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# Photoluminescence color tuning of phosphorescent bis-cyclometalated iridium(III) complexes by ancillary ligand replacement

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### ABSTRACT

A series of bis-cyclometalated iridium(III) complexes bearing various types of 1.3-diketonate ancillary ligands were prepared, and their photoluminescent (PL) properties were investigated, especially focusing on the emission color tuning. When the dipivaloylmethanate ancillary ligand ( $O^{-0-1a}$ ) was replaced by conjugated 1,3-diketonates such as 1,3-bis(3,4-dibutoxyphenyl)propane-1,3-dionate (**0^0-1b**) and 1,3bis(4-(dibenzo[b,d]furan-4-yl)phenyl)propane-1,3-dionate (**0^0-1c**), the blue-emitting bis[2-(3,5bis(trifluoromethyl)phenyl)pyridinato-N,C<sup>2'</sup>]iridium(III) (Ir-1) and bluish green-emitting bis[2phenylpyridinato- $N,C^{2'}$  [iridium(III) (**Ir-2**) complexes exhibited significantly red-shifted phosphorescence in solution ( $\lambda_{PI}$ ; 474–604 nm and 521–661 nm for **Ir-1a–c** and **Ir-2a–c**, respectively: the subscripts **a**, **b**, and **c** corresponding to **0^0-1a**-**c**). On the other hand, the ancillary ligand replacement was less effective on tuning the emission color of the green-emitting bis[2-(2,4-bis(trifluoromethyl) phenyl)pyridinato-N, $C^2$  |iridium(III) complex ( $\lambda_{PL}$ ; 541–566 nm for **Ir-3a–c**), and no PL color change was observed for the red-emitting bis[1-(dibenzo[b,d]furan-4-yl)isoquinolinato- $N, C^3$ ]iridium(III) complex (Ir-4). The X-ray crystallographic analysis for Ir-1a-c revealed that these complexes adopt cis-C,C and trans-N,N configuration, indicating that the coordination geometry around the iridium center is not a main factor for the emission spectral differences caused by the O^O ancillary ligands. Furthermore, the ancillary ligand effect on the PL properties of the present iridium(III) complexes is independent on solvent polarity and concentrations. Taking these results into consideration, the ancillary ligand effect should be attributed to the electronic structures of the complexes, and the inter-ligand energy transfer from the triplet metal-to-ligand charge transfer level at the cyclometalated ligand (<sup>3</sup>MLCT<sub>C^N</sub>) to the ancillary ligand-related triplet level ( ${}^{3}LC_{0^{n}O}$  or  ${}^{3}MLCT_{0^{n}O}$ ) should play a significant role in the triplet exciton formation. The PL properties of Ir-1-Ir-4 in PMMA films were also investigated, and the remarkable blue shifts of  $\lambda_{PL}$ s due to rigidochromism were observed for **Ir-1b,c** and **Ir-2b,c** that have the aromatic O^O ancillary ligands. It was found that some of the complexes developed here exhibited larger  $\Phi_{\rm PI}$ s in PMMA films than in toluene solutions.

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### 1. Introduction

Organic light-emitting diodes (OLEDs) have attracted much interest of researchers for the last few decades due to their promising applications such as flat-panel displays and solid-state lightings [1,2]. In order to obtain high performance OLEDs, phosphorescent materials are frequently used as emitters because combination of statistically generated triplet excitons (75% of all) with those obtained from the singlet excitons (25% of all) *via* intersystem crossing can theoretically achieve the internal quantum efficiency ( $\eta_{int}$ ) of 100%, corresponding to four times magnitude of the maximum  $\eta_{int}$  of fluorescent OLEDs that utilize only singlet excitons. With this respect, organometallic complexes with heavy metal centers such as Pt(II) [3,4], Ir(III) [5–7], Ru(II) [8], and Os(II) [9,10] have been widely studied because the strong spin-orbit coupling gives rise to the efficient intersystem crossing from the singlet excited state to the triplet to facilitate the generation of triplet excitons. Especially, cyclometalated iridium(III) complexes have been intensely developed since the pioneering work on the phosphorescent OLED was reported by Thompson and Forrest [11]. Homoleptic tris-cyclometalated (Ir( $C^{\Lambda}N_{3}$ ) and heteroleptic bis-cyclometalated (Ir( $C^{\Lambda}N_{2}(LX)$ ) iridium(III) complexes are representative examples,

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where *C*<sup>N</sup> and *LX* represent an arylpyridine-type cyclometalated ligand and an anionic ancillary ligand such as 1,3-diketonate, respectively [6,12,13]. The cyclometalated ligands bring about the strong ligand field influence on the metal center *via* the *d*– $\pi$  orbital overlap. Thus, the energy gap of the metal-centered excited states (*d*–*d*<sup>\*</sup>) increase to suppress the non-radiative decay, and strong phosphores-cence is obtained from the triplet metal-to-ligand charge transfer (MLCT) state [3,14,15]. In addition, it has been well demonstrated that the skeletal variation as well as the modification by substituent groups in the *C*^*N* ligands affords effective color tuning of phosphorescence, so various types of *C*^*N* ligands have been enthusiastically investigated to obtain desired colors of phosphorescence [6,16–19].

We previously developed highly emissive red phosphorescent  $(C^{N})_{2}$ Ir(O^{O}) complexes (O^{O}; 1,3-diketonate ancillary ligand) [20]. The employment of a  $\pi$ -extended *C*^*N* ligand such as 1-(dibenzo [*b*,*d*]furan-4-yl)isoquinoline yielded pure red phosphorescence  $(\lambda_{PL} = 640 \text{ nm}, \text{ in toluene at } 298 \text{ K}).$  When 1,3-bis(3,4dibutoxyphenyl)propane-1,3-dionate was employed as an O^O ancillary ligand, a larger photoluminescence (PL) quantum yield was obtained ( $\Phi_{PL} = 0.61$ , in toluene at 298 K) in comparison with the dipivaloylmethanate derivative ( $\Phi_{PL} = 0.55$ , in toluene at 298 K), although the emission color of these complexes is independent on the O^O ligand. However, in the course of our investigation of the ancillary ligand effect on photoluminescent properties of bis-cyclometalated Ir(III) complexes, the 1,3-diphenylpropane-1,3-dionate-type ligands significantly affect the PL color of the complexes when they are combined with some C^N ligands. Taking it into consideration that the 0<sup>\0</sup> ancillary ligand has received less attention to tune and improve phosphorescent properties [21–23], the systematic investigation to elucidate how the ancillary ligand determine the emission properties should lead to understanding the emission mechanism of the biscyclometalated Ir(III) complex as well as designing new types of Ir(III)-based phosphorescent emitters for OLEDs.

In this study, we show how a series of  $O^{0}$  ancillary ligands affect PL properties of  $(C^{N})_{2}$ Ir $(O^{0})$  complexes bearing four types of  $C^{N}$  ligands (**Ir-1–Ir-4**, Fig. 1). We employ three types of  $O^{0}$  ancillary ligands that have different electronic structures from each other ( $O^{0}$ -1a– $O^{0}$ -1c, Fig. 1).

### 2. Experimental section

### 2.1. General procedures

<sup>1</sup>H NMR spectra were obtained on a Jeol JNM-ECX400 (400 MHz) spectrometer, using TMS (0.00 ppm) and residual

CHD<sub>2</sub>CN (1.95 ppm) as internal standards for CDCl<sub>3</sub> and CD<sub>3</sub>CN, respectively. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were measured on a Shimadzu-Kratos AXIMA-CFR PLUS TOF mass spectrometer using sinapinic acid as a matrix. Elemental analyses were carried out on a J-Science MICRO CORDER JM10 analyzer.

