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

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Synthesis

1,3-Diphenoxybenzene. Under a nitrogen atmosphere, 1,3-dibromobenzene (5.00 g, 0.02 mol), Phenol (5.19 g, 0.06 mol), Cs₂CO₃ (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 Na₂SO₄ 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%). ¹H NMR (400 MHz, CDCl₃): δ (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). ¹³C NMR (100 MHz, CDCl₃): δ (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 CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄ 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%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (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). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (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$_2$Cl$_2$. The organic layer was dried over anhydrous Na$_2$SO$_4$ 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%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (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). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (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\(_3\))\(_4\) (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\(_2\)Cl\(_2\) : ethyl acetate = 17:1 (v/v). The title product was obtained as a white solid (0.69 g, 64%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) (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). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) (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](image)

**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\(_3\))\(_4\) (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\(_2\)Cl\(_2\) : ethyl acetate = 16:1 (v/v). The title product was obtained as a white solid (1.19 g, 60%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) (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). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) (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 $^1$H and $^{13}$C NMR spectra for the asymmetric OBA-based Ir(III) complexes.
Cont. Fig. S1
**X-ray crystallography experimental information.** The single crystal of the mononuclear Ir(III) complex $\text{IrQ-P}$ 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.$^2$

![TGA curves for these unsymmetric OBA-based ppy-type Ir(III) complexes.](#)

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

![Cyclic voltammograms 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.