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# Photostable ester-substituted bis-cyclometalated cationic iridium(III) complexes for continuous

monitoring oxygen

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Three bis-cyclometalated cationic Ir(III) complexes Ir1, Ir2 and Ir3 with an ester substituent at the 4position of the phenyl ring on the 2-phenylpyridine (ppy) have been synthesized and fully characterized. The emission maxima of ester-substituted Ir(III) complexes show notably blue-shift compared to the parent complex Ir0  $[Ir(ppy)_2(phen)]^+PF_6$  (phen = 1,10-phenanthroline). The influences of an ester group 10 on the photoelectric properties of the Ir(III) complexes have been investigated systematically. The oxygen sensing films prepared from ethyl cellulose immobilized with Ir(III) complexes exhibit excellent operational stability, high photostability and quick response to oxygen. Ir1~Ir3 demonstrate extended luminescent lifetimes relative to Ir0, and display better sensitivity on changes of oxygen partial pressures.

# **1** Introduction

- 15 Oxygen measurements are of great importance in many environmental and biomedical applications.<sup>1,2</sup> Compared with traditional techniques, optical oxygen methods have many including high sensitivity, advantages immunity to electromagnetic interference, virtually non-invasive, no oxygen 20 consumption, and fast response times.<sup>3</sup> Thus, they have become extremely popular in the last two decades. The dynamic quenching of luminescence of the oxygen sensitive probes by molecular oxygen is the most widely used sensing mechanism for the optical detection of this gas.4,5 An ideal oxygen sensitive 25 probe should possess several key requirements: efficient emission (high quantum yield) for improved sensitivity, long luminescent lifetime (from hundreds of nanoseconds to microseconds) to be
- quenched efficiently by oxygen. Equally important is high photostability of the probes to construct robust oxygen sensing 30 systems.<sup>6</sup> In recent years, many heavy metal complexes as oxygen-sensitive probes have been developed in the fabrication of oxygen-sensing devices by dissolved in a solvent or immobilized in a polymer matrix.7-11 Among them, Ir(III)
- complexes are particularly suitable for the use in oxygen sensing, 35 due to their relatively long lifetimes, high emission quantum yields, and flexible tuning of photophysical and electrochemical properties by the coordinating ligands.<sup>12,13</sup>

The substituent effect has been recognized as an important factor for adjusting the photoelectric properties of the luminescence

40 metal complexes. Several groups have demonstrated that the colours or quantum yields of metal complexes could be effectively influenced by different substituents, such as CF<sub>3</sub>, F, COOR, Me, OMe, and so on.<sup>14-16</sup> For example, introducing an ester substituent onto the cyclometalating ligands of Ir(III)

- 45 complexes could tune the emission wave-length red-shift for developing efficient organic light-emitting diodes<sup>17,18</sup> and lightemitting electrochemical cells.<sup>19</sup> Moreover, the water-soluble carboxylate Ir(III) complexes obtained from the hydrolysis of the ester-substituted complexes showed a promising application in 50 bioprocessing.<sup>20,21</sup> It is worth mentioning that, in 2012, Marín-Suárez and co-workers<sup>22</sup> described the use of ester-substituted blue phosphorescent neutral Ir(III) complexes immobilized in the AP200/19 polymer for efficient oxygen detection at a low concentration. These reports demonstrate that the ester group is 55 an interesting substituent for adjusting the photoelectric properties of the corresponding metal complexes. To the best of our knowledge, no example of ester-substituted biscyclometalated cationic Ir(III) complexes for oxygen sensing has been reported yet.
- 60 In the present paper, three new bis-cyclometalated cationic Ir(III) complexes  $[Ir(C^N)_2(phen)]^+PF_6^-$  (Ir1~Ir3) modified with -COOEt were synthesized. The chemical structures of these complexes are illustrated in Fig. 1.



65 Fig. 1 Chemical structures of the Ir(III) complexes for this study.

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Their photophysical and electrochemical properties have been fully investigated. In addition, we fabricated the ethyl cellulose (EC) films immobilized with these Ir(III) complexes to evaluate their oxygen sensitivity and photostability.

