

Supporting Information

**Highly Efficient Blue Electrophosphorescent Polymers with Fluorinated Poly(arylene ether  
phosphine oxide) as Backbone**

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## Experimental

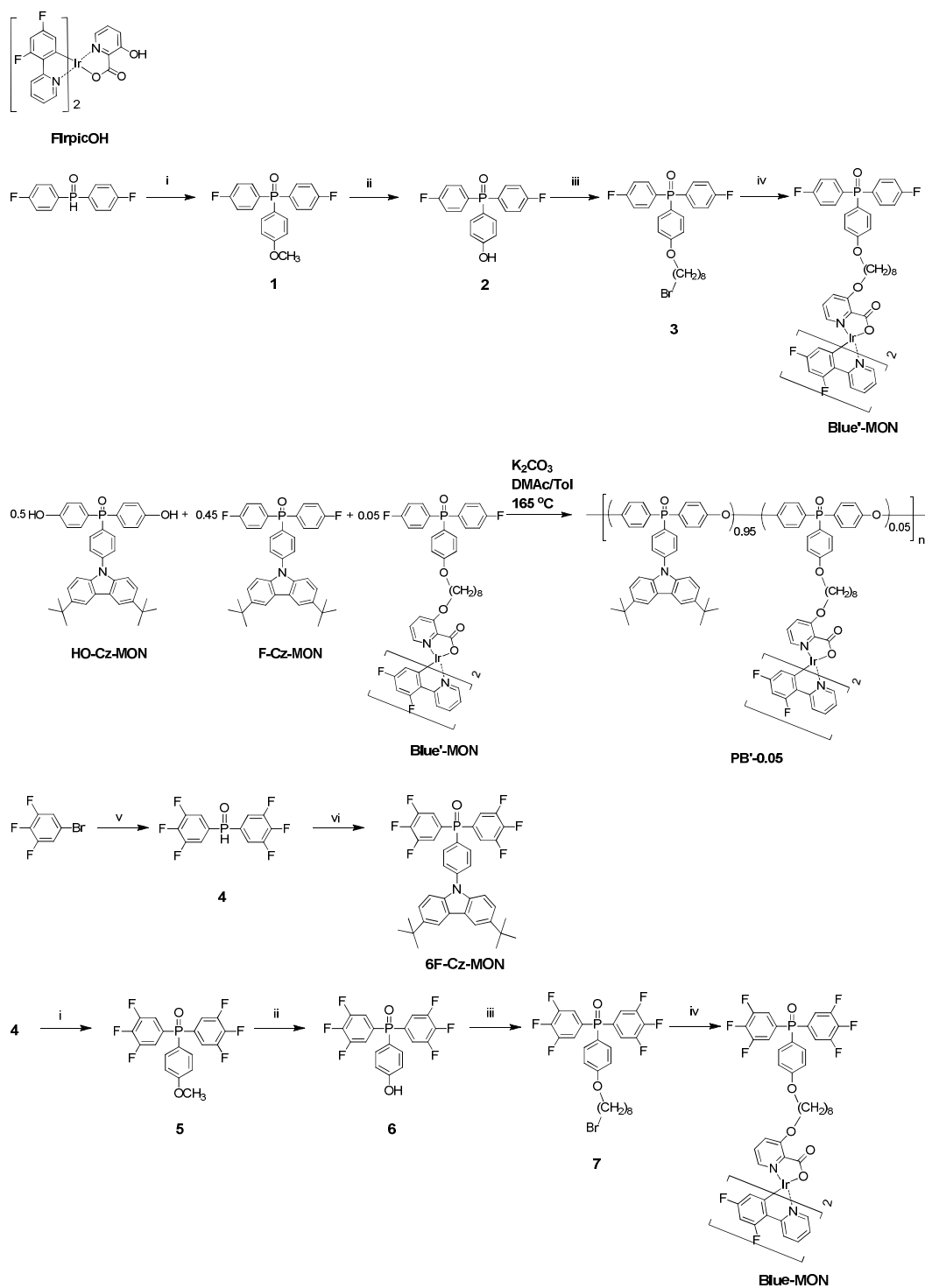
*General Information:* All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified according to the standard procedures. NMR spectra were recorded with Bruker Avance NMR spectrometers. Elemental analysis was performed using a Bio-Rad elemental analysis system. MALDI-TOF mass spectra were performed on an AXIMA CFR MS apparatus (COMPACT). TPCz (3,6-bis(diphenylphosphoryl)-9-(4-(diphenylphosphoryl)phenyl)-9H-carbazole) and FIrpic were prepared in our lab. The synthesis of HO-Cz-MON, F-Cz-MON, FIrpicOH and 9-(4-bromophenyl)-3,6-di-*tert*-butyl-9H-carbazole has been described in previous reports.<sup>[1]</sup>

