical properties of the corresponding Ir(III) complexes has been investigated systematically. In addition, the oxygen sensitivity, operational stability and photostability of these Ir(III) complexes were also studied.

#### 2. Experimental

#### 2.1. Materials and measurements

All starting materials were purchased from commercial suppliers and used without further purification. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a 400 MHz Varian Unity Inova spectrometer. Mass spectra were recorded with a MALDI micro MX spectrometer. FT-IR spectra were recorded on a Nicolet-6700 IR Spectrometer using KBr disks and wave numbers were given in  $cm^{-1}$ . Melting points were determined using X-4 digital melting point apparatus. UV-Vis absorption spectra were recorded on a Lambda 750s spectrometer. Fluorescence spectra were recorded with a HITACHI F-7000 spectrofluorimeter. Phosphorescence quantum yields were measured relative to  $[Ir(ppy)_3]$  ( $\Phi_{PL} = 0.4$  in CH<sub>2</sub>Cl<sub>2</sub>, under deoxygenated conditions). Phosphorescence lifetimes were measured on an Edinburgh FLS920 Spectrometer. Cyclic voltammograms of the Ir(III) complexes were recorded on an electrochemical workstation (BAS100 B/W, USA) at room temperature in a 0.1 M [Bu<sub>4</sub>N]PF<sub>6</sub> solution under argon gas protection. Emission intensity response of sensing films of the Ir(III) complexes were recorded with a HITACHI F-7000 spectrofluorimeter. The preparation of the ethylcellulose (EC) oxygen sensing films and photostability test were performed following a protocol previously developed by us [26]. The weight content of all Ir(III) complexes immobilized in the EC film is 0.5 wt% and the photostability was investigated upon continuous irradiation with a 16 W 254 nm UV lamp (WFH-204B, the power density on the film is 23.4 W m<sup>-2</sup>). The structures of these Ir(III) complexes were optimized using density functional theory (DFT) with the B3LYP functional and 6-31G(d)/LanL2DZ basis set. The LanL2DZ basis set was used to treat the iridium atom, whereas the 6-31G(d) basis set was used to treat all other atoms. All the calculations were performed using Gaussian 09 software package [27]. CH<sub>2</sub>Cl<sub>2</sub> was used as the solvent for the calculations (CPCM model).

# 2.2. Synthesis

Chemical structures and the detailed synthetic protocols of the Ir(III) complexes are shown in Scheme 1. Cyclometalating ligands and the Ir(III) complexes were synthesized according to the reported method [23,24]. All the Ir(III) complexes were synthesized in two steps from the cyclometalation of  $IrCl_3 \cdot 3H_2O$  with the corresponding ligand to form the chloride-bridged dimer initially, followed by treatment with the picolinic acid in the presence of Na<sub>2</sub>CO<sub>3</sub>.

# 2.2.1. Synthetic procedure of C<sup>N</sup> cyclometalating ligand

The different C<sup>N</sup> cyclometalating ligands containing a diphenylphosphoryl group were synthesized by the method developed previously for analogous compounds (see Supporting Information).

**5Me-POFdFppy**: Yield 70.2%, white solid, Mp: 108–110 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.46 (s, 1H), 8.19–8.12 (m, 1H), 7.79–7.72 (m, 4H), 7.52–7.40 (m, 8H), 6.98 (td, *J* = 8.9, 3.8 Hz, 1H), 2.28 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  163.7, 161.4, 161.0, 158.9, 149.2, 147.7, 136.0, 135.7, 135.6, 132.6, 131.5, 131.4, 131.1, 130.2, 130.1, 129.7, 129.6, 127.9, 127.8, 127.6, 127.5, 124.1, 123.9, 123.0, 122.9, 112.1, 111.9, 111.8, 110.0, 109.8, 109.6, 109.1, 108.9, 108.7, 17.1. IR (KBr):  $\nu$  3060, 2972, 2925, 1607, 1583, 1464, 1439, 1402, 1198, 1117, 1096, 1050, 1002, 881, 824, 752, 723, 696, 587, 561, 521 cm<sup>-1</sup>. HRMS (MALDI-TOF): calcd. for C<sub>24</sub>H<sub>18</sub>NOF<sub>2</sub>P 405.1094, found 405.1089.

**5F-POFdFppy:** Yield 79.1%, white solid, Mp: 168–170 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.53 (d, *J* = 2.9 Hz, 1H), 8.28–8.11 (m, 1H), 7.86–7.74 (m, 4H), 7.70–7.64 (m, 1H), 7.59–7.53 (m, 2H), 7.53–7.45 (m, 4H), 7.44–7.36 (m, 1H), 7.09–6.97 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  164.9, 162.5, 162.2, 160.0, 159.8, 157.5, 147.6, 138.3, 138.0, 136.8, 136.6, 133.4, 132.4, 132.2, 131.2, 131.1, 128.7, 128.5, 125.5, 125.3, 124.1, 124.0, 123.9, 123.4, 123.2, 113.3, 113.1, 113.0, 111.3, 111.1,



Scheme 1. Chemical structures and synthetic routes to these Ir(III) complexes. (i) IrCl<sub>3</sub>·3H<sub>2</sub>O, EtOCH<sub>2</sub>CH<sub>2</sub>OH/H<sub>2</sub>O, 3:1 (v/v), 120 °C, N<sub>2</sub>, 24 h (ii) Na<sub>2</sub>CO<sub>3</sub>, picolinic acid, CH<sub>2</sub>Cl<sub>2</sub>/EtOH, 4:1 (v/v), 40 °C, N<sub>2</sub>, 12 h.