## **5 2 Results and discussion**

# 2.1 Crystal structure of Ir2

The perspective view of **Ir2** is shown in Fig. 2 and selected crystallographic data are provided in Table S1 (see ESI). It can be seen that the Ir(III) center in **Ir2** adopts a distorted octahedral <sup>10</sup> coordination geometry with *cis*-metalated carbons and *trans* nitrogen atoms. The distance of Ir–N (N^N ligands) is 2.143(4) Å, which is longer than that of Ir–N (C^N ligands) (2.059(4) Å). The N–Ir–N and C–Ir–N angles are 77.4° and 80.5°, which are similar to the previously reported.<sup>23-25</sup> The cation of **Ir2** is connected to <sup>15</sup> the anion PF<sub>6</sub><sup>-</sup> by weak intra- and intermolecular C–H---F–P hydrogen bonds with an average H---F distance of 2.62 Å and intramolecular N–H---F–P hydrogen bonds with an average H----F distance of 2.22 Å.



20 Fig. 2 Perspective view of Ir2 (the thermal ellipsoids drawn at 30% probability level and hydrogen atoms are omitted for clarity).

#### 2.2 Photophysical and electrochemical properties

- UV-visible absorption spectra (Fig. 3) of all the Ir(III) complexes were measured in CH<sub>2</sub>Cl<sub>2</sub> at room temperature (Table 1). All <sup>25</sup> Ir(III) complexes exhibit two major absorption bands in their UVvis absorption spectra, which are primarily due to the spinallowed intraligand ( ${}^{1}\pi{-}\pi{*}$ ) transitions. The weak absorption bands in the range 385~460 nm can be assigned to both spinallowed and spin-forbidden metal-to-ligand charge transfer <sup>30</sup> ( ${}^{1}MLCT$  and  ${}^{3}MLCT$ ) transitions.<sup>26,27</sup> The four spectra have similar band positions, however, obvious differences in
- absorption coefficient are observed. **Ir1~Ir3** have larger molar absorption coefficient in the visible region than that of **Ir0**. For example, the second bands of **Ir1~Ir3** around 270 nm are similar <sup>35</sup> with absorption coefficient above 76,500 M<sup>-1</sup>cm<sup>-1</sup>, they are
- stronger than Ir0 (38,000 M<sup>-1</sup> cm<sup>-1</sup>). The excitation spectra of Ir0~Ir3 are almost the same as those of the absorption spectra (see Fig. S1, ESI), illustrating that phosphorescence shown in Fig. 3 comes from the target Ir(III) complexes, and not from <sup>40</sup> impurities. The emission maxima of Ir1~Ir3 ( $\lambda_{max}$  at 541, 506
- and 547 nm) in CH<sub>2</sub>Cl<sub>2</sub> show notably blue-shift relative to **Ir0** ( $\lambda_{max}$  at 570 nm). The tuning of the emission maxima in the estersubstituted complexes can be rationalized by taking into account the donor-acceptor characters of the substituents and their impact 45 on the HOMO and LUMO energy levels. The emission spectra of





Fig. 3 Absorption spectra (up) and emission spectra (down) of the Ir0~Ir3 ( $1.0 \times 10^{-5}$  M) ( $\lambda_{ex} = 400$  nm) in CH<sub>2</sub>Cl<sub>2</sub> solution, at ambient temperature.

<sup>55</sup> The onset oxidation potentials of **Ir0~Ir3** are at 1.20 V, 1.36 V. 1.43 V and 1.31 V, indicating that the introduction of the ester group into the cyclometalating ligand stabilizes the metal center as it is more difficult to oxidize. These complexes exhibit reduction wave at similar potentials between -1.33 V and -1.38 60 V, which can be assigned to the reduction of the phenanthroline ligands (see Fig. S3, ESI). Specifically, Ir2 shows the highest quantum efficiency  $(\Phi_p)$  and onset oxidation potential than other three complexes, which is probably attributed to the addition of a fluorine atom on the pyridine ring. The C-F bond of the 65 cyclometalating ligand can increase the phosphorescent quantum yield and stabilize the HOMO energy level.31-34 Obviously, the luminescent lifetimes ( $\tau$ ) of Ir1~Ir3 are longer than that of Ir0 in deaerated CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN, respectively. The reason for this might be that coordination of ester group with a Ir(III) center in 70 the complexes Ir1~Ir3, the electron from the triplet metal-toligand charge transfer (<sup>3</sup>MLCT) to the short-lived and nonemissive triplet metal-centered (<sup>3</sup>MC) state is suppressed, and the energy difference between <sup>3</sup>MLCT and <sup>3</sup>MC states increases, resulting in reduced radiationless decay and prolonging the

75 luminescence lifetime.<sup>35-37</sup>



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#### Table 1. Photophysical and electrochemical data for Ir0~Ir3.