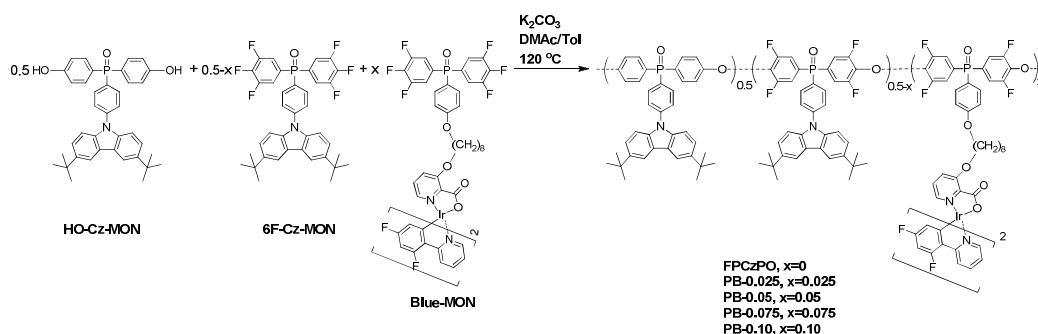
*Measurements and Characterization:* Molecular weight of the polymers were determined by gel permeation chromatography (GPC) on a Waters 410 instrument with polystyrene as a standard and THF as the eluent. Thermal properties of the polymers were analyzed with a Perkin-Elmer-TGA 7 instrument under nitrogen at a heating rate of 10 °C/min. UV-visible (UV-vis) absorption and photoluminescent spectra were measured with a Perkin-Elmer Lambda 35 UV-vis spectrometer and a Perkin-Elmer LS 50B spectrofluorometer, respectively. Phosphorescent spectra at 77 K were measured in toluene. Cyclic Voltammetry experiments were performed on an EG&G 283 (Princeton Applied Research) potentiostat/galvanostat system. The films of FPCzPO and PCzPO were tested in acetonitrile using ferrocene as an internal reference and n-Bu<sub>4</sub>NClO<sub>4</sub> as the supporting electrolyte. The HOMO energy levels were calculated according to the equation  $E_{\text{HOMO}} = -e [E_{\text{onset, ox}} + 4.8\text{V}]$ , in which  $E_{\text{onset, ox}}$  was the onset of the oxidation potential. The LUMO energy levels were calculated according to the equation  $E_{\text{LUMO}} = -e [E_{\text{onset, red}} + 4.8\text{V}]$ , where  $E_{\text{onset, red}}$  was the onset of the reduction potential.

*Polymer Light-emitting Diode (PLED) Fabrication and Measurements:* To fabricate PLEDs, a 40-nm-thick poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) film was first deposited on the pre-cleaned ITO-glass substrates (20Ω per square) and subsequently baked at 120 °C for 40 min. Then, solutions of the polymers in chlorobenzene were spin-coated onto PEDOT:PSS as the emissive layer (EML). The thickness of the EML was about 40 nm. Successively, a 50-nm-thick film of TPCz was thermally evaporated on top of the EML at a base pressure less than 10<sup>-6</sup> Torr (1 Torr=133.32 Pa). Finally, 1 nm LiF and 100 nm Al were deposited

as the cathode through a shadow mask with an array of  $14 \text{ mm}^2$  openings. The EL spectra and CIE coordinates were measured using a PR650 spectra colorimeter. The current–voltage and brightness–voltage curves of devices were measured using a Keithley 2400/2000 source meter and a calibrated silicon photodiode. All the measurements were carried out at room temperature under ambient conditions.

Scheme S1. Synthetic routes for the polymers.