110.9, 110.4, 110.2, 110.0. IR (KBr):  $\nu$  3080, 3055, 1609, 1591, 1462, 1439, 1409, 1238, 1205, 1117, 1070, 1000, 824, 792, 753, 723, 696, 586, 559, 523 cm  $^{-1}$ . HRMS (MALDI-TOF): calcd. for  $C_{23}H_{15}NOF_{3}P$  409.0843, found 409.0841.

**5CF<sub>3</sub>-POFdFppy**: Yield 39.3%, white solid, Mp: 91–93 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.91 (d, *J* = 2.2 Hz, 1H), 8.35–8.21 (m, 1H), 7.94–7.88 (m, 1H), 7.85–7.71 (m, 5H), 7.58–7.51 (m, 2H), 7.51–7.41 (m, 4H), 7.09–7.01 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  165.4, 163.0, 162.9, 160.4, 154.8, 146.6, 137.1, 135.1, 133.8, 133.3, 132.1, 131.2, 131.1, 128.7, 128.6, 128.2, 128.1, 125.6, 125.3, 124.7, 124.1, 124.0, 123.7, 123.5, 122.0, 119.3, 113.6, 113.5, 113.2, 111.7, 111.5, 111.3, 110.8, 110.6, 110.4. IR (KBr): *v* 3055, 2972, 2926, 1604, 1463, 1439, 1419, 1329, 1196, 1134, 1088, 1003, 854, 821, 777, 752, 720, 695, 591, 546, 525, 517 cm<sup>-1</sup>. HRMS (MALDI-TOF): calcd. for C<sub>24</sub>H<sub>15</sub>NOF<sub>5</sub>P 459.0811, found 459.0797.

#### 2.2.2. Synthetic procedure of Ir(III) complexes

A mixture of  $IrCl_3 \cdot 3H_2O$  and 2.5 equiv. of C°N cyclometalating ligand was heated at 120 °C in 2-ethoxyethanol/water (3:1, v/v) for 24 h under a nitrogen atmosphere. Upon cooling to room temperature, the mixture was poured into water and the formed precipitate was filtered, washed by ethanol and *n*-hexane, to obtain the chloro-bridged dimer. Without further purification, the dimer was mixed with 3.0 equiv. picolinic acid and 5.0 equiv. Na<sub>2</sub>CO<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>/ethanol (4:1, v/v). The reaction mixture was stirred at 40 °C for 12 h under a nitrogen atmosphere, then the reaction mixture was dried over MgSO<sub>4</sub> and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (10:1, v/v) as eluent to obtain the desired Ir(III) complex.

**5Me-POFIrpic**: Yield 70.0%, yellow-green solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.48 (s, 1H), 8.33 (d, *J* = 7.6 Hz, 1H), 8.02–7.93 (m, 3H), 7.84–7.69 (m, 9H), 7.56–7.40 (m, 15H), 7.09 (s, 1H), 5.74 (dd, *J* = 9.9, 3.9 Hz, 1H), 5.58 (dd, *J* = 10.0, 4.0 Hz, 1H), 2.29 (s, 3H), 2.08 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  172.6, 164.1, 163.8, 162.6, 162.2, 161.9, 161.5, 161.2, 160.6, 160.2, 160.0, 159.6, 158.7, 151.0, 148.4, 148.2, 147.7, 139.5, 138.8, 134.3, 134.1, 133.8, 133.3, 133.0, 132.7, 132.0, 131.9, 131.8, 131.7, 131.2, 131.1, 129.9, 129.6, 128.8, 128.6, 128.5, 128.4, 128.3, 123.6123.4, 123.2, 123.0, 116.0, 115.8, 103.7, 103.5, 103.3, 103.1, 102.7, 102.5, 102.3, 102.1, 18.4, 18.3. IR (KBr):  $\nu$  3057, 2969, 2924, 1662, 1641, 1596, 1523, 1488, 1285, 1187, 1118, 1101, 1051, 1018, 885, 865, 839, 752, 735, 722, 698, 602, 524 cm<sup>-1</sup>. HRMS (MALDI-TOF): calcd. for C<sub>54</sub>H<sub>38</sub>N<sub>3</sub>O<sub>4</sub>F<sub>4</sub>P<sub>2</sub>Ir 1123.1903, found 1124.1915 ([M+H]<sup>+</sup>).