Complexes	$\lambda_{abs}(nm)^{a}$	$\lambda_{em}(nm)^{b}$	$\Phi_p^{\ c}$	$\tau(\mu s)^d$	$\tau(\mu s)^e$	$E_{red}^{onset}\left(\mathbf{V}\right)^{\mathrm{f}}$	$E_{ox}^{onset}\left(V\right)^{f}$	HOMO (eV) <sup>g</sup>	LUMO (eN)	/ ACLE(XGY)ine
Ir0	231(2.99),265(3.81)385(0.50), 417(0.22)	570	0.23	0.80	1.13	-1.36	1.20	-5.60 DC	-3.07	0.50,0.49
Ir1	231(7.53),269(7.97)398(0.38),426(0.58)	541	0.22	2.02	3.81	-1.35	1.36	-5.76	-3.13	0.34,0.60
Ir2	231(5.33),272(7.65)400(0.70),428(0.60)	<b>506</b> ,539	0.38	3.09	4.57	-1.33	1.43	-5.83	-3.19	0.31,0.62
Ir3	232(5.35),271(8.25)399(0.76),425(0.62)	547	0.29	1.35	3.21	-1.38	1.31	-5.71	-3.12	0.36,0.59

<sup>a</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub> at a concentration of 10<sup>-5</sup> M and extinction coefficients (10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>) are shown in parentheses. <sup>b</sup> The emission maxima are the values in bold style. <sup>c</sup> The quantum yields ( $\Phi_p$ ) in degassed CH<sub>2</sub>Cl<sub>2</sub> solution were measured with [Ir(ppy)<sub>2</sub>(acac)] ( $\Phi_p$ = 0.34) as a standard ( $\lambda_{ex}$ = 400 nm). <sup>d</sup> In degassed CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>e</sup> In degassed CH<sub>3</sub>CN solution. <sup>f</sup> 0.1 M [Bu<sub>4</sub>N]PF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub>, scan rate 100 mV·s<sup>-1</sup>, measured using saturated calomel electrode (SCE) as the standard. <sup>g</sup> E<sub>HOMO</sub> (eV) = -e(4.4+E<sup>oxstefl</sup><sub>ox</sub>). <sup>h</sup> E<sub>LUMO</sub> (eV) = E<sub>HOMO</sub> + E<sub>00</sub>. All measured at ambient temperature.

Fable 2.	Contour	plots c	of fr	ontier	molecular	orbitals	of Ir0	~ <b>Ir3</b> i	n ground sta	te.



#### 2.3 Theoretical calculations

- <sup>5</sup> In order to understand the impacts of the substituents on the photophysical and electrochemical behavior of these Ir(III) complexes, density functional theory (DFT) calculations for Ir(III) complexes were performed. As reported in Table 2, the HOMO distribution primarily resides on the iridium center and <sup>10</sup> cyclometalating ligands, the LUMO distribution is localized on the whole phenanthroline ligand. The HOMO–LUMO gaps calculated for **Ir0~Ir3** are 2.66 eV, 2.76 eV, 2.84 eV and 2.73 eV, respectively. The complexes **Ir0~Ir3** show different HOMO–LUMO gaps from 2.66 eV to 2.84 eV, which is attributed to the total of the substituent of the substituent of the substituent of the substituent.
- <sup>15</sup> introduction of different substituents on the cyclometalated complexes. The enhanced photoelectric properties of estersubstituted complexes may have great opportunities to improve their oxygen sensitivity. Considering the measuring conditions and basis sets of calculation, the difference between experimental <sup>20</sup> values and calculated values is acceptable.