Reagents and conditions:

i) *p*-bromoanisole, Pd(PPh<sub>3</sub>)<sub>4</sub>, *N*-methylmorpholine and toluene, 105 °C; ii) BBr<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, -78 °C; iii) K<sub>2</sub>CO<sub>3</sub>, 1,8-dibromooctane, acetone, reflux; iv) K<sub>2</sub>CO<sub>3</sub>, FlrpicOH, DMF, 60 °C. v) (1) Mg, tetrahydrofuran, (2) diethylphosphite, (3) NH<sub>4</sub>Cl; vi) 9-(4-bromophenyl)-3,6-di-*tert*-butyl-9H-carbazole, Pd(PPh<sub>3</sub>)<sub>4</sub>, *N*-methylmorpholine and toluene, 100 °C;

#### Synthetic Procedures:

**Bis(4-fluorophenyl)(4-methoxyphenyl)phosphine oxide (1):** Bis(4-fluorophenyl)phosphine oxide (10 g, 41.2 mmol), *p*-bromoanisole (9.24 g, 49.0 mmol), *N*-methylmorpholine (6.25 g, 61.8 mmol) and tetrakis(triphenylphosphine)palladium(0) (9.5 g, 8.24 mmol) was added consecutively to 80 mL toluene (Tol) under argon. The mixture was then heated at 100 °C for 8 hours. After cooling to room temperature, the obtained suspension was directly applied to a silica gel column using petroleum ether/ethyl acetate = 1/1 as eluent to give the crude product. Crystallization from a mixture of petroleum ether and CH<sub>2</sub>Cl<sub>2</sub> gave the pure product as white crystal (12.5 g) in a yield of 88%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.68 - 7.61 (m, 4H), 7.55 (dd, *J* = 11.6, 8.6 Hz, 2H), 7.21 - 7.11 (m, 4H), 6.98 (dd, *J* = 8.7, 2.0 Hz, 2H), 3.86 (s, 3H).

**Bis(4-fluorophenyl)(4-hydroxyphenyl)phosphine oxide (2):** Into a 50 mL flask were placed **1** (1.38 g, 4 mmol) and dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The stirred mixture was cooled to -78 °C and then boron tribromide (1.88 mL, 20 mmol) was added. The reaction mixture was warmed to room temperature, stirred for 24 h, and poured into cold water. The mixture was extracted with ethyl acetate and the organic layers was washed with NaHCO<sub>3</sub> aqueous and water. After drying, the organic layers was concentrated and applied to a silica gel column using CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH = 30/1 as eluent to give the product (1.19 g) as white powder in a yield of 90%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sup>6</sup>, δ): 10.28

(s, 1H), 7.67 - 7.61 (m, 4H), 7.45 – 7.33 (m, 6H), 6.92 (dd,  $J$  = 8.6, 2.2 Hz, 2H).

*(4-((8-bromooctyl)oxy)phenyl)bis(4-fluorophenyl)phosphine oxide (3):* **2** (2.05 g, 6.21 mmol), 1, 8-dibromooctane (2.88 ml, 18.63 mmol),  $K_2CO_3$  (5 g, 36 mmol) and acetone (30 mL) were added into a 100 mL flask and stirred at reflux for 12 hours. After cooling to room temperature, the mixture was filtrated and the filter residue was washed with  $CH_2Cl_2$ . The combined filtrate was concentrated and chromatographed by silica gel column using petroleum ether/ethyl acetate = 2/3 as eluent to give the product (2.63 g) as colorless oil in a yield of 85%.  $^1H$  NMR (300 MHz,  $CDCl_3$ ,  $\delta$ ): 7.69 – 7.61 (m, 4H), 7.54 (dd,  $J$  = 11.6, 8.7 Hz, 2H), 7.16 (td,  $J$  = 8.7, 2.0 Hz, 4H), 6.96 (dd,  $J$  = 8.8, 2.2 Hz, 2H), 4.01 (t,  $J$  = 6.4 Hz, 2H), 3.43 (t,  $J$  = 6.7 Hz, 2H), 1.97 – 1.73 (m, 4H), 1.60 – 1.41 (m, 4H).

Blue'-MON: FirpicOH (2.50 g, 3.52 mmol), **3** (2.08 g, 4.22 mmol),  $K_2CO_3$  (10 g, 72 mmol) and DMF (30 mL) were added into a 50 mL flask and stirred at 60 °C for 12 hours. After cooling to room temperature, the mixture was extracted with  $CH_2Cl_2$  and the organic layers was washed with water. The organic layers was dried, concentrated and applied to a silica gel column using ethyl acetate as eluent to give the product (3.44 g) as green powder in a yield of 87%.  $^1H$  NMR (300 MHz,  $CDCl_3$ ,  $\delta$ ): 8.80 (d,  $J$  = 5.4 Hz, 1H), 8.25 (dd,  $J$  = 14.1, 8.9 Hz, 2H), 7.76 (t,  $J$  = 7.9 Hz, 2H), 7.69 – 7.60 (m, 4H), 7.55 – 7.38 (m, 5H), 7.30 – 7.25 (m, 1H), 7.21 – 7.12 (m, 5H), 6.99 – 6.93 (m, 3H), 6.49 – 6.38 (m, 2H), 5.80 (d,  $J$  = 8.7 Hz, 1H), 5.32 (dd,  $J$  = 8.7 Hz, 2.1 Hz, 1H), 4.12 – 4.03 (m, 2H), 4.01 (t,  $J$  = 6.2 Hz, 2H), 2.05 – 1.91 (m, 2H), 1.91 – 1.77 (m, 2H), 1.77 – 1.43 (m, 8H). MALDI-TOF MS: calcd for  $C_{54}H_{43}F_6IrN_3O_5P$ : 1151.3 found: 1152.3  $[M+H]^+$ . Anal. calcd for  $C_{54}H_{43}F_6IrN_3O_5P$ : C, 56.34; H, 3.77; N, 3.65. found: C, 56.14; H, 3.70; N, 3.50.