The preparation of 2-(3.5-bis(trifluoromethyl)phenyl)pyridine (HC^N-1), 2-(2,4-bis(trifluoromethyl)phenyl)pyridine (HC^N-3). and 1-(dibenzo[b,d]furan-4-yl)isoquinoline (**HC^N-4**) were previously reported [20,24]. 2-Phenylpyridine (HC^N-2) was purchased from Tokyo Chemical Industry Co., Ltd. For the preparation of 1,3bis(4-(dibenzo[b,d]furan-4-yl)phenyl)propane-1,3-dione (HO^O-1c), 4-iodoacetophenone and ethyl 4-iodobenzoate were purchased from Wako Pure Chemical Industries, Ltd. (Dibenzo[*b*,*d*] furan-4-yl)boronic acid was purchased from Sigma-Aldrich Co. As a catalyst for the Suzuki-Miyaura cross-coupling reaction, Pd(PPh<sub>3</sub>)<sub>4</sub> was purchased from Wako Pure Chemical Industries, Ltd, and used just as obtained. Dipivaroylmethane (HO^O-1a) was purchased from Tokyo Chemical Industry Co., Ltd. The preparation of 1,3-bis(3,4-dibutoxyphenyl)propane-1,3-dione (HO^O-1b) was previously reported [25]. For the preparation of Ir-1-Ir-4, 2ethoxyethanol was purchased from Wako Pure Chemical Industries, Ltd.

### 2.2. Preparation of materials

### 2.2.1. Synthesis of 1-[4-(dibenzo[b,d]furan-4-yl)phenyl]ethanone(1)

To a mixture of 4-iodoacetophenone (1.36 g, 5.52 mmol), (dibenzo[b,d]furan-4-yl)boronic acid (1.02 g, 4.81 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (197 mg, 0.170 mmol) in 1,2-dimethoxyethane (50 mL) was added sodium carbonate (1.35 g, 12.7 mmol) in water (5 mL). Then, the mixture was heated at 70 °C for 15 h under nitrogen. After cooling, the solvent was removed on a rotary evaporator. The residue was dissolved in chloroform (200 mL), and the solution was washed with water (150 mL  $\times$  2) and sat. brine (150 mL), and then dried over anhydrous MgSO<sub>4</sub>. The solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography using chloroform as eluent. The obtained solid was further washed with hexane to afford a white solid of 1 (1.22 g, 4.26 mmol, 89%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.68 (s, 3H), 7,38 (dt, J = 0.9 and 7.8 Hz, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.49 (dt, J = 0.9 and 7.8 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.64 (dd, J = 0.9 and 7.8 Hz, 1H), 7.98–8.01 (m, 2H), 8.03 (d, *J* = 8.3 Hz, 2H), 8.13 (d, *J* = 8.3 Hz, 2H); MALDI-TOF MS m/z 287 ([M + H]<sup>+</sup>). Anal. Calcd for C<sub>20</sub>H<sub>14</sub>O<sub>2</sub>: C, 83.90; H, 4.93. Found: C, 83.55; H, 4.99.



Fig. 1. The structures of bis-cyclometalated iridium(III) complexes Ir-1-Ir-4, each of which is classified to three categories (a-c) with respect to the diketonate ancillary ligand.

### 2.2.2. Synthesis of ethyl 4-(dibenzo[b,d]furan-4-yl)benzoate (2)

To a mixture of ethyl 4-iodobenzoate (1.26 g, 4.56 mmol), (dibenzo[*b*,*d*]furan-4-yl)boronic acid (1.09 g, 5.14 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (153 mg, 0.132 mmol) in a solvent mixture of toluene (100 mL) and ethanol (10 mL) was added sodium carbonate (0.806 g, 7.60 mmol) in water (4 mL). Then, the mixture was heated at 80 °C for 20 h under nitrogen. After cooling, ethyl acetate (100 mL) and water (100 mL) were added, and the insoluble materials were removed by filtration. The filtrate was divided into two layers, and the upper organic layer was separated using a separation funnel. The lower was extracted with ethyl acetate (50 mL  $\times$  2). All the organic layers were combined, washed with water (200 mL  $\times$  2) and sat. brine (200 mL), and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography using dichloromethane/hexane (2:1, v/v) as eluent to afford a white solid of **2** (1.25 g, 3.95 mmol, 87%);  $^{1}\mathrm{H}$  NMR (400 MHz, CDCl\_3)  $\delta$  1.43 (t, J = 7.2 Hz, 3H), 4.43 (q, J = 7.2 Hz, 2H), 7,37 (dt, J = 1.2 and 7.8 Hz, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.48 (dt, J = 1.2 and 7.8 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.64 (dd, J = 1.2 and 7.8 Hz, 1H), 7.97–8.01 (m, 4H), 8.21 (d, J = 8.3 Hz, 2H); MALDI-TOF MS m/z 317 ([M + H]<sup>+</sup>). Anal. Calcd for C<sub>21</sub>H<sub>16</sub>O<sub>3</sub>: C, 79.73; H, 5.10. Found: C, 79.78; H, 5.15.

## 2.2.3. Synthesis of 1,3-bis[4-(dibenzo[b,d]furan-4-yl)phenyl] propane-1,3-dione (HO^O-1c)

To a mixture of 2 (1.46 g, 4.62 mmol) and sodium hydride (60% oil dispersion, 845 mg, 14.1 mmol) in THF (7.2 mL) was added dropwise a solution of 1 (1.24 g, 4.33 mmol) in THF (7.2 mL) over 2 h with a dropping funnel. Then, the mixture was heated at 60 °C for 15 h under nitrogen. After cooling, water (30 mL) added to the reaction mixture on an ice bath, and the mixture was acidified to pH 3 with 1.2 M HClaq. Then, chloroform (200 mL) was added, and the organic layer was separated using a separation funnel. The aqueous layer was further extracted with chloroform (100 mL  $\times$  3). All the organic layers were combined, washed with sat. NaHCO<sub>3</sub> (300 mL  $\times$  3), H<sub>2</sub>O (300 mL  $\times$  2), and sat. brine (300 mL  $\times$  2), and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed on a rotary evaporator, and the residue was purified by recrystallization from chloroform to afford a yellow solid of HO^O-1c in 39% (950 mg, 1.71 mmol); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN) δ 3.52 (br s, 2H), 7.41 (t, J = 7.8 Hz, 2H), 7.47–7.54 (m, 4H), 7.62 (d, J = 7.8 Hz, 2H), 7.71 (dd, J = 1.4 and 7.8 Hz, 2H), 8.03 (d, J = 8.6 Hz, 4H), 8.08-8.11 (m, 4H), 8.15 (d, J = 8.6 Hz, 4H); MALDI-TOF MS m/z 557 ([M + H]<sup>+</sup>). Anal. Calcd for C<sub>39</sub>H<sub>24</sub>O<sub>4</sub>: C, 84.16; H, 4.35. Found: C, 83.87; H, 4.40.

## 2.2.4. Synthesis of $\mu$ -chloro-bridged iridium(III) dimers [(C^N)<sub>2</sub>lr( $\mu$ -Cl)]<sub>2</sub>; the general procedure

These compounds were prepared according to the conventional procedure [12,24]. To a solution of the cyclometalated ligand HC<sup>N</sup> (2.5 mmol) in 2-ethoxyethanol (50 mL) was added a solution of IrCl<sub>3</sub>·3H<sub>2</sub>O (1.2 mmol) in water (15 mL), and the mixture was heated on an oil bath for 24 h, where the bath temperature was kept at 100 °C. After cooling, water (300 mL) was added, and the precipitate was collected by filtration. The obtained precipitate was washed with ethanol (20 mL) and hexane (20 mL) to afford the  $\mu$ -chloro-bridged iridium(III) dimer [(C<sup>^</sup>N)<sub>2</sub>Ir( $\mu$ -Cl)]<sub>2</sub>. These materials were highly insoluble, and thus, used in the next reaction without further purification.

