

## Supporting Information

### Novel Cyclometalated Iridium(III) Complex Containing dibenzo-24-crown-8: Synthesis, Luminescence and Application in Highly Efficient Green Phosphorescent OLEDs

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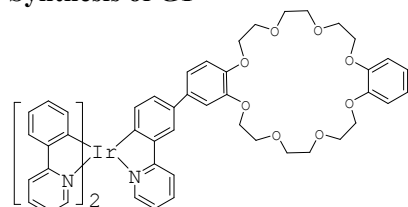
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## Experimental Section

### Materials and equipment

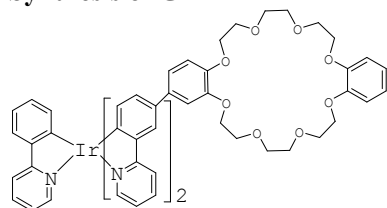
Ir(PPy)<sub>3</sub> [*fac*-tris(2-phenylpyridinato)iridium] (**1**),<sup>S1</sup> bromination of Ir(PPy)<sub>3</sub> (**2-4**),<sup>S2</sup> and 4-(boronic acid pinacol ester)-dibenzo-24-crown-8 (**5**)<sup>S3</sup> were prepared according to the reported procedures. All reactions were performed under nitrogen. All solvents were carefully dried and distilled prior to use. Commercially available reagents were used without further purification unless otherwise stated.

### Synthesis of G1



Pd(PPh<sub>3</sub>)<sub>4</sub> (30 mg, 0.025 mmol) was added to a mixture of compound **2** (368 mg, 0.5 mmol), compound **5** (345 mg, 0.6 mmol), and 2.0 M K<sub>2</sub>CO<sub>3</sub> solution (20.0 mL) in toluene (40.0 mL) and ethanol (20.0 mL). The mixture was degassed and heated to 90 °C with vigorously stirring for 24 h under N<sub>2</sub>. After being cooled to room temperature, the mixture was poured into water. The organic phase was separated and the aqueous phase was extracted with dichloromethane (3×30 mL). The combined organic layers were dried over MgSO<sub>4</sub> and evaporated to remove the solvents under vacuum. The residue was purified by column chromatography (ethyl acetate/dichloromethane = 1/1, v/v) to provide G1 (352 mg) as a yellow solid in 64% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ (ppm): 7.99–7.94 (d, *J* = 8.19 Hz, 2H), 7.91–7.88 (d, *J* = 8.19 Hz, 2H), 7.82 (s, 1H), 7.64–7.55 (m, 9H), 7.15 (s, 5H), 7.05–7.02 (m, 1H), 6.93–6.84 (m, 18H), 4.18–4.12 (m, 8H), 3.91–3.90 (m, 8H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS) δ (ppm): 166.73, 160.81, 160.20, 148.95, 147.51, 147.24, 147.02, 144.23, 144.22, 143.65, 137.36, 137.12, 136.17, 136.05, 132.42, 132.36, 129.97, 128.63, 123.92, 122.14, 122.01, 121.42, 119.95, 119.17, 118.90, 114.43, 114.16, 112.70, 69.95, 69.92, 69.52, 69.48, 69.3 6. Elemental Anal. Calcd. for C<sub>57</sub>H<sub>54</sub>IrN<sub>3</sub>O<sub>8</sub>: C, 62.17; H, 4.94; N, 3.82; Found: C, 62.23; H, 4.96; N, 3.74. MALDI-TOF (*m/z*): calcd for [M]<sup>+</sup> 1101.354, found [M + Na]<sup>+</sup> 1124.359.

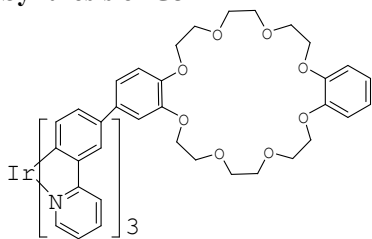
### Synthesis of G2



Pd(PPh<sub>3</sub>)<sub>4</sub> (60 mg, 0.05 mmol) was added to a mixture of compound **3** (260 mg, 0.32 mmol), compound **5** (525 mg, 0.96 mmol), and 2.0 M K<sub>2</sub>CO<sub>3</sub> solution (15.0 mL) in toluene (30.0 mL) and ethanol (15.0 mL). The mixture was degassed and heated to 90 °C with vigorously stirring for 36 h under N<sub>2</sub>. After being cooled to room temperature, the mixture was poured into water. The organic phase was separated and the aqueous phase was extracted with dichloromethane (3×30 mL). The combined organic layers were dried over MgSO<sub>4</sub> and evaporated to remove the solvents under vacuum. The residue was purified by column chromatography (ethyl acetate/dichloromethane = 2/1, v/v) to provide G2 (302 mg) as a yellow solid in 61% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ (ppm): 7.98–7.95 (d, *J* = 8.19 Hz, 2H), 7.90–7.87 (d, *J* = 8.19 Hz, 1H), 7.80 (s, 2H), 7.63–7.54 (m, 7H), 7.13 (s, 4H), 7.06–7.03 (m, 2H), 6.94–6.85 (m, 18H), 4.19–4.13 (m, 16H), 3.92–3.91 (m, 16H), 3.83 (s, 16H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS) δ (ppm): 166.72, 160.80, 160.22, 148.97, 147.50, 147.20, 147.05, 144.26, 144.21, 143.66, 137.38, 137.11, 136.18, 136.07, 132.40, 132.36, 129.95, 128.64, 123.95, 122.15, 122.02, 121.44, 119.93, 119.19, 118.91, 114.44, 114.18, 112.72,

71.23, 69.97, 69.93, 69.54, 69.46, 69.38. Elemental Anal. Calcd. for  $C_{81}H_{84}IrN_3O_{16}$ : C, 62.86; H, 5.47; N, 2.71; Found: C, 62.98; H, 5.36; N, 2.64. MALDI-TOF ( $m/z$ ): calcd for  $[M]^+$  1547.548, found  $[M + Na]^+$  1570.540.