PB'-0.05: Under argon, HO-Cz-MON (0.2938 g, 0.5 mmol), F-Cz-MON (0.2663 g, 0.45 mmol), Blue'-MON (0.0562 g, 0.05 mmol),  $K_2CO_3$  (0.21 g, 1.5 mmol), *N,N*-dimethylacetamide (DMAc) (3.0 mL) and toluene (3.0 mL) were added to a 10 mL flask equipped with a magnetic stir bar, a oil-water separator, a condenser and a gas adapter. The reaction was stirred at 140 °C for 3 hours and then 165 °C for 16 hours. After that, a solution of F-Cz-MON (0.0295 g, 0.05 mmol) in 1 mL DMAc was added and the mixture was stirred at 165 °C for another 8 hours. After cooling to room temperature, the mixture was extracted with  $CH_2Cl_2$ . The organic phase was washed with

water and then dried over Na<sub>2</sub>SO<sub>4</sub>. The solution was concentrated and then precipitated in methanol to afford the polymer as green fiber (0.40 g) in a yield of 70%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.11 (s, 2H), 7.94 – 7.64 (m, 8H), 7.48 - 7.34 (br, 4H), 7.19 (d, *J* = 7.2 Hz, 4H), 4.06 – 3.91 (m, 0.05H), 1.43 (s, 18H).<sup>[2]</sup>

*Bis(3,4,5-trifluorophenyl)phosphine oxide (4)*: Diethylphosphite (5.85 mL, 45.5 mmol) was added dropwise at 0 °C to a solution of 3, 4, 5-trifluorophenylmagnesium bromide in tetrahydrofuran which was prepared from 3, 4, 5-trifluoro bromobenzene (17.9 mL, 150 mmol) and magnesium (3.96 g, 165 mmol). The mixture was aged for 30 minutes at 0 °C, then stirred at ambient temperature for 16 hours. After that it was cooled again to 0 °C, and 75 mL NH<sub>4</sub>Cl aqueous was then added slowly. The mixture was extracted with diethyl ether and the organic phase was washed with NaHCO<sub>3</sub> aqueous and brine, then it was dried over Na<sub>2</sub>SO<sub>4</sub>. After the solvent had been completely removed, the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate = 3/1 as eluent to give the product (13.9 g) as white powder in 96% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.01 (d, *J* = 503.6, 1H), 7.39 – 7.31 (m, 4H).

6F-Cz-MON: **4** (5 g, 16.1 mmol), 9-(4-bromophenyl)-3,6-di-tert-butyl-9*H*-carbazole (5.82 g, 13.4 mmol), *N*-methylmorpholine (2.71 g, 26.8 mmol) and tetrakis(triphenylphosphine)palladium(0) (3.10 g, 2.68 mmol) was added consecutively to 20 mL toluene under argon. The mixture was then heated at 100 °C for 8 hours. After cooling to room temperature, the obtained suspension was directly applied to a silica gel column using petroleum ether/ethyl acetate = 6/1 as eluent to give the crude product. Crystallization from a mixture of petroleum ether and CH<sub>2</sub>Cl<sub>2</sub> gave the pure product as white crystal (8.0 g) in a yield of 90%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.13 (d, *J* = 1.4 Hz, 2H), 7.87 – 7.77 (m, 4H), 7.48 (dd, *J* = 8.7, 1.8 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.39 (dd, *J* = 12.6, 6.3 Hz, 4H), 1.46 (s, 18H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, δ): 152.85, 150.29, 144.09, 143.24, 138.19, 133.58, 133.48, 128.34, 127.30, 126.45, 126.32, 124.10, 123.96, 116.52, 109.11, 34.76, 31.90. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, δ (vs. fluorobenzene)): -16.67 (dd, *J* = 19.9 Hz, 0.5 Hz, 4F), -38.57 (t, *J* = 19.9 Hz, 2F). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 298K, δ): 24.19. MALDI-TOF MS: calcd for C<sub>38</sub>H<sub>32</sub>F<sub>6</sub>NOP: 663.2. found: 664.1 [M+H]<sup>+</sup>. Anal. calcd for C<sub>38</sub>H<sub>32</sub>F<sub>6</sub>NOP: C, 68.77; H, 4.86; N, 2.11. found: C, 68.53; H, 4.80; N, 2.03.