### 2.2.5. Synthesis of $(C^N)_2 Ir(O^O)$ ; the general procedure

A mixture of  $[(C^N)_2 Ir(\mu-Cl)]_2$ , 1,3-diketone HO^O (1.5–2 eq of  $[(C^N)_2 Ir(\mu-Cl)]_2$ ), and Na<sub>2</sub>CO<sub>3</sub> (9–10 eq of  $[(C^N)_2 Ir(\mu-Cl)]_2$ ) in 2-ethoxyethanol was heated at 100 °C under nitrogen. After cooling, the solvent was removed on a rotary evaporator. The residue was dissolved in dichloromethane, and the solution was washed with

water and sat. brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed on a rotary evaporator, and the residue was purified by alumina column chromatography. Further purification by recrystallization from chloroform/hexane gave a crystal of the  $(C^{N})_2 Ir(O^{O})$  complex. The preparation of **Ir-1a** [26], **Ir-2a** [6], **Ir-4a** [20], and **Ir-4b** [20] were prepared according to the reported procedures.

2.2.5.1. Bis[2-(3,5-bis(trifluoromethyl)phenyl)pyridinato-N,C<sup>2'</sup> |iridium(III) [1,3-bis(3,4-dibutoxyphenyl)propane-1,3-dionate-0,0] (Ir-**1b**). A mixture of [(**C^N-1**)<sub>2</sub>Ir(µ-Cl)]<sub>2</sub> (184 mg, 0.114 mmol), **HO^O-**1b (110 mg, 0.214 mmol), and Na<sub>2</sub>CO<sub>3</sub> (96 mg, 0.905 mmol) in 2ethoxyethanol (33 mL) was heated at 100 °C for 1.5 h under nitrogen. Subsequent isolation and purification were carried out according to the general procedure. The column chromatography was eluted with dichloromethane; yield, 80% (220 mg, 0.171 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.93–0.98 (m, 12H), 1.40–1.49 (m, 8H), 1,69–1.81 (m, 8H), 3.82 (t, J = 6.4 Hz, 4H), 3.98 (m, 4H), 6.32 (s, 1H), 6.74 (d, *J* = 8.2 Hz, 2H), 6.94 (t, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 1.8 Hz, 2H), 7.21 (dd, *J* = 1.8 and 7.8 Hz, 2H), 7.56 (s, 2H), 7.74 (dt, J = 1.8 and 7.8 Hz, 2H), 7.96 (d, J = 8.2 Hz, 2H), 8.11 (s, 2H), 8.20 (d, *J* = 7.8 Hz, 2H); MALDI-TOF MS *m*/*z* 1284 ([M]<sup>+</sup>). Anal. Calcd for C<sub>57</sub>H<sub>55</sub>F<sub>12</sub>IrN<sub>2</sub>O<sub>6</sub>: C, 53.31; H, 4.32; N, 2.18. Found: C, 53.31; H, 4.35; N, 2.30.

### 2.2.5.2. Bis[2-(3,5-bis(trifluoromethyl)phenyl)pyridinato-N,C<sup>2'</sup> ]iri-

dium(III) [1,3-bis(4-(dibenzo[b,d]furan-4-yl)phenyl)propane-1,3dionate-0,0] (Ir-1c). A mixture of [(C^N-1)<sub>2</sub>Ir(µ-Cl)]<sub>2</sub> (300 mg, 0.186 mmol), HO^O-1c (142 mg, 0.255 mmol), and Na<sub>2</sub>CO<sub>3</sub> (193 mg, 1.82 mmol) in 2-ethoxyethanol (50 mL) was heated at 100 °C for 6 h under nitrogen. Subsequent isolation and purification were carried out according to the general procedure. The column chromatography was eluted with dichloromethane; yield, 38% (128 mg, 0.0964 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.66 (s, 1H), 7.02 (t, J = 6.4 Hz, 2H), 7,37 (dt, J = 1.4 and 7.8 Hz, 2H), 7.43 (t, J = 7.8 Hz, 2H), 7.48 (dt, *I* = 1.4 and 7.8 Hz, 2H), 7.57–7.59 (m, 4H), 7.61 (d, *I* = 1.8 Hz, 2H), 7.78–7.82 (m, 6H), 7.88 (d, *I* = 8.3 Hz, 4H), 7.98 (m, 4H), 8.05 (d, J = 7.8 Hz, 2H), 8.18 (d, J = 1.8 Hz, 2H), 8.30 (d, J = 6.4 Hz, 2H); MALDI-TOF MS m/z 1328 ([M]<sup>+</sup>). Anal. Calcd for C<sub>65</sub>H<sub>35</sub>F<sub>12</sub>IrN<sub>2</sub>O<sub>4</sub>: C, 58.78; H, 2.66; N, 2.11. Found: C, 58.81; H, 3.07; N, 2.17.

2.2.5.3. Bis[2-phenylpyridinato-N,C<sup>2'</sup>]iridium(III) [1,3-bis(3,4dibutoxyphenyl)propane-1,3-dionate-0,0] (Ir-2b). A mixture of [(*C*^*N*-2)<sub>2</sub>Ir(μ-Cl)]<sub>2</sub> (500 mg, 0.466 mmol), HO<sup>^</sup>O-1b (469 mg, 0.914 mmol), and Na<sub>2</sub>CO<sub>3</sub> (433 mg, 4.09 mmol) in 2-ethoxyethanol (65 mL) was heated at 100 °C for 5 h under nitrogen. Subsequent isolation and purification were carried out according to the general procedure. The column chromatography was eluted with dichloromethane/hexane (1:2, v/v); yield, 70% (648 mg, 0.640 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.91–0.96 (m, 12H), 1.37-1.50 (m, 8H), 1,67-1.80 (m, 8H), 3.89 (m, 4H), 3.98 (t, J = 6.4 Hz, 4H), 6.38 (d, J = 7.8 Hz, 2H), 6.40 (s, 1H), 6.71 (t, J = 7.8 Hz, 2H), 6.75 (d, J = 8.2 Hz, 2H), 6.82 (t, J = 7.8 Hz, 2H), 7.02 (t, J = 6.0 Hz, 2H), 7.29 (d, J = 1.8 Hz, 2H), 7.38 (dd, J = 1.4 and 8.2 Hz, 2H), 7.56 (d, J = 7.8 Hz, 2H), 7.66 (t, J = 1.4 and 8.2 Hz, 2H), 7.83 (d, J = 8.2 Hz, 2H), 8.59 (d, J = 6.0 Hz, 2H); MALDI-TOF MS m/z 1012 ([M]<sup>+</sup>). Anal. Calcd for C<sub>53</sub>H<sub>59</sub>IrN<sub>2</sub>O<sub>6</sub>: C, 62.89; H, 5.87; N, 2.77. Found: C, 62.87; H, 5.79; N, 2.75.

2.2.5.4. Bis[2-phenylpyridinato- $N,C^{2^{\prime}}$ ]iridium(III) [1,3-bis(4-(dibenzo [b,d]furan-4-yl)phenyl)propane-1,3-dionate-O,O] (**Ir-2c**). A mixture of [(**C^N-2**)<sub>2</sub>Ir(µ-Cl)]<sub>2</sub> (268 mg, 0.250 mmol), **HO^O-1c** (200 mg, 0.359 mmol), and Na<sub>2</sub>CO<sub>3</sub> (234 mg, 2.21 mmol) in 2-ethoxyethanol (35 mL) was heated at 100 °C for 3.5 h under nitrogen. Subsequent

isolation and purification were carried out according to the general procedure. The column chromatography was eluted with dichloromethane; yield, 38% (144 mg, 0.136 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.42 (dd, *J* = 0.9 and 7.3 Hz, 2H), 6.77–6.79 (m, 3H), 6.89 (dt, *J* = 1.1 and 7.8 Hz, 2H), 7.09 (dt, *J* = 1.4 and 7.8 Hz, 2H), 7.36 (dt, *J* = 1.1 and 7.3 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.46 (dt, *J* = 1.1 and 7.3 Hz, 2H), 7.56–7.63 (m, 6H), 7.72 (dt, *J* = 1.4 and 7.8 Hz, 2H), 7.85–7.90 (m, 6H), 7.95 (dd, *J* = 1.4 and 7.8 Hz, 2H), 7.98 (d, *J* = 7.8 Hz, 2H), 8.03 (d, *J* = 8.7 Hz, 4H), 8.68 (dd, *J* = 0.9 and 6.0 Hz, 2H); MALDI-TOF MS *m*/*z* 1056 ([M]<sup>+</sup>). Anal. Calcd for C<sub>61</sub>H<sub>39</sub>IrN<sub>2</sub>O<sub>4</sub>: C, 69.37; H, 3.72; N, 2.65. Found: C, 69.43; H, 4.11; N, 2.56.