**5F-POFIrpic**: Yield 48.1%, yellow-green solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.62 (t, *J* = 2.4 Hz, 1H), 8.38 (d, *J* = 7.7 Hz, 1H), 8.22–8.01 (m, 3H), 7.86–7.68 (m, 9H), 7.60–7.37 (m, 15H), 7.19 (t, *J* = 2.5 Hz, 1H), 5.76 (dd, *J* = 9.7, 3.8 Hz, 1H), 5.59 (dd, *J* = 9.7, 3.8 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  172.3, 164.5, 164.1, 162.8, 162.4, 161.8, 161.6, 161.5, 160.2, 159.8, 158.9, 158.7, 157.4, 156.4, 150.8, 148.4, 139.5, 137.4, 137.1, 136.9, 136.6, 134.0, 133.6, 132.9, 132.8, 132.5, 132.1, 132.0, 131.9, 131.2, 131.0, 129.3, 129.1, 128.8, 128.7, 128.6, 128.5, 128.4, 126.5, 126.3, 125.0, 124.8, 124.6, 124.4, 116.0, 115.7, 104.5, 104.3, 104.1, 103.5, 103.3, 103.1. IR (KBr):  $\nu$  3060, 2970, 1664, 1644, 1597, 1524, 1486, 1438, 1405, 1269, 1187, 1100, 1051, 1019, 855, 750, 732, 721, 698, 601, 540, 524 cm<sup>-1</sup>. HRMS (MALDI-TOF): calcd. for C<sub>52</sub>H<sub>32</sub>N<sub>3</sub>O<sub>4</sub>F<sub>6</sub>P<sub>2</sub>Ir 1131.1401, found 1132.1443 ([M+H]<sup>+</sup>), 1154.1273 ([M+Na]<sup>+</sup>).

**5CF<sub>3</sub>-POFIrpic**: Yield 44.6%, yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.98 (s, 1H), 8.39 (d, J = 7.7 Hz, 1H), 8.28 (t, J = 10.2 Hz, 2H), 8.09 (td, J = 7.7, 1.2 Hz, 1H), 8.01–7.88 (m, 2H), 7.88–7.64 (m, 9H), 7.65–7.37 (m, 14H), 5.75 (dd, J = 9.5, 3.7 Hz, 1H), 5.57 (dd, J = 9.6, 3.7 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  172.0, 168.1, 166.8, 165.3, 165.0, 164.5, 164.0, 162.7, 162.4, 161.9, 161.4, 160.4, 159.4, 150.7,

148.5, 145.5, 144.6, 139.8, 136.2, 133.7, 133.5, 133.3, 132.6, 132.4, 132.2, 132.1, 132.0, 131.2, 131.1, 131.0, 129.4, 129.2, 128.9, 128.8, 128.7, 128.6, 128.5, 126.5, 126.2, 125.9, 124.0, 123.7, 123.5, 123.3, 123.2, 123.0, 120.4, 120.3, 116.3, 116.0, 105.0, 104.8, 104.0, 103.8. IR (KBr):  $\nu$  3059, 2965, 2927, 1667, 1619, 1597, 1523, 1331, 1286, 1183, 1139, 1094, 1055, 1020, 863, 847, 758, 723, 702, 695, 620, 589, 530, 519 cm<sup>-1</sup>. HRMS (MALDI-TOF): calcd. for C<sub>54</sub>H<sub>32</sub>N<sub>3</sub>O<sub>4</sub>F<sub>10</sub>P<sub>2</sub>Ir 1231.1338, found 1232.1439 ([M+H]<sup>+</sup>), 1270.1063 ([M+K]<sup>+</sup>).

# 3. Results and discussion

# 3.1. Photophysical properties

UV-Vis absorption spectra and emission spectra of all Ir(III) complexes in CH<sub>2</sub>Cl<sub>2</sub> at room temperature are presented in Fig. 1 and the pertinent data are summarized in Table 1. The intense short wavelength absorptions are primarily due to the spin-allowed intra-ligand ( $^{1}\pi$ - $\pi^{*}$ ) transitions. The long wavelength (inset of Fig. 1(a)) with lower extinction coefficient absorption can be assigned to mixing among singlet and triplet metal-to-ligand charge transfer ( $^{1}$ MLCT and  $^{3}$ MLCT) transitions [28,29].

These diphenylphosphoryl-substituted bis-cyclometalated Ir(III) complexes exhibit intense emission bands at 455–492 nm (Fig. 1(b)). Introducing a CH<sub>3</sub> group at the 4-position of the pyridyl ring results in a slight blue-shift of 3 nm for **4Me-POFIrpic** ( $\lambda_{max}$  at



**Fig. 1.** Absorption (a) and emission spectra (b) of Ir(III) complexes  $(1.0 \times 10^{-5} \text{ M in CH}_2\text{Cl}_2)$  at room temperature. The inset in (a) shows the magnified spectra from 300 to 450 nm. The inset in (b) shows the emission photographs in CH<sub>2</sub>Cl<sub>2</sub> (excited at 365 nm by a UV lamp).

455 nm) in comparison with **POFIrpic** ( $\lambda_{max}$  at 458 nm), while the CH<sub>3</sub> substituent at 5-position of pyridyl ring, a red-shift of 4 nm for **5Me-POFIrpic** ( $\lambda_{max}$  at 462 nm) is reached. Instead of a CH<sub>3</sub> with a F group at 5-position of pyridyl ring, **5F-POFIrpic** ( $\lambda_{max}$  at 464 nm) gives a red-shift of approximately 6 nm versus the emission of the complex **POFIrpic**. Introducing a CF<sub>3</sub> group at the same position for **5CF<sub>3</sub>-POFIrpic**, an almost featureless emission band was observed ( $\lambda_{max}$  at 477 nm), which is red-shifted by about 19 nm relative to **POFIrpic**. Compared with other Ir(III) complexes, a red-shifted emission spectrum was achieved for **5CF<sub>3</sub>-POFIrpic**, which may result from the stabilization of the LUMO to a larger extent than the HOMO due to the electron-withdrawing CF<sub>3</sub>, thus leading to a smaller energy gap (see the computational results).