*(4-methoxyphenyl)bis(3,4,5-trifluorophenyl)phosphine oxide (5)*. This compound was prepared from **4** and *p*-bromoanisole according to the procedure for the synthesis of **1**. Column chromatography on silica gel using petroleum ether/ethyl acetate = 1/1 as eluent afforded the desired product as white powder in 57% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.53 (dd, *J* = 12 Hz, 8.8 Hz, 2H), 7.31 - 7.25 (m, 4H), 7.03 (dd, *J* = 8.8 Hz, 2.4 Hz, 2H), 3.88 (s, 3H).

*(4-hydroxyphenyl)bis(3,4,5-trifluorophenyl)phosphine oxide (6)*. This compound was prepared from **5** according to the procedure for the synthesis of **2**. Column chromatography on silica gel using petroleum ether/ethyl acetate = 1/1 as eluent afforded the desired product as white powder in a yield of 87%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sup>6</sup>, δ): 10.3 (s, 1H), 7.65 - 7.58 (m, 4H), 7.47 (dd, *J* = 12.1, 8.6 Hz, 2H), 6.94 (dd, *J* = 8.6, 2.4 Hz, 2H).

*(4-((8-bromooctyl)oxy)phenyl)bis(3,4,5-trifluorophenyl)phosphine oxide (7)*. This compound was prepared from **6** and **1**, 8-dibromooctane according to the procedure for the synthesis of **3**. Column chromatography on silica gel using petroleum ether/ethyl acetate = 1/1 as eluent afforded the desired product as colorless oil in a yield of 95%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.51 (dd, *J* = 12.0, 8.8 Hz, 2H), 7.31 - 7.25 (m, 4H), 7.01 (dd, *J* = 8.9, 2.5 Hz, 2H), 4.02 (t, *J* = 6.5 Hz, 2H), 3.41 (t, *J* = 6.8 Hz, 2H), 1.92 - 1.75 (m, 4H), 1.49 - 1.42 (m, 4H), 1.41 - 1.30 (m, 4H).

Blue-MON: This compound was prepared from FIrpicOH (0.071 g, 0.1 mmol) and **7** (0.089 g, 0.15 mmol) according to the procedure for the synthesis of Blue'-MON. Column chromatography on silica gel using ethyl acetate as eluent afforded the desired product as green powder in a yield of 91%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.80 (d, *J* = 5.7 Hz, 1H), 8.24 (dd, *J* = 19.3, 8.6 Hz, 2H), 7.75 (t, *J* = 7.9 Hz, 2H), 7.50 (dd, *J* = 12.0, 8.8 Hz, 2H), 7.45 (dd, *J* = 13.4, 7.0 Hz, 2H), 7.40 (s, 1H), 7.30 - 7.24 (m, 5H), 7.18 (t, *J* = 6.6 Hz, 1H), 7.00 (dd, *J* = 8.9, 2.5 Hz, 2H), 6.95 (d, *J* = 6.1 Hz, 1H), 6.50 - 6.31 (m, 2H), 5.80 (dd, *J* = 8.7, 2.3 Hz, 1H), 5.52 (dd, *J* = 8.7, 2.3 Hz, 1H), 4.13 - 4.05 (m, 2H), 4.00 (t, *J* = 6.5 Hz, 2H), 1.97 - 1.91 (m, 2H), 1.83 - 1.76 (m, 2H), 1.63 - 1.35 (m, 8H). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 298K, δ): 24.77. MALDI-TOF MS: calcd for C<sub>54</sub>H<sub>39</sub>F<sub>10</sub>IrN<sub>3</sub>O<sub>5</sub>P: 1223.2. found: 1224.2 [M+H]<sup>+</sup>. Anal. calcd for C<sub>54</sub>H<sub>39</sub>F<sub>10</sub>IrN<sub>3</sub>O<sub>5</sub>P: C, 53.03; H, 3.21; N, 3.44. found: C,



52.80; H, 3.18; N, 3.24.