### 2.2.5.5. Bis[2-(2,4-bis(trifluoromethyl)phenyl)pyridinato-N, $C^{2'}$ ]iri-

dium(III) [2,2,6,6-tetramethylheptane-3,5-dionate-0,0] (**Ir-3a**). A mixture of  $[(C^N-3)_2Ir(\mu-CI)]_2$  (177 mg, 0.109 mmol), **HO^O-1a** (41 mg, 0.222 mmol), and Na<sub>2</sub>CO<sub>3</sub> (95 mg, 0.896 mmol) in 2-ethoxyethanol (33 mL) was heated at 100 °C for 2 h under nitrogen. Subsequent isolation and purification were carried out according to the general procedure. The column chromatography was eluted with chloroform/hexane (1:2, v/v); yield, 71% (150 mg, 0.157 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  0.86 (s, 18H), 5.51 (s, 1H), 6,65 (s, 2H), 7.25–7.26 (m, 2H, masked by residual CHCl<sub>3</sub>), 7.49 (s, 2H), 7.86 (dt, *J* = 1.4 and 7.8 Hz, 2H), 8.36–8.41 (m, 4H); MALDI-TOF MS *m*/*z* 956 ([M]<sup>+</sup>). Anal. Calcd for C<sub>37</sub>H<sub>31</sub>F<sub>12</sub>IrN<sub>2</sub>O<sub>2</sub>: C, 46.49; H, 3.27; N, 2.93. Found: C, 46.48; H, 3.52; N, 2.97.

### 2.2.5.6. Bis[2-(2,4-bis(trifluoromethyl)phenyl)pyridinate-N,C<sup>2'</sup> |iri-

dium(III) [1.3-bis(3.4-dibutoxyphenyl)propane-1.3-dionate-0.0] (Ir-**3b**). A mixture of [(**C^N-3**)<sub>2</sub>Ir(µ-Cl)]<sub>2</sub> (177 mg, 0.109 mmol), **HO^O-**1b (109 mg, 0.213 mmol), and Na<sub>2</sub>CO<sub>3</sub> (95 mg, 0.896 mmol) in 2ethoxyethanol (33 mL) was heated at 100 °C for 2.5 h under nitrogen. Subsequent isolation and purification were carried out according to the general procedure. The column chromatography was eluted with chloroform/hexane (2:1, v/v); yield, 60% (163 mg, 0.127 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  0.91 (t, *J* = 6.9 Hz, 6H), 0.94 (t, J = 6.9 Hz, 6H), 1.36 - 1.51 (m, 8H), 1.70 (quint, J = 6.9 Hz, 4H),1.77 (quint, J = 6.9 Hz, 4H), 3.80–3.86 (m, 4H), 3.99 (t, J = 6.9 Hz, 4H), 6.47 (s, 1H), 6.63 (s, 2H), 6.78 (d, J=8.7 Hz, 2H), 7.17 (d, J = 2.3 Hz, 2H), 7.22 (t, J = 6.4 Hz, 2H), 7.34 (dd, J = 1.8 and 8.7 Hz, 2H), 7.52 (s, 2H), 7.86 (t, J = 7.3 Hz, 2H), 8.39 (d, J = 8.7 Hz, 2H), 8.62 (d, J = 6.4 Hz, 2H); MALDI-TOF MS m/z 1284 ([M]<sup>+</sup>). Anal. Calcd for C<sub>57</sub>H<sub>56</sub>F<sub>12</sub>IrN<sub>2</sub>O<sub>6</sub>: C, 53.31; H, 4.32; N, 2.18. Found: C, 53.60; H, 4.34; N, 2.26.

2.2.5.7. Bis[2-(2,4-bis(trifluoromethyl)phenyl)pyridinate-N, $C^2$  ]iridium(III) [1,3-bis(4-(dibenzo[b,d]furan-4-yl)phenyl)propane-1,3-dionate-O,O] (**Ir-3c**). A mixture of [(**C^N-3**)<sub>2</sub>Ir( $\mu$ -Cl)]<sub>2</sub> (130 mg, 0.0804 mmol), **HO^O-1c** (70 mg, 0.126 mmol), and Na<sub>2</sub>CO<sub>3</sub> (95 mg, 0.896 mmol) in 2-ethoxyethanol (15 mL) was heated at 100 °C for 3 h under nitrogen. Subsequent isolation and purification were carried out according to the general procedure. The column chromatography was eluted with dichloromethane/hexane (1:1, v/v); yield, 44% (74.0 mg, 0.0557 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.67 (s, 2H), 6.83 (s, 1H), 7.28–7.31 (m, 2H), 7.36 (dt, *J* = 1.1 and 7.8 Hz, 2H), 7.41–7.49 (m, 4H), 7.56–7.59 (m, 6H), 7.89–7.93 (m, 6H), 7.95–8.00 (m, 8H), 8.45 (d, *J* = 8.3 Hz, 2H), 8.73 (d, *J* = 6.0 Hz, 2H); MALDI-TOF MS *m*/*z* 1328 ([M]<sup>+</sup>). Anal. Calcd for C<sub>65</sub>H<sub>35</sub>F<sub>12</sub>IrN<sub>2</sub>O<sub>4</sub>: C, 58.78; H, 2.66; N, 2.11. Found: C, 58.55; H, 3.08; N, 2.16.

# 2.2.5.8. Bis[1-(dibenzo[b,d]furan-4-yl)isoquinolinato-N,C<sup>3'</sup> Jiridium(III) [1,3-bis(4-(dibenzo[b,d]furan-4-yl)phenyl)propane-1,3-dionate-0,O]

(**Ir-4c**). A mixture of  $[(C^N-4)_2 Ir(\mu-CI)]_2$  (500 mg, 0.306 mmol), **HO^O-1c** (276 mg, 0.496 mmol), and Na<sub>2</sub>CO<sub>3</sub> (270 mg, 2.55 mmol) in 2-ethoxyethanol (45 mL) was heated at 100 °C for 5 h under nitrogen. Subsequent isolation and purification were carried out

according to the general procedure. The column chromatography was eluted with dichloromethane/hexane (1:2, v/v); yield, 34% (225 mg, 0.168 mmol); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.50 (d, J = 7.8 Hz, 2H), 6.80 (s, 1H), 7.24–7.31 (m, 2H, masked by residual CHCl<sub>3</sub>), 7.33–7.39 (m, 8H), 7.43 (dt, J = 1.4 and 7.8 Hz, 2H), 7.51–7.54 (m, 6H), 7.58 (d, J = 6.4, 2H), 7.73–7.80 (m, 10H), 7.90–7.96 (m, 10H), 8.67 (d, J = 6.4 Hz, 2H), 9.20 (dd, J = 1.4 and 7.8 Hz, 2H); MALDI-TOF MS m/z 1336 ([M]<sup>+</sup>). Anal. Calcd for C<sub>81</sub>H<sub>47</sub>IrN<sub>2</sub>O<sub>6</sub>: C, 72.79; H, 3.54; N, 2.10. Found: C, 72.41; H, 3.79; N, 2.12.

### 2.3. X-ray structure determination

Diffraction data for **Ir-1a**–**Ir-1c** were collected on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71075$  Å). The cell parameters for **Ir-1a**–**Ir-1c** were collected at a temperature of  $23 \pm 1$  °C to a maximum  $2\theta$  value of 55.0°. The structures were solved by direct methods using the SIR2002 program for **Ir-1a** [27] and the SIR92 program for **Ir-1b** and **Ir-1c** [28], and expanded using the DIRDIF99 [29] program. Anisotropic temperature factors were applied to the non-hydrogen atoms. The calculated positions of the hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure 3.8 [30] software packages of computer programs. The crystal data and refinement details of the crystal structure determination are given in Table 1.