#### 2.4 Oxygen sensing properties

Ir(III) complexes with a long-living excited state usually have a strong dynamic collision with triplet oxygen, which leads to a reduction of its decay time and/or emission intensity, and to the

25 formation of highly reactive singlet oxygen. The dynamic quenching process of Ir(III) complex by triplet oxygen can occur through two mechanisms: electron transfer and energy transfer. In both cases, a long luminescent lifetime will favor the process, enhancing the oxygen sensing ability of the complex. The process can be described as follows:  $Ir^{III} + O_2 \rightarrow Ir^{III} + O_2^*$ , where  $Ir^{III}$ denotes the complex and the "\*" indicates the excited state. The relationship between emission intensity (or luminescent lifetimes) and the concentration of oxygen is reflected by a two-site model to fit the curved Stern–Volmer plots (SVPs) in the oxygen 70 sensing film, which can be described as follows (Eq 1).<sup>38,39</sup>

$$\frac{I}{I_0} = \frac{\tau}{\tau_0} = \frac{f_1}{1 + K_{\text{SV1}} \cdot p_{\text{O}_2}} + \frac{f_2}{1 + K_{\text{SV2}} \cdot p_{\text{O}_2}} \qquad \text{Eq 1}$$

In the equation,  $I_0$  and  $\tau_0$  are the unquenched luminescent intensity and lifetime in an inert atmosphere, I and  $\tau$  are the corresponding quantities in the presence of oxygen.  $f_1$  and  $f_2$  are  $\tau_0$  the fractions of the total emission for each component ( $f_1 + f_2 = 1$ ),  $K_{SV1}$  and  $K_{SV2}$  are the Stern–Volmer constants for the two components.  $p_{O2}$  is the partial pressure of oxygen.



Scheme 1 The simple diagrams of optical oxygen sensing in <sup>55</sup> solution and EC.

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Fig. 4 Emission spectra of Ir0~Ir3 under different partial pressures of  $O_2$  in CH<sub>3</sub>CN solutions ( $1.0 \times 10^{-5}$  M) ( $\lambda_{ex} = 400$  nm, s at ambient temperature). In order to compare the quenching properties of the complexes in solution, the Y axis is set from -100.

First, we studied the oxygen sensing properties of **Ir0~Ir3** in solution. As expected, the emission intensity of complexes <sup>10</sup> decreased with the increase of oxygen concentration from 0 to 100% (Fig. 4), suggesting that oxygen has a significant effect on the emission intensity of these complexes. The luminescence is quenched by oxygen without distortions in the shape of the spectra.



Fig. 5 Phosphorescence decay profiles of Ir0~Ir3 in CH<sub>3</sub>CN solutions at the different concentrations of oxygen (0–9.61%) at ambient temperature.

- <sup>20</sup> The luminescent lifetimes ( $\tau$ ) of **Ir0~Ir3** in CH<sub>3</sub>CN solution (1.0 × 10<sup>-5</sup> M) were obtained for different oxygen concentrations at ambient temperature, the results are illuminated in Fig. 5. Interestingly, Fig. 5 shows markedly changed luminescent lifetimes ( $\tau$ ) in dependence on oxygen partial pressure. For
- <sup>25</sup> example, the luminescent lifetime (τ) of Ir2 is 4.57 μs in degassed CH<sub>3</sub>CN solution. The τ value reduces drastically to 0.42 μs in the presence of 9.61% O<sub>2</sub>. In contrast, the luminescent lifetime of Ir0 reduces from 1.13 μs to 0.11 μs under the same experimental conditions (see Table S5 and Fig. S8, ESI). Thus,
  <sup>30</sup> the dynamic ranges of response for Ir1~ir3 are larger than that of Ir0 under the conditions used.



**Fig. 6** Emission spectra of **Ir0~Ir3** in CH<sub>2</sub>Cl<sub>2</sub> solution (solid) and 0.5 wt % doped in **EC** (dash) ( $\lambda_{ex} = 400$  nm), at ambient <sup>35</sup> temperature.