*General Synthetic Procedure for the Polymers:* Under argon, 6F-Cz-MON, HO-Cz-MON, Blue-MON, K<sub>2</sub>CO<sub>3</sub> (0.21 g, 1.5 mmol), toluene (2.5 mL) and DMAc (2.5 mL) were added to a 10 mL flask and then stirred at 120 °C for 18 hours. After that, a solution of 6F-Cz-MON (10 mol% relative to HO-Cz-MON) in 1 mL DMAc was added and the mixture was stirred at 165 °C for another 8 hours. After cooling to room temperature, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was washed with water and dried over Na<sub>2</sub>SO<sub>4</sub>. The solution was concentrated and then precipitated in methanol to afford the polymers in 45~55% yield.

FPCzPO: White fiber. 6F-Cz-MON (0.1659 g, 0.25 mmol) and HO-Cz-MON (0.1469 g, 0.25 mmol) were used in the polymerization. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.11 (br, 4H), 7.96 – 7.61 (m, 12H), 7.54 – 7.34(m, 12H), 7.18 – 7.95(m, 4H) 1.44 (br, 36H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 159.77, 156.07 (dd, *J* =259.4, 18.7 Hz), 144.11, 143.68, 143.27, 142.03, 138.42, 138.18, 134.30, 134.20, 133.60, 130.70, 130.42, 129.64, 129.38, 127.79, 127.20, 126.71, 126.46, 126.33, 126.11, 125.98, 124.12, 123.96, 123.81, 116.52, 116.39, 115.85, 115.72, 109.12, 34.74, 31.91. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, δ (vs. fluorobenzene)): -8.02 (s, 4H). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 298K, δ): 27.04, 24.43. Anal. Calcd: C, 75.36; H, 5.66; N, 2.31. Found: C, 75.00; H, 5.76; N, 2.18.

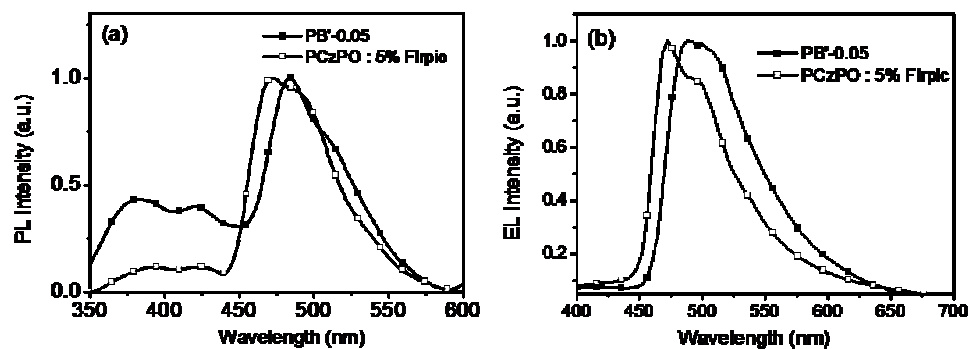
PB-0.025. Light-green fiber. 6F-Cz-MON (0.2521 g, 0.380 mmol), HO-Cz-MON (0.2351 g, 0.400 mmol) and Blue-MON (0.0245 g, 0.020 mmol) were used in the polymerization. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.10 (br, 4H), 7.92 – 7.61 (m, 12H), 7.52 – 7.32(m, 12H), 7.16 – 6.97 (m, 4H),

4.14 –3.84 (m, 0.15H), 1.42 (br, 36H).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 298K,  $\delta$ ): 26.96, 34.35. Anal. Calcd: C, 74.31; H, 5.57; N, 2.37. Found: C, 74.01; H, 5.67; N, 2.21.

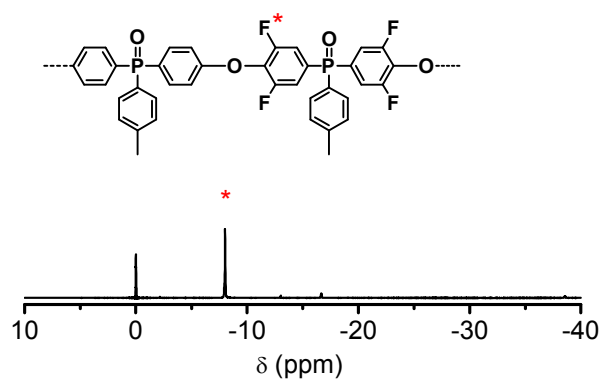
PB-0.05. Light-green fiber. 6F-Cz-MON (0.2389 g, 0.360 mmol), HO-Cz-MON (0.2351 g, 0.400 mmol) and Blue-MON (0.0490 g, 0.040 mmol) were used in the polymerization.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.11 (br, 4H), 7.95 – 7.62 (m, 12H), 7.51 – 7.34(m, 12H), 7.15 – 6.96 (m, 4H), 4.14 –3.84 (m, 0.35H), 1.43 (br, 36H).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 298K,  $\delta$ ):27.16, 24.37. Anal. Calcd: C, 73.50; H, 5.47; N, 2.43. Found: C, 73.21; H, 5.55; N, 2.38.