### 2.4. Photophysical characterization

UV—vis absorption and photoluminescence (PL) spectra were measured on a Shimadzu UV-3100 and a Jasco FP-6600 spectrophotometer, respectively, using a quartz cell. PL lifetimes were obtained on a Horiba Jobin Yvon FluoroCube spectroanalyzer using a 390 nm nanosecond-order LED light source. PL quantum yields were obtained on a Hamamatsu Photonics C9920 PL quantum yield measurement system. The sample solutions for optical and photophysical measurements were deaerated by argon bubbling followed by complete sealing, and the analyses were carried out just after preparation of the samples.

Table 1	
Crystal da	a and structure refineme

Compound	Ir-1a	Ir-1b	Ir-1c
Formula	C <sub>37</sub> H <sub>31</sub> N <sub>2</sub> O <sub>2</sub> F <sub>12</sub> Ir	C57H55N2O6F12Ir	C <sub>65</sub> H <sub>35</sub> N <sub>2</sub> O <sub>4</sub> F <sub>12</sub> Ir
Formula weight	955.86	1284.27	1328.20
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1(#2)	P-1(#2)	P-1(#2)
Lattice parameters			
a (Å)	11.3363 (5)	13.2698 (5)	13.6888 (12)
b (Å)	13.2534 (6)	13.4972 (6)	14.4881 (12)
c (Å)	14.7442 (7)	15.8762 (6)	17.0849 (14)
α ( <b>o</b> )	81.9281 (14)	88.6908 (14)	110.5895 (18)
β( <b>o</b> )	69.3969 (15)	78.3164 (12)	92.7006 (17)
γ(0)	69.9899 (15)	89.1659 (12)	105.3759 (19)
V (Å <sup>3</sup> )	1947.86 (15)	2783.72 (18)	3021.2 (4)
Ζ	2	2	2
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.630	1.532	1.460
$\mu ({\rm cm}^{-1})$	35.278	24.954	23.003
F (000)	936.00	1288.00	1312.00
T (K)	296	296	296
No. of unique	8721 (0.037)	12,614 (0.039)	13,320 (0.098)
reflections (R <sub>int</sub> )			
No. of reflections	6684	9640	6225
used $(I > 2.00\sigma(I))$			
$R_1; wR_2$	0.0326; 0.0418	0.0342; 0.0385	0.0692; 0.0861
GOF indicator	0.981	1.086	1.004

 $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|.$ 

 $wR_2 = [\Sigma \omega (|F_0| - |F_c|)^2 / \Sigma \omega F_0^2]^{1/2}.$ 

### 3. Results and discussion

### 3.1. Synthesis and structures

All bis-cyclometalated iridium(III) complexes (**Ir-1–Ir-4**) were prepared according to the conventional procedure reported by Thompson and coworkers [12]. That is, the preparation of the  $\mu$ -chlorobridged iridium(III) dimers followed by the ligand exchange with the corresponding diketonates yielded the bis-cyclometalated iridium(III) complexes. For the *C^N* ligands, 2-phenylpyridine (**HC^N-2**) was commercially available, and **HC^N-1**, **HC^N-3** and **HC^N-4** were prepared according to the reported procedures [20,24]. The preparation of the *O^O* ancillary ligand **HO^O-1b** was previously reported [25]. In this study, **HO^O-1c** was newly synthesized, as shown in Scheme 1. All the new compounds prepared here were identified by <sup>1</sup>H NMR and MALDI-TOF mass spectra as well as elemental analyses.

The ligand configuration of the present bis-cyclometalated iridium(III) complexes was investigated from the X-ray crystallographic analyses of **Ir-1a–Ir-1c**. The single crystals were obtained by slow diffusion of chloroform solutions of the complexes to hexane. In Fig. 2 are shown the ORTEP drawings of the structures of **Ir-1a–Ir-1c**, and the crystal data are summarized in Table 1. The selected bond lengths and angles around the iridium center are also summarized in Table 2.

Fig. 2 shows that each of **Ir-1a–Ir-1c** has a six-coordinated structure with *cis–C,C* and *trans–N,N* configuration as is observed for bis-cyclometalated iridium(III) complexes so far reported [12,16,31,32]. The C-Ir and N-Ir bond lengths as well as the C-Ir-C, C-Ir-N and N-Ir-N bond angles are almost the same among these three complexes (within 0.041 Å for the bond lengths and within 1.53° for the bond angles), indicating that the coordination geometry around the Ir(III) center is almost independent on the *O^O* ligand. For **Ir-1b**, the constituent atoms included in the 1,3-diphenylpropane-1,3-dionate skeleton exhibited deviation within 0.196 Å from the mean plane, showing that the *O^O* ligand in **Ir-1b** is extensively conjugated from one phenyl ring to the other. For **Ir-1c**, the  $\pi$ -planes of dibenzo[*b*,*d*]furan moieties are considerably

twisted from the  $\pi$ -conjugation of 1,3-diphenylpropane-1,3dionate skeleton. This result indicates that the  $\pi$ -extension is likely to be partially prevented due to the crystal packing forces.

### 3.2. Optical properties

UV—vis absorption and PL spectra of **Ir-1**—**Ir-4** were obtained in toluene at 298 K. These spectra are shown in Figs. 3 and 4, and the spectral data are also summarized in Table 3. All the spectra were taken for deaerated samples, kept away from luminescence quenching by oxygen.

As shown in Fig. 3a, Ir-1a exhibits the light absorption from the near UV to the visible region up to 490 nm. The absorption bands at <350 nm are assigned to the spin-allowed ligand-centered  $\pi-\pi^*$ transitions at the  $C^N$  ligand ( ${}^{1}LC_{C^N}$  transitions), and the next absorption band at 384 nm is assigned to the spin-allowed MLCT transition from Ir(III) to the C^N ligand (<sup>1</sup>MLCT<sub>C^N</sub> transition). The lowest-energy absorption band at 466 nm is assignable to the spinforbidden <sup>3</sup>MLCT transition (Ir(III) to C^N, <sup>3</sup>MLCT<sub>C^N</sub> transition). The relatively large molar absorption coefficient (419  $M^{-1}$  cm<sup>-1</sup> at 466 nm), comparable with that of the  ${}^{1}MLCT_{C^{N}}$  transition, indicates effective mixing of the  ${}^{3}MLCT_{C^{N}}$  level with the  ${}^{1}MLCT_{C^{N}}$  due to the strong spin-orbit coupling caused by the Ir(III) center. On the other hand, the relatively intense light absorption of Ir-1b and Ir-1c was observed in comparison with that of Ir-1a, obviously showing the overlap of the  ${}^{1}LC_{C^{n}N}$  and  ${}^{1}MLCT_{C^{n}N}$  transition bands with the  $\pi - \pi^{*}$ transition band at the  $\pi$ -conjugated O^O ligand (<sup>1</sup>LC<sub>0^0</sub> transition). For these complexes, the  ${}^{3}MLCT_{C^{N}}$  bands were also observed at *ca*. 465 nm as shoulder peaks. It is worthy to note that the onset of the absorption spectrum is red-shifted according to the extension of the  $\pi$ -conjugation of the O^O ancillary ligand from **Ir-1a** to **Ir-1c**, indicating that the lowest triplet energy level  $(T_1)$  is lowered using the  $\pi$ conjugated 0^0 ligands. Thus, one can see that the aromatic 0^0 ligands. **0^0-1b** and **0^0-1c**, participate in the determination of T<sub>1</sub>: The  ${}^{3}LC_{0,0}$  and  ${}^{3}MLCT_{0,0}$  levels should be considerably lowered upon employment of the aromatic ancillary ligands.





