

## Supporting Information

### White Light-Emitting Diodes Based on an All-Phosphorescent Supramolecular Polymer

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#### Experimental

**Materials.** 4-(boronic acid pinacol ester)dibenzo-24-crown-8 (**6**)<sup>1</sup>, monomers Flrpic-dCr and C<sub>6</sub>O<sub>4</sub>-dA were prepared according to the reported procedures.<sup>2</sup> All reactions were performed under nitrogen. All solvents were carefully dried and distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated.

#### Synthesis of 2-(9,9-dioctylfluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**).<sup>3</sup>

To a solution of compound 2-bromo-9,9-dioctylfluorene 5.0 g (10.65 mmol) in THF (100 mL) in a flame-dried 250 mL flask at -78 °C was added dropwise 5.04 mL (12.60 mmol) of *n*-butyllithium (2.5 M in hexane). The mixture was stirred at -78 °C for 1 h and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 2.83 mL (13.85 mmol) was added rapidly to the solution. After one additional hour at -78 °C, the resulting mixture was warmed to room temperature and stirred overnight. The mixture was poured into water, extracted with diethyl ether three times and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by recrystallization in methanol/acetone (*v/v* = 10/1) to obtain the product **2** (4.78 g) as a white crystal. Yield: 87 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS) δ (ppm): 8.03 (s, 1H), 7.77–7.83 (m, 4H), 7.32–7.34 (m, 2H), 1.14 (s, 12H). MS (ESI):

calcd for  $[M]^+$  516.4, found  $[M+1]^+$  517.6.

### **Synthesis of 5-bromo-2-(9,9-dioctylfluoren-2-yl)pyridine (3).**

2,5-dibromopyridine (2.11 g, 8.90 mmol), **2** (2.30 mg, 4.45 mmol), 2.0 M  $K_2CO_3$  solution (25.0 mL), toluene (50.0 mL) and ethanol (25.0 mL) were added into a two-necked flask (150 mL), then  $Pd(PPh_3)_4$  (415 mg, 0.356 mmol) was added. The mixture was degassed and heated to 90 °C with vigorously stirring for 24 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 ( $3 \times 50$  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 (petroleum ether/dichloromethane = 4/1, v/v) to provide colorless solid product **3** (1.73 g). Yield: 71%.  $^1H$  NMR (300 MHz,  $CDCl_3$ , TMS)  $\delta$  (ppm): 8.77 (s, 1H), 7.97 (s, 1H), 7.94–7.93 (d,  $J = 1.5$  Hz, 1H), 7.91–7.87 (d,  $J = 11.1$  Hz, 1H), 7.75–7.69 (m, 3H), 7.36–7.33 (m, 3H), 2.05–1.98 (m, 4H), 1.60–1.03 (m, 20H), 0.81–0.76 (t,  $J = 6.9$  Hz, 6H), 0.64–0.62 (m, 4H). MS (ESI): calcd for  $[M]^+$  545.3, found  $[M+1]^+$  546.7.

**Synthesis of 5.** A mixture of iridium trichloride hydrate (0.35 g, 1.0 mmol) and 5-bromo-2-(9,9-dioctylfluoren-2-yl)pyridine (**3**) (1.36 g, 2.50 mmol) in 2-ethoxyethanol (24 mL) and water (8 mL) was heated and refluxed for 24 h under nitrogen atmosphere. After being cooled to room temperature, the resulting precipitate was collected, and then washed respectively with water, ethanol and petroleum ether to afford 1.18 g chlorine-bridged iridium dimer **4** as an orange powder. The dimer was directly used in the following procedure.