As shown in Table 1, these Ir(III) complexes exhibit high phosphorescence quantum yields ( $\Phi_{PL}$ ) in the range of 54–64% in CH<sub>2</sub>Cl<sub>2</sub>. These  $\Phi_{PI}$  values are comparable to some previously reported bis-cyclometalated Ir(III) complexes [23,30-33], which consisted of an electron-withdrawing substituent at the 3' position of 2-(2',4'-difluorophenyl)pyridine as the cyclometalating ligand and a pic as the ancillary ligand. The phosphorescence lifetimes  $(\tau)$ of the Ir(III) complexes were 0.85-2.82 µs in CH<sub>2</sub>Cl<sub>2</sub> at room temperature (Table 1). The radiative decay rate ( $k_r \approx 1.95 - 7.53 \times 10^5$ s<sup>-1</sup>) and nonradiative decay rate ( $k_{\rm nr} \approx 1.56-4.23 \times 10^5 \text{ s}^{-1}$ ) of these complexes in CH<sub>2</sub>Cl<sub>2</sub> were calculated and are listed in Table 1. The relatively high radiative decay rate ( $k_r = 7.53 \times 10^5 \text{ s}^{-1}$ ) and short phosphorescence lifetime ( $\tau = 0.85 \ \mu s$ ) indicate that **5CF<sub>3</sub>-**POFIrpic emits from a more pronounced <sup>3</sup>MLCT excited state and is more influenced by the spin-orbit coupling (SOC) effect than those of other Ir(III) complexes [34,35].

#### 3.2. Electrochemical properties

The electrochemical behavior of these Ir(III) complexes were investigated by cyclic voltammetry (CV) in CH<sub>2</sub>Cl<sub>2</sub> (the cyclic voltamograms of these Ir(III) complexes see Fig. S2 in Supporting Information) and the corresponding data are listed in Table 2. Several groups reported that it was difficult in observing reversible reduction potentials for blue phosphorescent Ir(III) complexes [36–38]. Similarly, all investigated Ir(III) complexes except 5CF<sub>3</sub>-**POFIrpic** exhibited irreversible reduction waves (see Fig. S2 in Supporting Information). The reduction profile of **5CF<sub>3</sub>-POFIrpic** was found to be quasi-reversible, suggesting an electrochemical stability of **5CF<sub>3</sub>-POFIrpic** to some extent [39]. The onset oxidation potentials of these Ir(III) complexes are 1.40 (POFIrpic), 1.41 (4Me-**POFIrpic**), 1.34 (**5Me-POFIrpic**), 1.48 (**5F-POFIrpic**) and 1.51 (**5CF**<sub>3</sub>-**POFIrpic**) V. It was found that introducing the electron-donating group CH<sub>3</sub> at the 4-position of pyridyl ring has no significant effect on the onset oxidation potential compared with that of **POFIrpic**. However, a CH<sub>3</sub> group at the 5-position of pyridyl ring leads to a lower oxidation potential for 5Me-POFIrpic. By contrast, introducing an electron-withdrawing group F (5F-POFIrpic) or CF<sub>3</sub>

Table 1	
Photophysical data of these Ir(III) complexes.	

 $k_{\rm nr}{}^{\rm e}\,(10^5~{\rm s}^{-1})$  $\lambda_{em}^{b}(nm)$  $\tau^{d}(\mu s)$  $k_r^{e} (10^5 \text{ s}^{-1})$ Complexes  $\lambda_{abs}^{a}$  (nm)  $\Phi_{PL}$ POFIrpic 0.57 230(0.47), 257(0.49), 287(0.35), 373(0.05) 458, 487 sh 2.02 2.82 2.13 4Me-POFIrpic 230(0.42), 258(0.49), 283(0.35), 370(0.06) 455, 484 sh 0.54 2.33 2.32 1.97 5Me-POFIrpic 230(0.46), 258(0.53), 288(0.36), 372(0.07) 462, 492 sh 0.55 2.82 1.95 1.59 230(0.34), 258(0.35), 289(0.23), 375(0.04) **5F-POFIrpic** 464, 492 sh 0.60 2.57 2.33 1.56 5CF<sub>3</sub>-POFIrpic 230(0.41), 266(0.45), 290(0.37), 391(0.04) 477 0.64 0.85 7.53 4.23

<sup>a</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub> at a concentration of  $10^{-5}$  M and extinction coefficients ( $10^{5}$  Lmol<sup>-1</sup>cm<sup>-1</sup>) are shown in parentheses.

<sup>b</sup> In deoxygenated CH<sub>2</sub>Cl<sub>2</sub>; the symbol sh denotes the shoulder wavelength.