**Scheme 1.** Reagents and conditions: (i) 4-iodoacetophenone, Pd(PPh<sub>3</sub>)<sub>4</sub>, Na<sub>2</sub>CO<sub>3aq</sub>, 1,2-dimethoxyethane, 70 °C; (ii) ethyl 4-iodobenzoate, Pd(PPh<sub>3</sub>)<sub>4</sub>, Na<sub>2</sub>CO<sub>3aq</sub>, toluene, EtOH, 80 °C; (iii) NaH, THF, 60 °C; (iv) lrCl<sub>3</sub>·3H<sub>2</sub>O, 2-ethoxyethanol, 100 °C; (v) **HO^0-1**, Na<sub>2</sub>CO<sub>3</sub>, 2-ethoxyethanol, 100 °C.



Fig. 2. The ORTEP drawings of (a) Ir-1a, (b) Ir-1b, and (c) Ir-1c. The hydrogen atoms are omitted for clarity. The frame format of the geometry around the Ir(III) center is also illustrated in (d).

Similar spectral features are found for the electronic absorption spectra of **Ir-2a–Ir-2c** (Fig. 3b), and the <sup>3</sup>MLCT<sub>C^N</sub> transition band is slightly red-shifted to *ca.* 470 nm. The onset of the absorption spectrum is also red-shifted for **Ir-2b** and **Ir-2c**. This indicates that the O^O ancillary ligand contributes to determination of T<sub>1</sub> in the series of **Ir-2.** For **Ir-3** and **Ir-4**, the <sup>3</sup>MLCT<sub>C^N</sub> transition bands are further red-shifted (Fig. 3c,d); *ca.* 480 nm for **Ir-3** and *ca.* 560 nm for **Ir-4**. In both series, the spectral onset is almost constant (*ca.* 540 nm for **Ir-3** and *ca.* 650 nm for **Ir-4**), independent on the O^O ancillary ligand. Thus, it is likely that the O^O ligands do not have any influences on T<sub>1</sub> in the cases of **Ir-3** and **Ir-4**. The most red-shifted <sup>3</sup>MLCT<sub>C^N</sub> transition and spectral onset of **Ir-4** are obviously caused by the extensively conjugated *C^N* ligand.

### 3.3. Photoluminescent and photophysical properties

As shown in Fig. 4, the PL spectra of **Ir-1–Ir-4** were obtained in toluene at 298 K under deaerated conditions. PL lifetimes ( $\tau_{PL}s$ ) and PL quantum yields ( $\Phi_{PL}s$ ) of these complexes were also obtained, and these data are summarized in Table 3.

#### Table 2

Selected	i bond	distances and	d angles	around	the	Ir(III)	) center	for	lr-1	la-	lr-1	lc
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		Ir-1a	lr-1b	Ir-1c
Distance (Å)	Ir-01	2.088 (4)	2.104 (2)	2.098 (9)
	Ir–O2	2.098 (2)	2,131 (2)	2.104 (7)
	Ir–N1	2.037 (3)	2.038 (3)	2.039 (9)
	Ir–C1	2.011 (3)	2.049 (3)	2.032 (12)
	Ir-N2	2.020 (3)	2.033 (3)	2.004 (9)
	Ir–C2	2.008 (9)	2.033 (3)	2.016 (12)
Angle (°)	01-Ir-02	88.94 (13)	88.87 (9)	90.2 (3)
	N1-Ir-C1	80.57 (15)	80.31 (14)	80.7 (4)
	N2–Ir–C2	81.32 (19)	80.84 (15)	81.7 (4)

In the PL spectrum of **Ir-1a** (Fig. 4a), the PL maximum ( $\lambda_{PL}$ ) was observed at 474 nm, showing that Ir-1a emits blue in solution. The structured spectrum indicates that the considerable contribution of the  ${}^{3}LC_{C^{n}N}$  level to PL [33]. In the case of **Ir-1b**, the  $\lambda_{PL}$  was observed at 558 nm, shifted by 84 nm from that of Ir-1a. This red shift brought about the PL color shift to yellow (Fig. 4a, inset). In the case of Ir-1c, the employment of the more conjugated aromatic 0^0 ligand (**0^0-1c**) gave rise to a further red shift of the PL spectrum  $(\lambda_{PL} = 604 \text{ nm})$ . The solution of **Ir-1c** emitted reddish orange, and thus it is clearly noted that the O^O ancillary ligands with  $\pi$ extended structures significantly affect the photoluminescent properties of the C^N-1-based bis-cyclometalated complexes. The PL spectra of Ir-1b and Ir-1c are less structured and significantly broadened, indicating that the electronic character of the triplet energy levels of these complexes are different from that of Ir-1a. The detailed emission mechanisms are discussed below. The  $\tau_{PL}s$  of **Ir-1a**–**Ir-1c** were determined as 0.97  $\mu$ s ( $\chi^2 = 1.03$ ), 1.00  $\mu$ s ( $\chi^2 = 1.06$ ), and 0.21  $\mu$ s ( $\chi^2 = 1.09$ ), respectively, each of which was well fitted to single-exponential decay. Such short phosphorescence lifetimes are effective to suppress triplet-triplet annihilation in phosphorescent OLEDs [34]. The  $\phi_{PL}$ s of **Ir-1a–Ir-1c** were also determined as 0.91, 0.31, and 0.083 (in toluene at 298 K), respectively, significantly decreasing as the  $\lambda_{PL}$  is red-shifted. The PL spectral profiles of Ir-2 also varied with the O<sup>^</sup>O ancillary ligands (Fig. 4b), as discussed for Ir-1. The  $\lambda_{PL}$ s of Ir-2a–Ir-2c were observed at 521, 633, and 661 nm, respectively, significantly red-shifted from bluish green to deep red when the aromatic O^O ligands were employed. The  $\tau_{PL}s$  of Ir-2a-Ir-2c were determined as 0.29  $\mu s$  $(\chi^2 = 1.04)$ , 0.02 µs  $(\chi^2 = 1.10)$ , and 0.52 µs  $(\chi^2 = 1.08)$ , respectively, well fitted to single-exponential decay. Although the  $\tau_{PL}$  of Ir-2b was somewhat short, the energy gap more than 1.0 eV between the spin-allowed transition and the  $\lambda_{\text{PL}}$  clearly indicates that the



Fig. 3. UV-vis absorption spectra of (a) Ir-1, (b) Ir-2, (c) Ir-3, and (d) Ir-4 in deaerated toluene at 298 K.

observed emission is phosphorescence. The  $\Phi_{PL}$  of **Ir-2a**–**Ir-2c** were determined as 0.14, 0.006, and 0.003, respectively, significantly decreasing as the  $\lambda_{PL}$  is red-shifted.

On the other hand, different tendencies of PL spectral behavior from **Ir-1** and **Ir-2** were observed for **Ir-3** and **Ir-4**. In Fig. 4c are shown the PL spectra of **Ir-3a–Ir-3c**. Only slight red shifts were observed for the PL spectra even when the aromatic  $O^O$  ancillary ligands ( $\lambda_{PL}$ s of **Ir-3a–Ir-3c**; 541, 543, and 566 nm, respectively). The PL color shifts are less remarkable, varying from green to yellow (Fig. 4c, inset). The PL spectrum of **Ir-3b** is similar to that of **Ir-3a**, indicating that the triplet energy levels of these complexes are almost the same in spite of the ligand replacement from **0^0-1a** to **0^0-1b**. The  $\tau_{PL}$ s of **Ir-3a–Ir-3c** show single-exponential decay profiles, ranging from 1.09 µs to 1.25 µs with  $\chi^2$  values of 1.00–1.03. Contrary to **Ir-1** and **Ir-2**, each of **Ir-3a–Ir-3c** exhibits a relatively high  $\Phi_{PL}$  (0.43, 0.51, and 0.53 for **Ir-3a–Ir-3c**, respectively),



Fig. 4. Photoluminescence spectra of (a) Ir-1, (b) Ir-2, (c) Ir-3, and (d) Ir-4 in deaerated toluene at 298 K.