Dynamic quenching of the Ir(III) complexes (Ir0~Ir3) immobilized in polymer films by oxygen was also investigated, including polar rigid ethylcellulose (EC), apolar flexible poly(cyclohexene carbonate) (PCHC) and apolar rigid 40 polystyrene (**PS**). The results of oxygen sensing tests show that the  $K_{sv}^{app}$  value of EC film immobilized with Ir1 (Ir1/EC) is higher than those of others (see Fig. S6, ESI). This is because EC is easily penetrated by oxygen with a permeability coefficient Pof 1.1  $\times$  10  $^{\text{-12}}$  cm² Pa s<sup>-1</sup>, and is regarded as a standard host 45 material for oxygen sensing.40 Additionally, the contents of oxygen-sensitive probes in EC were optimized to reach the highest sensitivity. The results indicate that the optimum content of EC film immobilized with Ir1 is 0.50 mg/g and its  $K_{sv}^{app}$  value is up to 0.00861 Torr<sup>-1</sup> (see Table S4, ESI). The results show that at 50 this content the EC matrix protects the complexes from potential interference and avoids self-quenching efficiently. Thus, EC and 0.5 wt% Ir(III) complexes were chosen as standard conditions for oxygen sensing (see Fig. S7, ESI). Compared with the emission spectra in solution, the emission spectra of Ir0~Ir3 in EC films 55 exhibit blue-shifts (Fig. 6) due to the rigidochromic effect, thus, the intraligand excited state dominates in the EC film.  $^{41,42}$ According to Eq (1), the quenching behaviors of Ir0~Ir3 were analyzed at various concentrations of oxygen. As the results showed in Table 4, the complexes Ir1~Ir3 are also more sensitive 60 to oxygen than Ir0. The  $I_0/I_{100}$  values of EC film sensors immobilized with Ir0~Ir3 are 3.47, 6.20, 6.46, and 7.25, respectively. The most sensitive film is the oxygen-sensitive probe of Ir3 incorporated into EC, showing a  $K_{SV}^{app}$  of 0.01052 torr<sup>-1</sup> (7.99520 bar<sup>-1</sup>), which is about 2 times higher than the  $K_{sv}^{app}$ 65 of Ir0 (0.00417 torr<sup>-1</sup> or 3.16920 bar<sup>-1</sup>) under same conditions. A reproducibility test of oxygen sensing film of Ir0 was conducted. The error of  $I_0/I_{100}$  value was determined using the mean value of five Ir0/EC films (see Fig. S9, ESI). The  $I_0/I_{100}$  values of Ir0/EC films are calculated to be  $3.47 \pm 0.11$ , showing good 70 reproducibility.

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**Fig. 7** Time trace curves of **Ir0**~**Ir3** (0.5 wt%) immobilized in **EC** to  $O_2/N_2$  saturation cycles( $\lambda_{ex} = 400$  nm). In order to compare s the quenching properties of the films, the Y axis is set from 0.



Fig. 8 The partial enlarged drawing of  $O_2/N_2$  saturation cycles.

# 2.5 Operational stability and photostability

- <sup>10</sup> Fig. 7 shows an operational stability test conducted by the emission intensity of oxygen sensing films of **Ir0~Ir3**. It is clear that the emission intensity responses are fully reversible when the atmosphere varies periodically between 100%  $N_2$  and 100%  $O_2$  in 4000 s. The complete reversibility of the luminescence emission
- 15 of the oxygen sensitive films allows stable and continuous monitoring the concentration of oxygen. All of the sensing films demonstrate quick response times (< 4.5 s when changing from 0 to 100 vol%  $O_2$ ) and recovery times (< 6 s when changing from 100 to 0 vol%  $O_2$ ), respectively (Fig. 8). Thus it can be seen that
- 20 the oxygen sensing films of these cationic Ir(III) complexes show complete reversibility with short response time.
- In addition, the photostability of sensing films were studied upon continuous irradiation by a WFH-204B 254 nm UV lamp. The emission intensity of the Ir(III) complexes immobilized in EC 25 reduced in different degree (Fig. 9). In fact, 10.0%, 21.7%, 10.1%
- and 15.7% decreases in intensity of **Ir0~Ir3** are observed respectively, compared to 64.3% for **Ir(ppy)<sub>2</sub>(acac)** after 60 min of irradiation. It is clear that these cationic Ir(III) complexes are more stable than the neutral Ir(III) complex **Ir(ppy)<sub>2</sub>(acac)** upon
- 30 continuous illumination. The results in Table 3 show that