<sup>c</sup> The quantum yields ( $\Phi_{PL}$ ) in deoxygenated CH<sub>2</sub>Cl<sub>2</sub> were measured with Ir(ppy)<sub>3</sub> ( $\Phi_{PL} = 0.40$ ) as a standard. <sup>d</sup> Massured in deoxygenated CH<sub>2</sub>Cl<sub>2</sub>

<sup>d</sup> Measured in deoxygenated CH<sub>2</sub>Cl<sub>2</sub>.

<sup>e</sup> Calculated from  $k_r = \Phi_{PL} \times \tau^{-1}$ ,  $k_{nr} = \tau^{-1}$ -  $k_r$  in deoxygenated CH<sub>2</sub>Cl<sub>2</sub>.

(**5CF<sub>3</sub>-POFIrpic**) at the same position makes the oxidation process shift to a more positive potential, indicating the relative difficulty of oxidation. On the basis of the onset oxidation potentials and the absorption edge data, the HOMO and LUMO energy levels can be calculated and the results are presented in Table 2.

# 3.3. Theoretical calculations

Fig. 2 displays the energy levels and electron density distributions of the orbitals for all complexes by DFT calculations. It was observed that the five complexes have very small differences in the electron density distributions of the HOMOs, which are all mainly located on the iridium center and the ppy moiety of the cyclometalating ligands. However, unlike the case of the HOMOs, these complexes show differences in the electron density distributions of the LUMOs. For **POFIrpic**, the LUMO is primarily contributed from the ppy of one of the cyclometalating ligands as well as the pic ancillary ligand. Compared with **POFIrpic**, the introduction of an electron-donating CH<sub>3</sub> group in **4Me-POFIrpic** and **5Me-POFIrpic** have no significant influence on the electron density distribution of the LUMOs. The LUMO electron densities of 5F-POFIrpic are located on the cyclometalating ligand and a relatively small contribution from the pic ancillary ligand relative to those of the POFIrpic, 4Me-POFIrpic, 5Me-POFIrpic. In contrast, the presence of an electron-withdrawing group CF<sub>3</sub> on the cyclometalating ligand of 5CF<sub>3</sub>-POFIrpic redistributed the LUMO from the ancillary ligand entirely to the cyclometalating ligand. Taking the energy level of **POFIrpic** as a criterion, incorporation of a CH<sub>3</sub> group into the 4-position of the pyridyl ring in cyclometalating ligand, increased slightly the HOMO-LUMO energy gap of the corresponding complex, resulting in a blue-shift relative to **POFIrpic**. The HOMO-LUMO energy gaps for the other complexes are reduced and 5CF<sub>3</sub>-POFIrpic is the lowest one, which are consistent with experimental results.

To investigate the nature of the emissive excited state, the lowlying triplet states of these Ir(III) complexes were calculated based on their optimized geometry of the ground state ( $S_0$ ) using the

#### Table 2

Electrochemical data of these Ir(III) complexes.

Complexes	Eoset a [V]	$E_{g}^{b}$ [eV]	HOMO <sup>c</sup> [eV]	LUMO <sup>c</sup> [eV]	$E_{ox}^{*}^{d}$
POFIrpic	1.40	2.86	-5.80	-2.94	-1.46
4Me-POFIrpic	1.41	2.91	-5.81	-2.90	-1.50
5Me-POFIrpic	1.34	2.85	-5.74	-2.89	-1.51
5F-POFIrpic	1.48	2.79	-5.88	-3.09	-1.31
5CF <sub>3</sub> -POFIrpic	1.51	2.72	-5.91	-3.19	-1.21

 $^a$  0.1 M [Bu\_4N]PF\_6 in CH\_2Cl\_2, scan rate 100 mV s  $^{-1}$ , measured using saturated calomel electrode (SCE) as the standard.

 $^{\rm b}$  HOMO-LUMO gap (*E*<sub>g</sub>) measured according to the onset of UV-Vis absorption (*E*<sub>g</sub> = 1240/ $\lambda_{\rm onset}$  eV).

$$^{c}$$
  $E_{HOMO} (eV) = -e(4.4 + E_{ox}^{onset}), E_{LUMO} (eV) = E_{HOMO} + E_{g}$ 

$$E_{ox}^* = E_{ox}^{onset} - E_g.$$



Fig. 2. Calculated energy-level diagram and contour plots of the HOMO and LUMO for all investigated Ir(III) complexes.

time-dependent DFT (TD-DFT) approach. The vertical excitation energies and molecular orbitals involved in the excitations for the lowest energy triplet state are summarized in Table 3 (see Fig. S1 in the Supporting Information for the electron density maps of the frontier molecular orbital that are mainly involved in the lowestlying transition). TD-DFT calculations show that T<sub>1</sub> and T<sub>2</sub> states of these complexes are relatively close in energy (within 0.11 eV) and, in principle, the emission might originate not only from the  $T_1$ state but also from the higher-lying T<sub>2</sub> state [40,41]. For **POFIrpic**, the orbitals involved are HOMO-4, HOMO-3, HOMO-1, HOMO, LUMO, LUMO+1 and LUMO+2, which renders the T<sub>1</sub> and T<sub>2</sub> states of **POFIrpic** with considerable nature of <sup>3</sup>LC with some <sup>3</sup>MLCT and <sup>3</sup>LLCT character. The finding is in good agreement with the experimental observation, where the vibronic fine structure is present in emission spectrum. For 4Me-POFIrpic, 5Me-POFIrpic and 5F-**POFIrpic**, distributions of the triplet states are similar to that of **POFIrpic**. Their emissions also take place from the <sup>3</sup>LC state according to the calculated triplet states (Table 3) and the experimental results of photophysical characterizations (section 3.1). Based on the calculations, the <sup>3</sup>MLCT character of the emissive state is more pronounced in 5CF3-POFIrpic than in other Ir(III) complexes, which may explain its almost featureless emission spectrum.