PB-0.075. Light-green fiber. 6F-Cz-MON (0.2256 g, 0.340 mmol), HO-Cz-MON (0.2351 g, 0.400 mmol) and Blue-MON (0.0730 g, 0.060 mmol) were used in the polymerization.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.11 (br, 4H), 7.93 – 7.63 (m, 12H), 7.53 – 7.33(m, 12H), 7.16 – 6.88 (m, 4H), 4.14 –3.84 (m, 0.60H), 1.44 (br, 36H).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 298K,  $\delta$ ):27.2, 24.40. Anal. Calcd: C, 72.61; H, 5.39; N, 2.48. Found: C, 72.35; H, 5.35; N, 2.36.

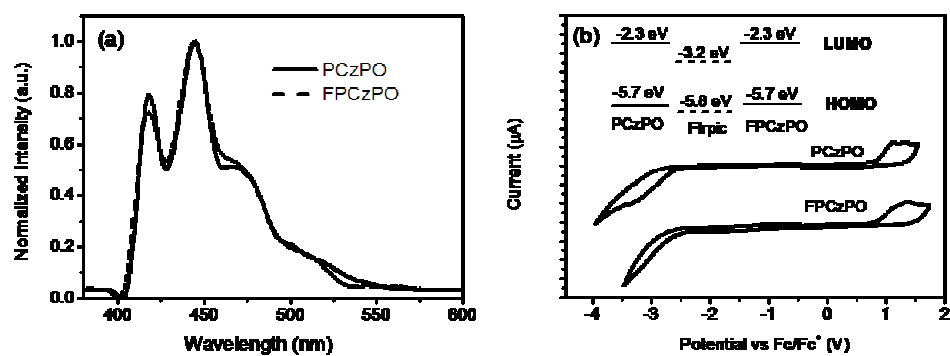
PB-0.10. Green fiber. 6F-Cz-MON (0.2123 g, 0.320 mmol), HO-Cz-MON (0.2351 g, 0.400 mmol) and Blue-MON (0.0978 g, 0.080 mmol) were used in the polymerization.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.10 (br, 4H), 7.92 – 7.57 (m, 12H), 7.51 – 7.26(m, 12H), 7.15 – 6.85 (m, 4H), 4.14 –3.84 (m, 0.79H), 1.43 (br, 36H).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 298K,  $\delta$ ):27.12, 24.40. Anal. Calcd: C, 71.60; H, 5.30; N, 2.54. Found: C, 71.32; H, 5.36; N, 2.35.



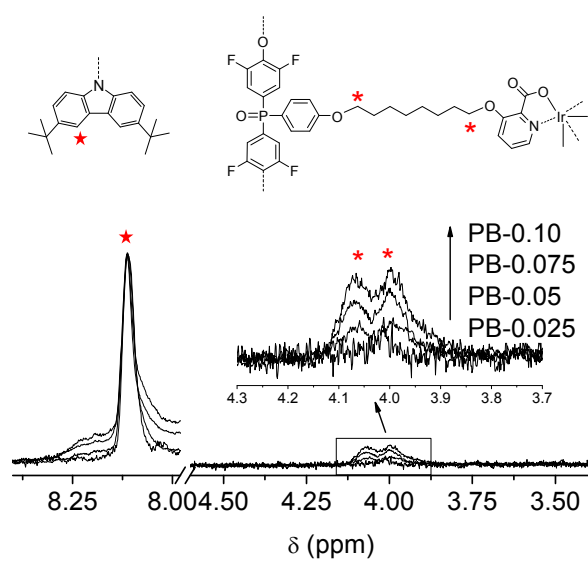
**Figure S1.** Comparison of the photoluminescent spectra (PL) (a) and the electroluminescent spectra (EL) (b) of polymer PB'-0.05 and the corresponding physical blend which is composed of 5 mol % Flrpic mixed with PCzPO. In PL spectrum, PB'-0.05 exhibits a bathochromic shift of 11 nm relative to the physical blend, while in EL spectrum, an even larger bathochromic shift of 18 nm is observed.