A mixture of **4** (1.18 g, 0.447 mmol), picolinic acid (138 mg, 1.12 mmol),  $Na_2CO_3$  (572 mg, 5.4 mmol) in 2-ethoxyethanol (20 mL) was refluxed for 24 h under nitrogen atmosphere, then was allowed to cool to room temperature and mixed with water (40 mL). The mixture was extracted with dichloromethane ( $3 \times 30$  mL). The resulting 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 = 1/1, v/v) to obtain **5** as an orange solid in 67% yield (842

mg).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  (ppm): 8.95–8.94 (d,  $J = 1.92$  Hz, 1H), 8.40–8.37 (d,  $J = 7.38$  Hz, 1H), 7.92–7.81 (m, 5H), 7.66–7.64 (d,  $J = 4.77$  Hz, 1H), 7.54–7.52 (d,  $J = 5.46$  Hz, 2H), 7.45 (s, 1H), 7.37–7.36 (m, 1H), 7.26–7.17 (m, 8H), 6.76 (s, 1H), 6.59 (s, 1H), 1.99–1.79 (m, 8H), 1.25–0.94 (m, 40H), 0.82–0.63 (m, 20H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  (ppm): 172.78, 168.68, 167.09, 152.18, 151.96, 151.83, 149.47, 148.61, 148.28, 147.52, 145.94, 144.32, 143.46, 142.91, 141.77, 140.22, 137.89, 128.54, 128.14, 127.56, 127.09, 126.52, 126.33, 123.33, 123.20, 122.99, 122.83, 119.91, 119.74, 119.27, 119.06, 116.00, 115.36, 54.36, 54.23, 40.42, 31.83, 31.79, 31.63, 29.42, 29.24, 29.14, 28.98, 23.94, 23.78, 22.58, 22.51, 14.07, 14.04, 13.99. MALDI-TOF ( $m/z$ ): calcd for  $[\text{M}]^+$  1405.501, found  $[\text{M} + \text{Na}]^+$  1428.373.

**Synthesis of monomer (FPyCr) $_2$ Irpic.**  $\text{Pd}(\text{PPh}_3)_4$  (105 mg, 0.09 mmol) was added to a mixture of **5** (842 mg, 0.6 mmol), **6** (1.03 g, 1.8 mmol), and 2.0 M  $\text{K}_2\text{CO}_3$  solution (20.0 mL) in toluene (30.0 mL) and ethanol (10.0 mL). The mixture was degassed and heated to 80 °C with vigorously stirring for 48 h under  $\text{N}_2$ . 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 (3×30 mL). The combined organic layers were dried over  $\text{MgSO}_4$  and evaporated to remove the solvents under vacuum. The residue was purified by column chromatography (ethyl acetate/dichloromethane = 2/1,  $v/v$ ) to provide monomer (FPyCr) $_2$ Irpic (617 mg) as an orange solid in 48% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  (ppm): 9.07 (s, 1H), 8.33–8.30 (d,  $J = 7.44$  Hz, 1H), 7.99–7.83 (m, 5H), 7.74–7.72 (d,  $J = 5.25$  Hz, 1H), 7.58 (s, 3H), 7.28–7.12 (m, 10H), 6.96–6.83 (m, 13H), 6.74–6.70 (d,  $J = 11.91$  Hz, 2H), 4.25–3.98 (m, 16H), 3.92 (s, 16H), 3.82 (s, 16H), 1.96–1.84 (m, 8H), 1.25–0.98 (m, 40H), 0.82–0.65 (m, 20H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  (ppm): 172.99, 169.67, 168.04, 152.62, 152.48, 149.15, 149.09, 149.02, 148.71, 148.21, 144.62, 144.13, 143.19, 143.01, 142.61, 141.96, 139.83, 139.36, 137.33, 136.79, 135.58, 135.25, 128.19, 127.83, 125.23, 123.31, 121.47, 119.15, 118.92, 118.68, 118.48, 114.42, 114.28, 113.87, 113.78, 71.24, 69.96, 69.41, 54.42, 54.29, 40.49, 31.84, 31.79, 31.64, 29.19, 29.15, 28.99, 24.00, 23.88, 22.58, 22.51, 14.07, 14.03, 14.00. Anal.