# 3.4. Oxygen sensitivity of the Ir(III) complexes in solution

The oxygen sensitivity of the Ir(III) complexes were investigated in CH<sub>3</sub>CN firstly. It was found that the emission intensity of all the Ir(III) complexes decreased with the increase of molecular oxygen concentrations from 0 to 100%. For example, changing from an N<sub>2</sub> atmosphere to 2.17% O<sub>2</sub> (mixture with N<sub>2</sub>, v/v) will significantly quench the emission intensity of the complex **5Me-POFIrpic** by over 80% (Fig. 3). In addition, the shape of the emission profile without distortions under different oxygen concentrations guarantees that the decreased phosphorescence can be attributed only to the oxygen quenching process [42]. A similar quenching effect was observed for other Ir(III) complexes (see Fig. S3 in Supporting Information).

In fluid solution, the relationship between the emission intensity of OSP and the concentration of quencher ( $O_2$ ) is reflected by the Stern-Volmer equation, which can be described as follows (eqn (1)) [13,43].

Table 3	
Calculated triplet states of these Ir(III) complexe	es by a TD-DFT approach.

Complexes	States	$E^{a}(eV)$	Composition <sup>b</sup>	CI <sup>c</sup>	Character
POFIrpic	T <sub>1</sub>	2.90	$H \to L{+}1$	0.3941	LC/LLCT
			$H \rightarrow L$	0.3558	LC/MLCT/LLCT
			$H-4 \rightarrow L+1$	0.1858	LC/LLCT
	T <sub>2</sub>	3.00	$H \rightarrow L+2$	0.4091	LC/MLCT/LLCT
			$H-3 \rightarrow L+2$	0.3427	LC
			$H-1 \rightarrow L+2$	0.2101	LC/MLCT/LLCT
4Me-POFIrpic	$T_1$	2.92	$H \rightarrow L+1$	0.4613	LC/LLCT
			$H \rightarrow L$	0.2460	LC/MLCT/LLCT
			$H-4 \rightarrow L+1$	0.2287	LC/LLCT
	T <sub>2</sub>	3.01	$H \rightarrow L+2$	0.4167	LC/MLCT/LLCT
			$H-3 \rightarrow L+2$	0.3493	LC
			$H-1 \rightarrow L+2$	0.1893	LC/MLCT/LLCT
5Me-POFIrpic	T <sub>1</sub>	2.87	$H \rightarrow L+1$	0.4636	LC/LLCT
			$H \rightarrow L$	0.2617	LC/MLCT/LLCT
			$H-4 \rightarrow L+1$	0.2125	LC/LLCT
	T <sub>2</sub>	2.98	$H \rightarrow L+2$	0.4144	LC/MLCT/LLCT
			$H-3 \rightarrow L+2$	0.3356	LC
			$H-1 \rightarrow L+2$	0.2413	LC/MLCT/LLCT
5F-POFIrpic	T <sub>1</sub>	2.84	$H \rightarrow L+1$	0.4037	LC/LLCT
			$H \rightarrow L$	0.3687	LC/MLCT/LLCT
	_		$H-4 \rightarrow L+1$	0.1839	LC/LLCT
	T <sub>2</sub>	2.94	$H-1 \rightarrow L$	0.4359	LC/MLCT/LLCT
			$H-3 \rightarrow L+2$	0.3153	LC
			$H \rightarrow L+2$	0.2109	LC/MLCT/LLCT
5CF <sub>3</sub> -POFIrpic	$T_1$	2.79	$H \rightarrow L$	0.5532	LC/MLCT/LLCT
			$H-4 \rightarrow L$	0.2499	LC/MLCT
			$H-3 \rightarrow L$	0.1616	LC/LLCT
	T <sub>2</sub>	2.90	$H \rightarrow L+1$	0.4270	LC/MLCT/LLCT
			$H-3 \rightarrow L+1$	0.3518	
			$H-1 \rightarrow L+1$	0.2039	MLCT/LLCT

<sup>a</sup> Calculated excitation energies for the triplet states.

<sup>b</sup> Only the main configurations are presented. H and L denote HOMO and LUMO, respectively.

<sup>c</sup> The Configuration-interaction (CI) coefficients are in absolute values. Oscillator strengths are zero because of the neglect of spin-orbit coupling in the TD-DFT calculations.

$$\frac{I_0}{I} = 1 + K_{\rm SV} \cdot p_{\rm O_2} \tag{1}$$

where *I* is the emission intensity, the subscript 0 denotes the value of the quantity in the absence of quencher,  $K_{SV}$  is the Stern-Volmer quenching constant and  $p_{O_2}$  is the partial pressure of oxygen.