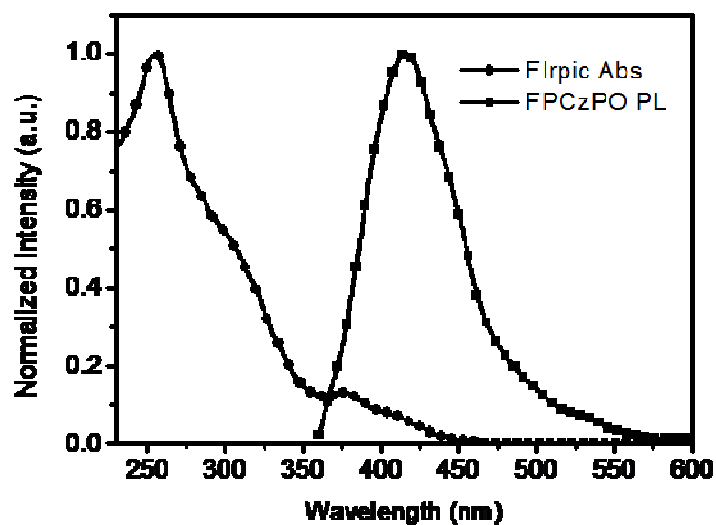
**Figure S2.**  $^{19}\text{F}$  NMR spectrum of FPCzPO using fluorobenzene as the internal standard.



**Figure S3.** Comparison of the phosphorescent spectra (a) and the electrochemical characteristics (b) of FPCzPO and PCzPO. Inset: relative energy levels of the materials.



**Figure S4.**  $^1\text{H}$  NMR spectra of PB-0.025 ~ PB-0.10.



**Figure S5.** Spectral overlap between the photoluminescent spectrum (PL) of FPCzPO in film and absorption spectrum (Abs) of FIrpic in dichloromethane.

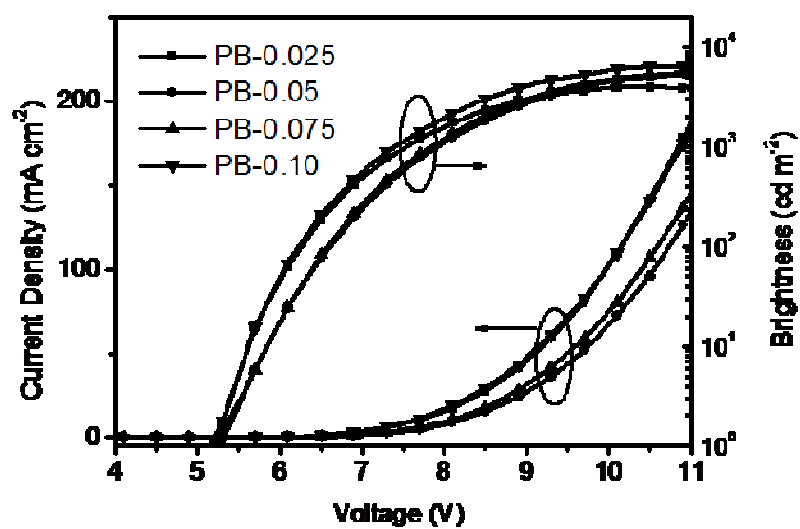


Figure S6. The current density and brightness versus voltage curves of the light-emitting devices.



**Table S1.** Properties of the polymers.

Polymer	Mn <sup>[a]</sup>	PDI <sup>[b]</sup>	Td <sup>[c]</sup>	Ir-complex loading (mol%)	
				Feed ratio	Calculated
FPCzPO	7, 800	1.64	493	---	---
PB-0.025	7, 500	1.73	393	0.025	0.018
PB-0.05	7, 700	1.70	382	0.05	0.042
PB-0.075	7, 600	1.68	383	0.075	0.070
PB-0.10	7, 800	1.67	379	0.10	0.090

[a] Number-average molecular weight, [b] Polydispersity index, [c] Decomposition temperature.

### Reference

- [1] a) T.-H. Kwon, M. K. Kim, J. Kwon, D.-Y. Shin, S. J. Park, C.-L. Lee, J.-J. Kim, J.-I. Hong, *Chem. Mater.* **2007**, *19*, 3673-3680; b) S. Shao, J. Ding, T. Ye, Z. Xie, L. Wang, X. Jing, F. Wang, *Adv. Mater.* **2011**, *23*, 3570-3574.
- [2] Here, similarly hereinafter, only the signals of the –CH<sub>2</sub>O– groups are given for clarity.