#### Table 3

UV-vis absorption and photoluminescence spectral data of **Ir-1-Ir-4** in toluene at 298 K.

Compd	UV-vis <sup>a,b</sup>	Photoluminescence <sup>a,b</sup>		
	$\lambda_{abs}$ (nm), $\epsilon$ (M <sup>-1</sup> cm <sup>-1</sup> )	$\lambda_{PL}(nm)$	$\tau_{PL}(\mu s\;(\chi^2))$	$\Phi_{\rm PL}$
Ir-1a	342 (7700), 384 (5800),	474, 506	0.97 (1.03)	0.91 <sup>c</sup>
	466 (419)			
Ir-1b	345 (26,400), 385 (27,400),	558	1.00 (1.06)	0.31
	463 [sh] (881)			
lr-1c	342 (40,700), 383 (24,600),	604	0.21 (1,09)	0.083
	467 [sh] (1360)			
lr-2a	341 (7470), 467 (2550)	521	0.29 (1.04)	0.14
Ir-2b	348 (28,500), 409 [sh] (13,900),	633	0.02 (1.10)	0.006
	466 [sh] (4120)			
Ir-2c	344 (41,600), 407 (16,000),	661	0.52 (1.08)	0.003
	466 [sh] (2480)			
Ir-3a	361 (5330), 393 (4390),	541	1.14 (1.03)	0.43
	479 (2560)			
lr-3b	336 (19,400), 383 (19,500),	543	1,25 (1.00)	0.51
	480 (2800)			
lr-3c	333 (29,400), 392 (17,200),	566	1.09 (1.00)	0.53
	\482 [sh] (2940)			
Ir-4a	338 (39,400), 421 (6560), 493 (5460),	639 <sup>d</sup>	1.04 (1.00) <sup>d</sup>	0.55 <sup>d</sup>
	557 [sh] (3160)			
Ir-4b	342 (51,400), 492 (5420),	640 <sup>d</sup>	1.07 (1.00) <sup>d</sup>	0.61 <sup>d</sup>
	558 [sh] (3440)			
Ir-4c	338 (53,700), 489 (6010),	637	0.41 (1.00)	0.20
	560 [sh] (3270)			

<sup>a</sup> Obtained in toluene solution at 298 K. [sh]; shoulder peak.

 $^{b}$  [Ir(III) complex] = 10  $\mu M.$ 

<sup>c</sup> Reported previously in ref. [26].

<sup>d</sup> Reported previously in ref. [20].

regardless of the O^O ancillary ligand. It is interesting that the PL spectra of **Ir-4a–Ir-4c** (Fig. 4d) are almost the same ( $\lambda_{PL}$ ; 637–640 nm), indicating that the O^O ancillary ligands do not affect the PL spectral profiles of these complexes. As shown in the inset in Fig. 4d, the emission color of **Ir-4** is pure red. The  $\tau_{PL}s$  of **Ir-4a–Ir-4c** fitted to single-exponential decay were 1.04 µs ( $\chi^2 = 1.00$ ), 1.07 µs ( $\chi^2 = 1.00$ ), and 0.41 µs ( $\chi^2 = 1.00$ ), respectively. The  $\Phi_{PL}s$  of **Ir-4a–Ir-4c** were determined as 0.55, 0.61, and 0.20 (in toluene at 298 K), respectively. The relatively small  $\Phi_{PL}$  of **Ir-4c** indicates that the O^O ancillary ligand **O^O-1c** affects the photophysical properties at some extent.

### 3.4. Ancillary ligand effect on photoluminescence behavior

As shown above, the replacement of aromatic 0<sup>^</sup>O ancillary ligand from **0^0-1a** to **0^0-1b** significantly affects the PL colors of bis-cyclometalated complexes Ir-1 and Ir-2. Here we discuss the mechanism of the ancillary ligand effect on the PL properties of Ir-1-Ir-4. In general, several factors should be taken into consideration when PL spectral changes upon ligand replacement are discussed. The first factor is the configurational difference among **Ir**-1a–Ir-1c [7,35]. As discussed in the X-ray crystallographic analysis, however, all these complexes have the same geometric structure, the six-coordinated cis-C,C and trans-N,N configuration. Thus, the configuration should not be a factor for the spectral differences caused by the O^O ancillary ligands. The second is the solvent effect on the PL spectra [36]. In order to verify this factor, the PL spectra of Ir-1a–Ir-1c were obtained in solvents with different polarity. The results are summarized in Table 4. As a result, no remarkable spectral differences were observed in solvents used here, indicating that the solvent polarity should not afford drastic PL spectral differences in the present series of bis-cyclometalated iridium(III) complexes. The third is the generation of the excimer-based emission upon extending the  $\pi$ -conjugation in the O^O ancillary ligand from **O^O**-1a to 0^0-1b and 0^0-1c [37,38]. However, no spectral changes were observed when the concentrations of the complexes varied

### Table 4

hotoluminescence spectral	data in	various	solvents	at 298 K. <sup>a</sup>
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Solvent	$\varepsilon_r^{b}$	$\lambda_{PL}(nm)$		
		Ir-1a	Ir-1b	Ir-1c
Toluene	2.43	473	557	604
Chloroform	4.89	474	558	607
1,2-Dichloroethane	10.74	474	560	607
Ethanol	25.00	474	559	609
Acetonitrile	36.00	474	558	609

 $^{a}$  The concentration of the complex was adjusted to 10  $\mu M.$ 

<sup>b</sup>  $\varepsilon_r$ : relative permittivity.

between  $0.1-100 \mu$ M. Therefore, from the results of the verification experiments, the *O*^O ligand effect on PL seen in **Ir-1** and **Ir-2** should be attributed to the differences in their own electronic structures, i.e. their T<sub>1</sub> characters.

Here we show the most possible mechanism of the PL behavior of the present bis-cyclometalated iridium(III) complexes upon employment of **0^0-1a**–**0^0-1c** as ancillary ligands (Fig. 5). Upon the <sup>1</sup>MLCT excitation from the Ir(III) center to the C^N ligand in the singlet manifold, highly efficient intersystem crossing (ISC) to the <sup>3</sup>MLCT<sub>C^N</sub> level occurs due to the strong spin-orbit coupling. The exciton at the <sup>3</sup>MLCT<sub>C^N</sub> level might be transferred to the emissive



Fig. 5. Possible mechanisms of the *O*^*O* ligand effects on PL for (a) **Ir-1**, (b) **Ir-3** and (c) **Ir-4**.



Fig. 6. Photoluminescence spectra in PMMA films doped with (a) Ir-1, (b) Ir-2, (c) Ir-3, and (d) Ir-4. In a sample film, the ratio of PMMA to the iridium complex was adjusted to 100/4 (wt/wt).