**Ir(ppy)<sub>2</sub>(acac)** has an oxidation potential of 0.71 V, which is considerably lower than these of the cationic Ir (III) complexes  $(E_{ox} = 1.20 \sim 1.43 \text{ V})$ . It has been reported that the transformation of a neutral Ir(III) complex into the cationic form could be a good <sup>35</sup> design strategy to appropriately tune the oxidation potential and the photostability.<sup>43,44</sup> The photooxidation of iridium complexes is enhanced by higher electron density and lower excited state oxidation potential.<sup>45</sup> The excited state  $E_{ox}^*$  potential can be calculated from the electrochemically determined ground state <sup>40</sup>  $E_{ox}$  potential and the energy gap ( $E_{00}$ ). The excited state oxidation potential of **Ir(ppy)<sub>2</sub>(acac)** (-1.83 V) is also lower than those of the cationic Ir (III) complexes (-1.21 ~ -1.33 V). The higher

the cationic Ir (III) complexes (-1.21  $\sim$  -1.33 V). The higher oxidation potentials of these cationic Ir (III) complexes make the molecules less reactive toward photooxidation processes and <sup>45</sup> increase the photostability.

**Table 3.** The excited state redox potentials for the Ir(III) complexes.

Complexes	$E_{ox}^{onset}$ (eV) <sup>a</sup>	$E_{00}(V)^{b}$	$E_{ox}^{*}$
Ir(ppy)2(acac)d	0.71	2.54	-1.83
Ir0	1.20	2.53	-1.33
Ir1	1.36	2.63	-1.27
Ir2	1.43	2.64	-1.21
Ir3	1.31	2.59	-1.28

<sup>a</sup> 0.1 M [Bu<sub>4</sub>N]PF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub>, scan rate 100 mV·s<sup>-1</sup>, measured using saturated calomel electrode (SCE) as the standard. <sup>b</sup>  $E_{00}$  were calculated from the intersection of the normalized absorption and emission spectra by equation of  $E_{00} = 1240/\lambda_{edge}$ . <sup>c</sup>  $E_{0x}^* = E_{ox}^* E_{00}$ . <sup>d</sup> Reference 49.



**Fig. 9** Photo-degradation histograms for **Ir0~Ir3** and <sup>50</sup> Ir(ppy)<sub>2</sub>(acac) immobilized in **EC** under continuous illumination for 60 min at ambient atmospheric conditions.

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Table 4. Parameters for the  $O_2$ -sensing film of the Ir(III) complexes with EC as the supporting matrix (fitting of the result to the two-site model).

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Complexes (0.5 wt%)	$f_1^a$	$f_2^a$	$K_{SV1}^{b}$	$K_{\rm SV2}^{\rm b}$	$r^{2c}$	<b>K<sup>appd</sup>ol: 10</b>	.1039/ <b>P52</b> DT02804C
Ir0	0.92270	0.07730	0.00452	0.0001	0.99827	0.00417	239.81
Ir1	0.96251	0.03749	0.00895	0.0001	0.99790	0.00861	116.14
Ir2	0.95945	0.04055	0.00983	0.0001	0.99651	0.00943	106.04
Ir3	0.96674	0.03326	0.01088	0.0000	0.99778	0.01052	95.06
<sup>a</sup> Ratio of the two portions of the $K_{eve}^{app} = f_1 K_{eve} + f_2 K_{eve}^{eve}$ The oxy	Ir(III) complexes. <sup>t</sup>	Quenching cons at which the initia	tant of the two po al emission intensi	ortions. <sup>c</sup> Determi	nation coefficients uenched by 50% a	s. <sup>d</sup> Weighted quer nd calculated as 1/	the network of the second sec

Importantly, all the ester-substituted complexes are more sensitive to oxygen than Ir0 both in solutions and doped in EC films. The corresponding orders of oxygen sensitivity are Ir3 > Ir1 > Ir2 > Ir0 and Ir3 > Ir2 > Ir1 > Ir0 (Fig. 10 (a) and (b)), respectively. To sum up, Ir1~Ir3 are promising candidates for oxygen sensing due to several reasons: (i) these complexes with a -COOEt substituent exhibit good solubility in organic solvents; (ii) the relatively larger ester-substituted complexes Ir1~Ir3 are less sensitive to self-quenching, triplet annihilation effects or radiationless decay than the smaller Ir0; (iii) the wide range of the luminescent lifetime will favour the quenching process.<sup>46,47</sup>



<sup>15</sup> Fig. 10 (a) Stern–Volmer plots (intensity ratios  $I_0/I$  versus  $O_2$  partial pressure) of Ir0~Ir3 in CH<sub>3</sub>CN solutions ( $1.0 \times 10^{-5}$  M); (b) Stern–Volmer plots of Ir0~Ir3 (0.5 wt%) immobilized into EC films ( $\lambda_{ex} = 400$  nm), at ambient temperature.