The  $I_0/I_{100}$  value is used to evaluate the O<sub>2</sub> sensing properties of phosphorescent OSPs, where  $I_0$  and  $I_{100}$  represent the detected



Fig. 3. Emission spectra of complex 5Me-POFIrpic (1.0  $\times$  10 $^{-5}$  M in CH\_3CN) under different oxygen concentration at room temperature.

luminescence intensities in 100% N<sub>2</sub> and 100% O<sub>2</sub> atmosphere, respectively [44]. Stern-Volmer plots of these Ir(III) complexes in CH<sub>3</sub>CN were studied (see Fig. S4 in Supporting Information). The  $I_0/I_{100}$  value is 64.2 for complex **5CF<sub>3</sub>-POFIrpic**. The  $I_0/I_{100}$  values of **POFIrpic**, **4Me-POFIrpic** and **5F-POFIrpic** are 105.8, 103.4 and 110.9, respectively. For **5Me-POFIrpic**, the highest quenching efficiency is increased to  $I_0/I_{100} = 150.3$ . Indeed, the incorporation of a CH<sub>3</sub> group at the 5-position of pyridyl ring in C<sup>N</sup> cyclometalating ligand is clearly advantageous in terms of increasing oxygen sensitivity compared with other complexes.

# 3.5. Oxygen sensitivity of the Ir(III) complexes in polymer films

The oxygen sensors with ethylcellulose (EC) as an efficient matrix have been reported [45,46]. Herein the oxygen sensitivity of the Ir(III) complexes were also studied in EC film. The dynamic response of the oxygen sensing film was tested against small steps of O<sub>2</sub> partial pressure variation (see Fig. S5 in Supporting Information). As shown in Table 4, the  $I_0/I_{100}$  values of these Ir(III) complexes immobilized into EC films are 4.47 (**POFIrpic**), 4.02 (**4Me-POFIrpic**), 5.88 (**5Me-POFIrpic**), 4.06 (**5F-POFIrpic**) and 3.93 (**5CF<sub>3</sub>-POFIrpic**).

For the heterogeneous oxygen sensing films, usually, a modified Stern-Volmer is required to quantify the quenching effect. A twosite model was proposed by Demas and co-workers [47,48], which has been generally accepted and widely used ever since [7,49,50]. In the two-site model, the OPS is taken (at least) two distinctly different environments into account, one ( $f_1$ ) being quenchable, the other ( $f_2$ ) either not being quenched at all, or being quenched at a very different rate ( $f_1 + f_2 = 1$ ). Each component shows different quenching constants ( $K_{SV1}$  and  $K_{SV2}$ ), it reads as follows (eqn (2)).

$$\frac{I}{I_0} = \frac{f_1}{1 + K_{\text{SV1}} \cdot p_{\text{O}_2}} + \frac{f_2}{1 + K_{\text{SV2}} \cdot p_{\text{O}_2}}$$
(2)

where  $I_0$  and I, are the emission intensities of a probe in the absence and presence of oxygen, respectively.  $p_{02}$  is the partial pressure of oxygen. The weighted quenching constant  $K_{sv}^{app}(K_{SV}^{app} = f_1 \cdot K_{SV1} + f_2 \cdot K_{SV2})$  is the guide of the sensitivity of an oxygen sensor, and higher values of  $K_{sv}^{app}$  indicate that the sensor is more sensitive to oxygen.

The Stern-Volmer plots for oxygen sensing films of these Ir(III) complexes immobilized in EC are shown in Fig. 4. The fitting results of the O<sub>2</sub> sensing data of these Ir(III) complexes are summarized in Table 4. The  $K_{S\nu}^{app}$  values of these Ir(III) complexes immobilized in EC film are 0.00583 (**POFIrpic**), 0.00518 (**4Me-POFIrpic**), 0.00793 (**5Me-POFIrpic**), 0.00522 (**5F-POFIrpic**) and 0.00459 (**5CF<sub>3</sub>-POFIrpic**) Torr<sup>-1</sup>. It is clear that the **5Me-POFIrpic** immobilized in EC exhibits the highest sensitivity to O<sub>2</sub> at a  $K_{SV}^{app}$  value up to 0.00793 Torr<sup>-1</sup>.

Generally, the complex **5Me-POFIrpic** shows higher oxygen sensitivity than the other Ir(III) complexes both in solution and doped in EC film. The presence of  $CH_3$  in C<sup>N</sup> cyclometalating ligand improves oxygen sensitivity since its emission decay lifetime is prolonged and thus increases sensing collision probability with  $O_2$  molecules. This indicates that rational chemical modification of the C<sup>N</sup> cyclometalating ligand can also pave the way to tune the oxygen sensitivity.



Fig. 4. Stern-Volmer plots for oxygen sensing films of the Ir(III) complexes immobilized in EC (intensity ratios  $I_0/I$  versus O<sub>2</sub> partial pressure).

Table 4

Parameters for the O<sub>2</sub>-sensing film of the Ir(III) complexes with EC as the supporting matrix (fitting of the result to the two-site model).