O^O-related triplet state ( ${}^{3}LC_{O^{\circ}O}$  and/or  ${}^{3}MLCT_{O^{\circ}O}$ ) when it is placed below the  ${}^{3}MLCT_{C^{N}}$  level (inter-ligand energy transfer, ILET). In the aliphatic diketonate ancillary ligand **0^0-1a**, the <sup>3</sup>LC<sub>0^0</sub> and <sup>3</sup>MLCT<sub>0^0</sub> levels should be unstabilized and enough high to prevent the exciton transfer from the  ${}^{3}MLCT_{C^{N}}$  level (Fig. 5a, path A), and thus the observed PL is predominantly based on the radiative decay from the <sup>3</sup>MLCT<sub>C^N</sub> level. On the other hand, the  ${}^{3}LC_{0^{0}0}$  and  ${}^{3}MLCT_{0^{0}0}$  levels of the aromatic 0^0 ancillary ligands such as **0^0-1b** and **0^0-1c** are expected to be lower than that of **0^0-1a** because of the increasing stability by the extended  $\pi$ -conjugation. This is clearly indicated by the red-shifted UV-vis onsets of Ir-1b and Ir-1c, as discussed in Section 3.2. Therefore, as the  ${}^{3}MLCT_{C^{N}}$  level is relatively high, the O^O-related triplet levels are placed below the  ${}^{3}MLCT_{C^{N}}$  level. As a result, the ILET occurs (Fig. 5a, path B), yielding the red-shift of the PL spectrum [21]. In Ir-2, the PL spectral differences caused by the ancillary ligands are attributed to the similar reason. In the case of red emissive Ir-4, any PL red shifts were not observed when the ancillary ligand was replaced from **0^0-1a** to **0^0-1b** and **0^0-1c**. This can be explained by the low-lying  ${}^{3}MLCT_{C^{n}N}$  level caused by the  $\pi$ extended C<sup> $\Lambda$ </sup> ligand of **Ir-4**. The ILET from the <sup>3</sup>MLCT<sub>C<sup> $\Lambda$ </sup></sub> level to the  ${}^{3}LC_{0,0}$  (or  ${}^{3}MLCT_{0,0}$ ) level is a less probable process, and the phosphorescent emission is based on the radiative decay from the  ${}^{3}MLCT_{C^{N}}$  level (Fig. 5c). According to this mechanism, the  ${}^{3}LC_{O^{n}O}$ (or  ${}^{3}MLCT_{0^{0}}$ ) level of **Ir-3b** is likely to lie at an energy level comparable to the  ${}^{3}MLCT_{C^{N}}$  level, and thus any remarkable PL color changes do not occur even when **0^0-1a** is replaced by **0^0-**1b (Fig. 5b, path A). In the case of Ir-3c, the O^O-related triplet level should be slightly lower than the  ${}^{3}MLCT_{C^{N}}$  level, and the red-shift of PL is modest upon replacing **0^0-1a** to **0^0-1c** (Fig. 5b, path B).

### 3.5. Photoluminescent properties in polymer thin films

From the viewpoint of application to solid-state electroluminescent devices, the PL properties in polymer thin films were investigated

for Ir-1-Ir-4. Poly(methyl methacrylate) (PMMA) was chosen as a matrix polymer because the absence of near UV-to-visible absorption allows us to estimate the intrinsic  $\Phi_{PL}$ s of the iridium complexes. The sample films were fabricated by a spin-coating method. In a sample film, the ratio of PMMA to the iridium complex was adjusted to 100/4 (wt/wt). The obtained PL spectra are shown in Fig. 6, and all the data are summarized in Table 5. In the series of Ir-1 (Fig. 6a), few spectral changes were observed for Ir-1a in comparison with the spectrum in solution shown in Fig. 4a, whereas significant blue shifts of  $\lambda_{PL}$  by 32 and 64 nm were observed for **Ir-1b** and **Ir-1c**, respectively. In the series of Ir-2, similar behavior was observed, where Ir-2b and Ir-2c exhibited blue shifts by 81 and 38 nm, respectively, in the PMMA films. These blue shifts should be due to so-called rigidochromism [39-41] that is likely to be caused by the aromatic O^O ligands. In the case of Ir-1a and Ir-2a, the C^N ligand mainly contributes to the T<sub>1</sub> level, as shown in Fig. 5, and thus the vectorial change of the molecular dipole is relatively small upon photo-excitation. On the other hand, the T<sub>1</sub> levels of the iridium complexes with aromatic O<sup>0</sup> ancillary

Table 5					
Photoluminescence	spectral da	ta of <b>Ir-1–Ir-4</b>	in	PMMA	films. <sup>a,b</sup>

Compd	$\lambda_{PL}(nm)$	$\Phi_{ m PL}$
Ir-1a	473, 505	0.51
Ir-1b	526	0.61
Ir-1c	540	0.40
Ir-2a	518	0.33
Ir-2b	552	0.058
Ir-2c	623	0.038
Ir-3a	538	0.49
Ir-3b	540	0.47
Ir-3c	536	0.29
Ir-4a	632	0.25
Ir-4b	635	0.25
Ir-4c	630	0.11

<sup>a</sup> Obtained in PMMA films at 298 K.

<sup>b</sup> The ratio of PMMA/Ir(III) complex was adjusted to 100/4 (wt/wt).

ligands such as **Ir-1b,c** and **Ir-2b,c** are based on the  $O^{O}$  ligands, that should bring about drastic vectorial changes of the molecular dipoles upon photo-excitation. As the PMMA molecules around the iridium complexes do not change their dipoles in the solid state, so the  $O^{O}$ related T<sub>1</sub> levels of **Ir-1b,c** and **Ir-2b,c** should be significantly unstabilized in the PMMA films. Therefore, these complexes exhibit remarkable rigidochromic behavior. It is interesting that **Ir-1** and **Ir-2** afford larger  $\Phi_{PL}$ s in PMMA matrices than in toluene solutions, except for **Ir-1a**. Especially, the  $\Phi_{PL}$  of **Ir-1c** was greatly enlarged from 0.083 to 0.40. These PL spectral features give great advantages in application to OLEDs.

In the series of **Ir-3** and **Ir-4**, the ancillary ligands do not affect their PL spectra in the PMMA films, except for **Ir-3a**, because their T<sub>1</sub> levels are based on considerable contributions from the *C^N* ligands rather than the *O^O* ligands, as shown in Fig. 5b and Fig. 5c, and thus any rigidochromic behavior was not observed. In the case of **Ir-3a**, one can see that the <sup>3</sup>MLCT<sub>C^N</sub> level is set at the T<sub>1</sub> level due to destabilization of the *O^O*-related triplet level, and thus the PL spectrum of **Ir-3a** is almost similar to those of **Ir-3b** and **Ir-3c**. The  $\Phi_{PLS}$  of **Ir-3** and **Ir-4** in PMMA films are not more than those in toluene solutions although the  $\Phi_{PL}$  of **Ir-3a** is exceptionally enhanced from 0.43 to 0.49.

### 4. Conclusions

Photoluminescent properties of bis-cyclometalated iridium(III) complexes bearing four types of C^N ligands Ir-1-Ir-4 were investigated, especially focusing on the influence of the O^O ancillary ligands on the PL color tuning. In the case of Ir-1 and Ir-2, PL spectra were significantly red-shifted by employing the aromatic O^O ancillary ligands (Ir-1; from 474 to 604 nm, Ir-2; from 521 to 661 nm), and the PL color was tuned from blue to deep red. In the case of Ir-3, the red shifts by the aromatic O^O ancillary ligands were guite modest (from 541 to 566 nm), and for red emissive Ir-4, any O^O ligand effects on the PL color were not found. These results can be explained by the relationship between the <sup>3</sup>MLCT<sub>C^N</sub> and O^O-related triplet levels. In general, the <sup>3</sup>MLCT<sub>C^N</sub> level is  $T_1$  in typical bis-cyclometalated iridium(III) complexes with aliphatic O^O ligands such as acetylacetonate and dipivaloylmethanate, whereas the employment of the aromatic O^O ancillary ligands lowers the  ${}^{3}LC_{0^{\circ}0}$  and/or  ${}^{3}MLCT$  levels below the <sup>3</sup>MLCT<sub>C<sup>N</sup></sub> level. As a result, the PL spectrum is red-shifted by the ILET from the  ${}^{3}MLCT_{C^{N}}$  to the O^O-related T<sub>1</sub> level. Thus, the color tuning by the O^O ancillary ligand is possible. We also investigated the PL properties of Ir-1-Ir-4 in PMMA films. For Ir-1 and Ir-2, the complexes with the aromatic ancillary ligands **0^0-1b** and **0^0-**1c showed remarkable rigidochromic behavior yielding considerable blue shifts of  $\lambda_{PL}$ s in comparison with those in solutions. These results should be caused by destabilization of the O^O-related T<sub>1</sub> levels. Some of the present iridium complexes exhibited the enhancement of their  $\Phi_{\rm PL}$ s in the PMMA films. We are currently investigating the electrophosphorescence behavior of these complexes by fabricating polymer-based OLEDs (PLEDs), and the O^O ligand effects on the PLED performance will be discussed elsewhere.

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