## **Electronic supplementary information**

## for

Unsymmetric 2-phenylpyridine (ppy)-type cyclometalated Ir(III) complexes bearing both 5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracene and phenylsulfonyl groups for tuning optoelectronic properties and electroluminescent abilities Yindi Zhang,<sup>a</sup> Xi Chen,<sup>a</sup> Dongdong Song,<sup>a</sup> Daokun Zhong,<sup>a</sup> Xiaolong Yang,<sup>a</sup> Yuanhui Sun,<sup>a</sup> Boao

Liu,<sup>a</sup> Guijiang Zhou\*<sup>a</sup> and Zhaoxin Wu\*<sup>b</sup>

<sup>a</sup> MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter, State Key Laboratory for Mechanical Behavior of Materials, Department of Chemistry, School of Science, Xi'an Jiaotong University, Xi'an 710049, P. R. China. E-mail: zhougj@mail.xjtu.edu.cn;

<sup>b</sup> Key Laboratory for Physical Electronics and Devices of the Ministry of Education, Faculty of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an 710049, P. R. China. E-mail: zhaoxinwu@mail.xjtu.edu.cn

Synthesis



**1,3-Diphenoxybenzene.** Under a nitrogen atmosphere, 1,3-dibromobenzene (5.00 g, 0.02 mol), Phenol (5.19 g, 0.06 mol), Cs<sub>2</sub>CO<sub>3</sub> (20.70 g, 0.06 mol) and CuBr (0.91 g, 0.01 mol) were heated to 160 °C in degassed 2-pyrrolidinone (35.00 ml) for 24 h. After cooling to room temperature, the mixture was extracted with petroleum ether. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure, then purified by column chromatography over silica gel using petroleum ether as the eluent. A white solid of the title compound was obtained (4.06 g, 72%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.32 (t, *J* = 8.0 Hz, 4H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 4H), 6.72–6.69 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 160.3, 158.3, 132.0, 131.5, 125.3, 120.8, 114.8, 110.9.



**OBA.** A solution of butyllithium in hexane (3.66 mL, 9.16 mmol) was added slowly to a solution of 1,3-diphenoxybenzene (2.00 g, 7.63 mmol) in *o*-xylene (30.00 mL) at 0 °C under a nitrogen atmosphere. After stirring at 70 °C for 4 h, borontribromide (0.87 mL, 9.16 mmol) was added slowly at -40 °C. After the reaction mixture was allowed to warm to room temperature for 1 h, *N*,*N*-diisopropylethylamine (2.66 mL, 15.26 mmol) was added at 0 °C. After stirring at 120 °C for 5 h, *N*,*N*-diisopropylethylamine (1.33 mL, 7.64 mmol) was added at 0 °C, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under

reduced pressure, then purified by column chromatography over silica gel using petroleum ether as the eluent. A white solid of the title compound was obtained (1.27 g, 62%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.69 (dd, J = 1.6, 7.8 Hz, 1H), 7.79 (t, J = 8.0 Hz, 1H), 7.70 (ddd, J = 1.6, 7.1, 8.5 Hz, 2H), 7.54 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 7.1, 7.8 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 160.5, 157.4, 134.6, 134.5, 133.6, 122.7, 118.5, 108.4.



**OBA-Br.** *N*-bromosuccinimide (0.33 g, 1.85 mmol) was added to a solution of **OBA** (0.50 g, 1.85 mmol) in THF (10.00 mL) at room temperature under nitrogen atmosphere. After the mixture was stirred at room temperature for 3 h, it was cooled to 0 °C and added to water, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure, then purified by column chromatography over silica gel using petroleum ether as the eluent. A white solid of the title compound was obtained (0.28 g, 65%) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.70 (d, *J* = 8.0 Hz, 2H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.78–7.71 (m, 2H), 7.68 (d, *J* = 4.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.45–7.39 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 176.8, 160.3, 153.1, 137.7, 134.6, 134.5, 134.0, 133.9, 123.4, 123.1, 118.8, 118.5, 110.1, 100.8.



**LS-P.** Under a nitrogen atmosphere, 1-bromo-4-(phenylsulfanyl)benzene (1.10 g, 3.70 mmol), 2-(tributylstannyl)pyridine (2.04 g, 5.56 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.21 g, 0.19 mmol) were added to degassed toluene (30.00 mL). The reaction mixture was heated to 110 °C and stirred for 16 h. After cooling to room temperature, the mixture was evaporated under reduced pressure, then purified by column chromatography over silica gel using CH<sub>2</sub>Cl<sub>2</sub> : ethyl acetate = 17:1 (v/v). The title product was obtained as a white solid (0.69 g, 64%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.70–8.68 (m, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.78–7.70 (m, 2H), 7.43–7.40 (m, 4H), 7.36–7.22 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 156.6, 150.0, 137.9, 137.3, 136.8, 135.1, 131.5, 131.0, 129.3, 127.6, 127.4, 122.2, 120.3.



**LS-M.** Under a nitrogen atmosphere, 1-bromo-3-(phenylsulfanyl)benzene (2.0 g, 6.73 mmol), 2-(tributylstannyl)pyridine (3.72 g, 10.1 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.39 g, 0.33 mmol) were added to degassed toluene (30.00 mL). The reaction mixture was heated to 110 °C and stirred for 16 h. After cooling to room temperature, the mixture was evaporated under reduced pressure, then purified by column chromatography over silica gel using CH<sub>2</sub>Cl<sub>2</sub> : ethyl acetate = 16:1 (v/v). The title product was obtained as a white solid (1.19 g, 60%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.69 (d, *J* = 4.8 Hz, 1H), 8.59 (s, 1H), 8.25–8.23 (m, 1H), 8.01–7.97 (m, 3H), 7.82–7.74 (m, 2H), 7.65–7.46 (m, 4H), 7.33–7.28 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 155.2, 149.9, 142.2, 140.8, 137.1, 133.3, 131.6, 129.8, 129.3, 127.9, 127.7, 125.9, 123.1, 120.7.



Fig. S1 <sup>1</sup>H and <sup>13</sup>C NMR spectra for the asymmetric OBA-based Ir(III) complexes.

Cont. Fig. S1



IrP-M















IrQ-M

**X-ray crystallography experimental information**. The single crystal of the mononuclear Ir(III) complex **IrQ-P** was cultivated by slowly diffusing its dichloromethane solution into hexane. The crystal was mounted on glass fiber and the data were collected on a Bruker SMART CCD diffractometer (Mo K $\alpha$  radiation and  $\lambda = 0.71073$  Å) in  $\Phi$  and  $\omega$  scan modes at *ca*. 293 K. Its structure was solved by direct methods followed by difference Fourier syntheses, and then refined by full-matrix least-squares techniques against  $F^2$  using SHELXL-97 program on a PC.<sup>2</sup>



Fig. S2 TGA curves for these unsymmetric OBA-based ppy-type Ir(III) complexes.



Fig. S3 Cyclic voltammograms for these unsymmetric OBA-based ppy-type Ir(III) complexes.



**Fig. S4** Current density-voltage-luminance (*J-V-L*) characteristics and EL efficiency-luminance curves for the optimized OLEDs: (a) Device A1 (b) Device A3.



**Fig. S5** Current density-voltage-luminance (*J-V-L*) characteristics and EL efficiency-luminance curves for the optimized OLEDs: (a) Device **B2** (b) Device **B3**.



Fig. S6 Current density-voltage-luminance (J-V-L) characteristics and EL efficiency-luminance curves for the optimized OLEDs: (a) Device C2 (b) Device C3.