Complexes	$\lambda_{em}$ (nm)	$I_0/I_{100}$	$f_1^a$	$f_2^a$	K <sub>SV1</sub> <sup>b</sup>	K <sub>SV2</sub> <sup>b</sup>	r <sup>2c</sup>	K <sup>app d</sup> <sub>SV</sub>	t <sub>res</sub> (s) <sup>e</sup>	t <sub>rec</sub> (s) <sup>e</sup>
POFIrpic	461, 488	4.47	0.94684	0.05316	0.00616	0.0000	0.99676	0.00583	4	5
4Me-POFIrpic	458, 485	4.02	0.92998	0.07002	0.00557	0.0000	0.99659	0.00518	4	6
5Me-POFIrpic	465, 494	5.88	0.95764	0.04236	0.00828	0.0002	0.99390	0.00793	4	5
5F-POFIrpic	467, 492	4.06	0.91921	0.08079	0.00568	0.0000	0.99597	0.00522	3	5
5CF₃-POFIrpic	480	3.93	0.95550	0.04450	0.00480	0.0001	0.99619	0.00459	5	6

<sup>a</sup> Ratio of the two portions of the Ir(III) complexes.

<sup>b</sup> Quenching constant of the two portions.

<sup>c</sup> Determination coefficients.

<sup>d</sup> Weighted quenching constant,  $K_{SV}^{app} = f_1 K_{SV1} + f_2 K_{SV2}$ .

<sup>e</sup> The response and recovery time for optical oxygen sensors are defined as the time for emission intensity changes to reach 95% of the whole variation when switching from 100% N<sub>2</sub> to 100% O<sub>2</sub> or vice versa.



Fig. 5. Reversibility and emission intensity response of sensing film of 5Me-POFIrPic immobilized in EC when cycling from 100% N<sub>2</sub> to 100% O<sub>2</sub> atmosphere.



Fig. 6. Photo-degradation histograms for the Ir(III) complexes/EC films under continuous illumination for 2.0 h at ambient atmospheric condition.

# 3.6. Operational stability and photostability of oxygen sensing films

Reversibility and stability are important factors to influence the overall performance of a sensor. Therefore, the operational stability and photostability tests of oxygen sensing films were conducted. The emission intensity is monitored when the oxygen sensing film is exposed to an atmosphere which periodically varies between 100% N<sub>2</sub> and 100% O<sub>2</sub> within 4000 s. All the oxygen sensing films demonstrated a stable optical signal during the quenching and recovering cycles (Fig. 5 and Fig. S6 in Supporting Information), suggesting that they have good operational stability. Fast response times of the Ir(III) complexes immobilized in EC films were obtained at around 3-5 s on going from O<sub>2</sub> to N<sub>2</sub> (Table 4). Additionally, no photobleaching phenomenon was observed with increasing exposure time, which indicates that they have very good photostability.

The photostability of the sensing films were further studied upon continuous irradiation by a 16 W UV lamp. As shown in Fig. 6, the emission intensity of the Ir(III) complexes immobilized in EC reduced by different degree after 2.0 h of irradiation. In fact, 46.7% (**POFIrpic**), 44.9% (**4Me-POFIrpic**), 49.4% (**5Me-POFIrpic**), 45.5% (**5F-POFIrpic**), and 29.9% (**5CF<sub>3</sub>-POFIrpic**) decreases in the intensity are observed. It was observed that introduction of a CH<sub>3</sub> group into the pyridyl ring has negative effects on the photostability of the corresponding complexes **4Me-POFIrPic** and **5Me-POFIrPic**. It is clear that introduction of an electron-withdrawing F or CF<sub>3</sub> group on the 5-position of the pyridyl ring has a positive effect on the photostability. Especially, the complex **5CF<sub>3</sub>-POFIrPic** demonstrated the highest photostability. The increase in the excited state  $E_{ox}^*$  potentials correlates well with higher photostability of **5CF<sub>3</sub>-POFIrPic** compared to the others (Table 2). It is reasoned that the Ir(III) complex with a CF<sub>3</sub> substituent on the pyridyl ring may be more resistant to photobleaching processes and this has increased photostability [51].

#### 4. Conclusions

In summary, a series of diphenylphosphoryl-substituted biscyclometalated Ir(III) complexes were synthesized and their photophysical, electrochemical and oxygen sensing properties were studied in detail. These Ir(III) complexes exhibit intense emission bands at 455–492 nm and high photoluminescence quantum yields in the range of 54–64% in CH<sub>2</sub>Cl<sub>2</sub>. Introducing a CH<sub>3</sub> group at 4-position of pyridyl ring, resulting in the emission band of **4Me-POFIrpic** being blue-shifted relative to that of the un-substituted **POFIrpic**. Whilst introducing a CH<sub>3</sub>, F or CF<sub>3</sub> group at 5-position of pyridyl ring gives emission bands of the corresponding Ir(III) complexes (**5Me-POFIrpic**, **5F-POFIrpic**, **5CF<sub>3</sub>-POFIrpic**) redshifted in comparison with that of **POFIrpic**. **5Me-POFIrpic** performs the best oxygen sensitivity and **5CF<sub>3</sub>-POFIrpic** exhibits the highest photostability.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2017.05.056.

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