

Supplemental Information

General Procedure for the Suzuki Coupling Polymerization. To a stirred mixture of 9,9-di-n-hexylfluorene-2,7-bisboronate (1 equiv.), dibromoarene (1.05 equiv.), tetrakis-(triphenylphosphine)palladium (1 wt %) and Alquat 336 (10 wt %) in toluene (10 mL) under nitrogen was added a solution of (3.3 equiv.) 2M aqueous potassium carbonate. The mixture was heated to reflux for 3 days. The polymerization was end-capped with phenylboronic acid for 6 h, followed by bromobenzene for another 6h. The reaction mixture was cooled, added dropwise into a methanol/water (2:1 v/v) solution. The precipitated polymer fibers were collected by filtration. The crude polymer was further purified by dissolving into THF, and re-precipitated in methanol for several times.

PF-CNP(3:1). The general procedure described above was followed using 9,9-di-n-hexylfluorene-2,7-bisboronate (237 mg, 0.5 mmol), 9,9-di-n-hexylfluorene-2,7-dibromide (129 mg, 0.2625 mmol) and 1,4-dibromo-2,5-dicyanobenzene (75 mg, 0.2625 mmol) in the presence of tetrakis-(triphenylphosphine)palladium (2.4 mg), Alquat 336 (24 mg) and K_2CO_3 (0.8 mL). Yield: 229 mg (78 %). 1H NMR (300 MHz, $CDCl_3$) δ 0.79 (t, J = 6.6 Hz, 18H), 1.15 (b, 48H), 2.19 (s, 12H), 7.81-7.64 (m, 12H), 7.99-7.84 (m, 6H), 8.08 (s, 2 H). Anal. Calcd for $C_{83}H_{98}N_2$: C, 88.72; H, 8.79; N, 2.49. Found: C, 88.87; H, 8.77; N, 2.20.

PF-CNP(1:1). The general procedure described above was followed using 9,9-di-n-hexylfluorene-2,7-bisboronate (190 mg, 0.4 mmol) and 1,4-dibromo-2,5-dicyanobenzene (109 mg, 0.38 mmol) in the presence of tetrakis-(triphenylphosphine)palladium (2 mg), Alquat 336 (20 mg) and K_2CO_3 (0.6 mL). Yield: 170 mg (97 %). 1H NMR (300 MHz, $CDCl_3$) δ 0.79 (t, J = 6.6 Hz, 6H), 1.12 (b, 16H), 1.55 (s, 4H), 7.68-7.63 (m, 4H), 7.98-7.94 (m, 2H), 8.22 (s, 2 H). Anal. Calcd for $C_{33}H_{34}N_2$: C, 86.42; H, 7.47; N, 6.11. Found: C, 86.69; H, 7.64; N, 6.01.

UV-Vis absorption spectra of the polymer films were measured using a Perkin-Elmer Lambda-9 UV/VIS/NIR spectrophotometer. PL and EL spectra were recorded using an Oriel InstaSpec IV CCD camera. The thickness of the films was measured on a Sloan Dektak 3030 surface profilometer. Cyclic voltammetry (CV) was conducted at room temperature in a typical three-electrode cell with a working electrode (ITO glass), a reference electrode (Ag/Ag^+ , externally referenced against Fc/Fc^+ , 0.12 V), and a counter electrode (Pt gauze) under a nitrogen atmosphere at a sweeping rate of 100 mV/s (CV-50W Voltammetric Analyzer, BAS). CV measurements for polymer films were done in an electrolyte solution of 0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile.

The light-emitting devices were fabricated on ITO substrates that had been ultrasonicated sequentially in detergent, de-ionized water, isopropanol and acetone, and had been treated with O_2 plasma for 10 min before use. All the evaporation of the metal electrodes was carried out in a vacuum evaporator inside an argon atmosphere dry box. For electron-only devices, a 60-nm-thick layer of Al was evaporated on top of the ITO substrate. The substrate was then moved out of the dry box and a layer of the copolymer spin-coated onto the substrate immediately. The copolymer layer was spin-coated from their toluene solutions (10~12 mg/mL) at 1600-2000 rpm. The samples were then moved into the dry box again for cathode evaporation. For LED devices, a layer of PEDOT (Bayer Corp) was spin-coated at a spin rate of 4000 rpm from its water solution (1.3 wt %) onto the ITO substrates and cured at 160 °C for 10 min under nitrogen. The thickness is about 35~40 nm. Then a layer of copolymer was spin-coated. For the hole-only devices, the copolymer layer was directly spin-coated onto the precleaned ITO substrate. The samples were then transferred into a vacuum evaporator inside an argon atmosphere dry box. For LED and electron-only devices, a layer of 30-nm-thick calcium (Ca) was vacuum deposited

at below 1×10^{-6} Torr through a mask, and another protecting layer of 120-nm-thick silver (Ag) was vacuum deposited. For hole-only devices, a layer of 100-nm-thick of Au was deposited. The active device area was about 8 mm^2 . All device testing was carried out in air at room temperature. Current-voltage characteristics were measured on a Hewlett Packard 4155B semiconductor parameter analyzer. The power of EL emission was measured using a Newport 2835-C multi-function optical meter. Photometric units (cd/m^2) were calculated using the forward output power and the EL spectra of the devices, assuming Lambertian distribution of the EL emission.