# **3** Conclusions

- <sup>20</sup> In conclusion, three new ester-substituted bis-cyclometalated cationic Ir(III) complexes (Ir1~Ir3) were synthesized and their photoelectric properties were studied in detail. Ir1~Ir3 have larger molar absorption coefficient in the visible region and higher oxidation potentials than Ir0. The prolonged luminescent
- <sup>25</sup> lifetimes of Ir1~Ir3 compared with Ir0 provide larger dynamic range of response to molecular oxygen. Moreover, these cationic Ir(III) complexes exhibit good operational stability in continuous monitoring oxygen and excellent photostability against continuous irradiation. This study demonstrates that the
- <sup>30</sup> introduction of an ester group on the cyclometalating ligand can tune the luminescent lifetime and oxygen sensing property of the corresponding bis-cyclometalated cationic Ir(III) complex. This concept might bring a useful perspective in the development of new phosphorescent materials with high performances.

# 35 4 Experimental

6

#### 4.1 Materials and instruments

All starting materials were purchased from commercial suppliers and used without further purification. The solvents were treated as required prior to use. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were <sup>40</sup> recorded on a Varian Unity Inova spectrophotometer. Mass spectra were recorded with a MALDI micro MX spectrometer. UV/Vis absorption spectra were recorded on an HP8453 UV/Vis spectrophotometer. Emission spectra were recorded with a HITACHI F-7000 fluorescence spectrophotometer ( $\lambda_{ex} = 400$  nm).

- <sup>45</sup> Luminescent lifetimes were measured on an Edinburgh FLS920 Spectrometer. Cyclic voltammograms of the Ir(III) complexes were recorded on an electrochemical workstation (BAS100B/W, USA). Crystallographic data were collected using a Bruker SMART CCD diffractometer and graphite-monochromated <sup>50</sup> Mo-K*a* radiation ( $\lambda = 0.71073$  Å). CCDC reference number for
- Ir2 is 1045430. The starting geometry was from the single-crystal structure of complex Ir2. DFT calculations (full geometry optimization) were carried out by B3LYP. The LanL2DZ basis set was used to treat the iridium atom, whereas the  $6-31G^*$  basis set was used to treat all other atoms. All these calculations were
- performed with the Gaussian 09 software package.<sup>48</sup>

### 4.2 Synthesis

**Synthesis of C^N ligands.** The different C^N ligands containing an ester substituent were synthesized by the method developed <sup>60</sup> previously for analogous compounds (See ESI).