Calcd. for C<sub>122</sub>H<sub>156</sub>IrN<sub>3</sub>O<sub>18</sub>: C, 68.32; H, 7.33; N, 1.96; Found: C, 68.59; H, 7.55; N, 1.82. MALDI-TOF (m/z): calcd for [M]<sup>+</sup> 2142.101, found [M + Na]<sup>+</sup> 2164.538.

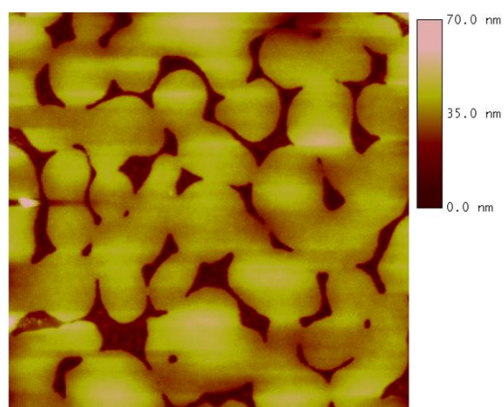
**Synthesis of Supramolecular Phosphorescent Polymers.** Monomers (FPyCr)<sub>2</sub>Irpic, FIrpic-dCr and C<sub>6</sub>O<sub>4</sub>-dA are dissolved at a certain molar ratio in a solution of CHCl<sub>3</sub>-CH<sub>3</sub>CN (1/1, v/v). The resulting solution was left for evaporation at room temperature. The obtained supramolecular phosphorescent polymers are denoted as SPP01, SPP02, SPP04, SPP08 and SPP1, corresponding respectively, to the monomer molar ratios of (FPyCr)<sub>2</sub>Irpic:FIrpic-dCr:C<sub>6</sub>O<sub>4</sub>-dA as 0.1:99.9:100, 0.2:99.8:100, 0.4:99.6:100, 0.8:99.2:100 and 1:99:100, without any further purification.

**Measurements and Characterization.** <sup>1</sup>H and <sup>13</sup>C spectra were recorded on a Bruker 300 MHz spectrometer operating at 300 and 75 MHz at room temperature. Chemical shifts were reported as δ values (ppm) relative to an internal tetramethylsilane (TMS) standard. Time-of-flight mass spectrometry (TOF-MS) was performed in the positive ion mode with a matrix of dithranol using a Bruker-autoflex III smartbeam. The differential scanning calorimetry (DSC) measurements were carried out with a Netzsch DSC 204 under N<sub>2</sub> flow at heating and cooling rates of 10 °C min<sup>-1</sup>. The glass transition temperature (T<sub>g</sub>) was determined from the second heating scan. UV-vis absorption spectra were measured on a HP 8453 spectrophotometer. PL spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. The phosphorescence quantum yield of monomer (FPyCr)<sub>2</sub>Irpic was determined in CH<sub>2</sub>Cl<sub>2</sub> solution at 293 K against *fac*-[Ir(ppy)<sub>3</sub>] (Hppy = 2-phenylpyridine) as a reference (Φ<sub>p</sub> = 0.90).<sup>4</sup>

**PLEDs Fabrication and Measurements.** 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 precleaned and O<sub>2</sub>-plasma-treated ITO substrates. Then the PEDOT:PSS layer was baked at 150 °C for 20 min to remove residual water, and the devices were moved into a glove box under the argon-protected environment. SPPs(50%)+mCP (25%)+OXD-7(25%) (30 mg mL<sup>-1</sup> in *o*-DCB) were spin-coated onto PEDOT:PSS at

a speed of 2000 rpm to yield the emitting layers with a thickness of ca. 90 nm. 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 EML 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.

**Figure S1.** AFM height images for ((FPyCr)<sub>2</sub>Irpic/Flirpic-dCr=1/99)(50-wt%) +mCP(25-wt%)+ OXD-7(25-wt%) film. The images are 5  $\mu\text{m}$   $\times$  5  $\mu\text{m}$



### Reference:

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