### Synthesis of G3



$Pd(PPh_3)_4$  (47 mg, 0.04 mmol) was added to a mixture of compound **4** (178 mg, 0.2 mmol), compound **5** (437 mg, 0.8 mmol), and 2.0 M  $K_2CO_3$  solution (15.0 mL) in toluene (40.0 mL), ethanol (15.0 mL) and THF (10.0 mL). The mixture was degassed and heated to 90 °C with vigorously stirring for 46 h under  $N_2$ . After being cooled to room temperature, the mixture was poured into water. The organic phase was separated and the aqueous phase was extracted with dichloromethane ( $3 \times 30$  mL). The combined organic layers were dried over  $MgSO_4$  and evaporated to remove the solvents under vacuum. The residue was purified by column chromatography (ethyl acetate/dichloromethane = 2/1, v/v) to provide G3 (267 mg) as a yellow solid in 67% yield.  $^1H$  NMR (300 MHz,  $CDCl_3$ , TMS)  $\delta$  (ppm): 7.99–7.96 (d,  $J = 8.19$  Hz, 3H), 7.84 (s, 3H), 7.65–7.60 (t,  $J = 7.74$  Hz, 3H), 7.56–7.55 (d,  $J = 4.62$  Hz, 3H), 7.12–7.03 (t,  $J = 13.71$  Hz, 9H), 6.84 (s, 21H), 4.20–4.08 (m, 24H), 3.92 (s, 24H), 3.83 (s, 24H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ , TMS)  $\delta$  (ppm): 166.52, 148.95, 147.51, 147.19, 144.22, 137.36, 136.13, 132.49, 128.69, 122.20, 121.42, 119.19, 118.98, 114.36, 114.12, 112.69, 71.25, 69.93, 69.55, 69.47, 69.39. Elemental Anal. Calcd. for  $C_{101}H_{114}IrN_3O_{24}$ : C, 63.24; H, 5.76; N, 2.11; Found: C, 63.28; H, 5.73; N, 2.34. MALDI-TOF ( $m/z$ ): calcd for  $[M]^+$  1993.742, found  $[M + Na]^+$  2016.748.

### Measurements and Characterization

$^1H$  and  $^{13}C$  spectra were recorded on a Bruker 300 MHz spectrometer operating at 300 MHz at room temperature. Chemical shifts were reported as  $\delta$  values (ppm) relative to an internal tetramethylsilane (TMS) standard. Thermogravimetric analysis (TGA) was measured on a Netzsch TG 209 instrument under nitrogen atmosphere at a heating rate of 20 °C  $min^{-1}$  and  $T_d$  was reported as the temperatures at 5% weight losses. Cyclic voltammetry was carried out on a CHI660A electrochemical workstation in a solution of tetrabutylammonium hexafluorophosphate ( $Bu_4NPF_6$ ) (0.1 M) in acetonitrile at a scan rate of 50 mV/s at room temperature under the protection of argon. A platinum electrode was used as the working electrode. A Pt wire was used as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. UV-vis absorption spectra were measured on a HP 8453 spectrophotometer. PL spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer.

### Fabrication of PLEDs

The ITO-coated glass substrates were ultrasonically cleaned with deionized water, acetone, detergent, deionized water, and isopropyl alcohol. Then a layer of 40 nm thick poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) (H.C.Stack, 4083) was spin-coated onto the pre-cleaned and  $O_2$ -plasma-treated ITO substrates. After that, the PEDOT:PSS layer was baked at 150 °C for 20 min to remove residual water, and then the devices were moved into a glove box under the argon-protected environment. A mixture of the iridium complex with PVK + PBD (30 mg  $mL^{-1}$  in *o*-DCB) were spin-coated onto PEDOT:PSS at a speed of 2000 rpm to yield 90 nm thickness emitting layers. The samples were transferred into a chamber and kept under vacuum ( $3.0 \times 10^{-4}$  Pa) for 2 h. Then cesium fluoride (CsF) with a thickness of 1.5 nm and aluminum with a thickness of 100 nm were subsequently deposited on top of the emitting layer to form the cathode. The current density ( $J$ ) and brightness ( $L$ ) versus voltage ( $V$ ) data were collected using a Keithley 236 source meter and silicon photodiode. After typical encapsulation with UV epoxy and cover glass, the devices were taken out from the dry box and the luminance was calibrated by a PR-705 SpectraScan Spectrophotometer (Photo Research) with simultaneous acquisitions of the EL spectra.

[S1] A. B. Tamayo, B. D. Alleyne, P. I. Djurovich, S. Lamansky, I. Tsyba, N. N. Ho, R. Bau and M. E. Thompson, *J. Am. Chem. Soc.*, 2003, **125**, 7377.

[S2] P. Stossel, H. Spreitzer and H. Becker. US Pat., 20040138455A1, 2004.

[S3] J. Zhang, K. Zhang, X. Huang, W. Cai, C. Zhou, S. Liu, F. Huang and Y. Cao, *J. Mater. Chem.*, 2012, **22**, 12759.