- **Synthesis of the Ir(III) complexes Ir1~Ir3.** IrCl<sub>3</sub>·3H<sub>2</sub>O was reacted with 2.5 equiv. cyclometalating ligand in a mixture of 2-ethoxyethanol and water (15 mL/5 mL) at 120 °C for 24 h to afford a cyclometalated iridium bridged-chloride dimer. Without
- <sup>65</sup> further purification the dimer was mixed with 3.0 equiv. phenanthroline in a mixture of dichloromethane (10 mL) and methanol (5 mL). The reaction mixture was stirred under refluxing for 12 h. After cooling down to room temperature, 10 equiv. KPF<sub>6</sub> was added and the mixture was stirred for 1 h. The 70 solvent was evaporated under reduced pressure and the residue
- was re-dissolved in dichloromethane. The organic layer was washed with water and dried over  $Na_2SO_4$ . Further purification for each complex was achieved using column chromatography.
- Ir1. Yield 68.2%, a yellow solid. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): <sup>75</sup>  $\delta$  8.92 (d, *J* = 8.4 Hz, 2H), 8.41 (d, *J* = 7.0 Hz, 4H), 8.24 - 8.19 (m, 2H), 8.10 (d, *J* = 8.3 Hz, 2H), 8.06 - 7.95 (m, 4H), 7.67 -7.52 (m, 4H), 7.13 (t, *J* = 6.6 Hz, 2H), 6.87 (d, *J* = 1.6 Hz, 2H), 4.14 (q, *J* = 7.0 Hz, 4H), 1.17 (t, *J* = 7.1 Hz, 6H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  166.5, 166.4, 150.8, 149.5, 149.2, 148.2,
- <sup>80</sup> 148.2, 146.7, 139.3, 138.5, 132.3, 131.8, 131.6, 128.9, 126.6, 124.7, 124.4, 120.8, 60.9, 14.2. HRMS (m/z; EI): calcd. for  $C_{40}H_{32}N_4O_4Ir [M PF_6]^+$  825.2053; found 825.2122.
- Ir2. Yield 58.4%, a yellow-green solid. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.91 (dd, *J* = 8.3 Hz, 1.3 Hz, 2H), 8.52 (dd, *J* = 9.2 ss Hz, 5.4 Hz, 2H), 8.39 (s, 2H), 8.17 (dd, *J* = 5.1 Hz, 1.2 Hz, 2H),
- 8.11 (dd, *J* = 11.3 Hz, 5.5 Hz, 4H), 8.01 (dd, *J* = 8.3 Hz, 5.1 Hz, 2H), 7.68 7.58 (m, 4H), 6.85 (d, *J* = 1.6 Hz, 2H), 4.16 (q, *J* =

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7.1 Hz, 4H), 1.19 (t, J = 7.1 Hz, 6H). <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  165.4, 162.8, 159.3, 157.3, 151.2, 147.8, 146.3, 139.1, 138.6, 138.3, 131.4, 130.3, 128.3, 127.2, 127.0, 125.1, 123.7, 122.7, 60.4, 14.2. HRMS (m/z; EI): calcd. for  ${}^{5}C_{40}H_{30}F_{2}N_{4}O_{4}$ Ir [M – PF<sub>6</sub>]<sup>+</sup> 861.1864; found 861.1914.

- **Ir3.** Yield 61.3%, a yellow solid. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.91 (dd, J = 8.3 Hz, 1.2 Hz, 2H), 8.40 (s, 2H), 8.31 (d, J = 8.5 Hz, 2H), 8.20 (dd, J = 5.1 Hz, 1.3 Hz, 2H), 8.04 (dd, J = 8.3 Hz, 4.4 Hz, 4H), 7.86 (d, J = 9.5 Hz, 2H), 7.61 (dd, J = 8.1 Hz, 1.6 Hz, 10 2H), 7.30 (s, 2H), 6.85 (d, J = 1.6 Hz, 2H), 4.13 (q, J = 7.1 Hz, 4H), 2.01 (s, 6H), 1.18 (t, J = 7.1 Hz, 6H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  166.0, 163.5, 151.4, 149.6, 149.3, 148.8, 146.6,
- 140.3, 139.4, 135.6, 131.9, 131.6, 130.4, 128.8, 127.7, 125.0, 124.0, 121.4, 60.9, 18.0, 14.4. HRMS (m/z; EI): calcd. for 15  $C_{42}H_{36}N_4O_4Ir [M PF_6]^+$  853.2366; found 853.2413.

## 4.3 Oxygen sensing film preparation and photostability test

Oxygen sensing films were prepared according to the literature:<sup>49</sup> EC (9.95 mg) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (0.90 mL) and then 0.10 mL Ir(III) complex (0.50 mg/mL) in CH<sub>2</sub>Cl<sub>2</sub> was added to the <sup>20</sup> solution. The mixture was treated via ultrasonic for 10 min at room temperature. Then, 0.10 mL of the solution was coated on a silica glass disk (diameter 1.4 cm). The solvent was evaporated at room temperature and a thin film was obtained. The samples with different loading levels and different matrixes were prepared with <sup>25</sup> procedure similar to that described above. The photostability of

these complexes in **EC** films was investigated by illuminating the films with a WFH–204B 254 nm UV lamp at a distance of 3 cm in the air. The power density on the film is  $23.4 \text{ W/m}^2$ .

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