

Supporting Information

Highly Reproducible Organic Field-Effect Transistor from Pseudo 3-Dimensional Triphenylamine-Based Amorphous Conjugated Copolymer

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Experimental Section

Materials and Instruments

All starting materials were purchased either from Aldrich or Acros and used without further purification. All solvents are ACS grade unless otherwise noted. Anhydrous THF was obtained by distillation from sodium/benzophenone prior to use. Anhydrous toluene was used as received. 3,6-dithien-2-yl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (**DTDPP**),¹ 2-decyl-tetradecylbromide,² and *N*-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline³ were prepared according to established literature procedures. ¹H NMR and ¹³C NMR spectra were recorded on a VNMRS 600 (Varian, USA) spectrophotometer using CDCl₃ as solvent and tetramethylsilane (TMS) as the internal standard and MALDI-MS spectra were obtained from Ultraflex III (Bruker, Germany). UV-Vis spectra were taken on Cary 5000 (Varian USA) spectrophotometer. Number-average (M_n) and weight average (M_w) molecular weights, and polydispersity index (PDI) of the polymer products were determined by gel permeation chromatography (GPC) with Agilent 1200 HPLC Chemstation using a series of mono disperse polystyrene as

standards in THF (HPLC grade) at 308 K. Cyclic voltammetry (CV) measurements were performed on Solartron SI 1287 with a three-electrode cell in a 0.1 M tetra-*n*-butylammonium hexafluorophosphate (*n*-Bu₄NPF₆) solution in acetonitrile at a scan rate of 50 mV/s at room temperature under argon. A silver wire, a platinum wire and a platinum disk were used as the reference electrode, counter electrode and working electrode respectively. The Ag/Ag⁺ reference electrode was calibrated using a ferrocene/ferrocenium redox couple as an external standard, whose oxidation potential is set at -4.8 eV with respect to zero vacuum level. The HOMO energy levels were obtained from the equation $\text{HOMO (eV)} = -(E_{(\text{ox})}^{\text{onset}} - E_{(\text{ferrocene})}^{\text{onset}} + 4.8)$. The LUMO levels of polymers were obtained from the equation $\text{LUMO (eV)} = -(E_{(\text{red})}^{\text{onset}} - E_{(\text{ferrocene})}^{\text{onset}} + 4.8)$.

OFET device Preparation and Measurement: All p-type OFETs were fabricated on heavily doped n-type silicon (Si) wafers each covered with a thermally grown silicon dioxide (SiO₂) layer with thickness of 200 nm. The doped Si wafer acts as a gate electrode, and the SiO₂ layer functions as the gate insulator. The active layer was deposited by spin-coating at 2500 rpm. All solutions were prepared at 0.5 wt.% concentration in chlorobenzene. The thickness of the deposited films was about 60 nm. Prior to vapor-deposition of source-drain electrodes, the films were dried on a hot plate stabilized at 80 °C for 30 minutes. All fabrication processes were carried out in a glove box filled with N₂. Source and drain electrodes using Au were deposited by thermal evaporation using a shadow mask. The thickness of source and drain electrodes was 50 nm. Channel length (L) and channel width (W) was 50 μm and 1.5 mm, respectively. All OFET devices were made in the top contact geometry. Electrical characterization was performed using a Keithley semiconductor parametric analyzer (Keithley 4200) under N₂ atmosphere. The electron mobility (μ) was determined using the following equation in the saturation regime;

$$I_{ds} = (WC_i/2L) \times \mu \times (V_{gs} - V_T)^2,$$

where C_i is the capacitance per unit area of the SiO₂ dielectric ($C_i=15$ nF/cm²), V_T is the threshold voltage.

Synthesis of 3,6-Dithien-2-yl-2,5-di(2-decyltetradecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione

A solution of 2-decyltetradecylbromide 9.1 g (21.7 mmol) in anhydrous DMF (20 mL) was added dropwise to a mixture of 3,6-dithien-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (2.8 g, 9.42 mmol) and K₂CO₃ (3.0 g, 21.6 mmol) in anhydrous DMF (55 mL). The mixture was maintained at 120 °C overnight. The reaction was cooled to room temperature and poured into water (100 mL). The mixture was extracted into CHCl₃, washed with brine, and dried over MgSO₄. The solvent was evaporated under reduced pressure. The crude product was purified by chromatography on silica with 0-30% dichloromethane in hexane as eluent. Isolated yield = 5.1 g (55 %) as a thick viscous dark purplish oil. ¹H NMR (CDCl₃, 600 MHz): δ ppm 8.88 (d, $J = 3.85$, 2H), 7.62 (d, $J = 4.9$, 2H), 7.27 (d, $J = 8.89$, 2H), 4.03 (d, $J = 7.71$ 4H), 1.91 (m, 2H), 1.30-1.21 (m, 80H), 0.89-0.87 (m, 12H). ¹³C NMR (CDCl₃, 150 MHz): δ ppm 161.75, 140.43, 135.19, 130.44, 129.84, 120.38, 107.95, 46.23, 37.75, 31.93, 29.69, 29.67, 29.65, 29.38, 29.37, 29.36, 26.22, 22.70, 22.69, 14.13. MALDI-TOF MS (m/z) 973.59 (M⁺). Anal. Calcd for C₆₂H₁₀₄N₂O₂S₂: C, 76.48; H, 10.77; N, 2.88. Found: C, 77.04; H, 10.97; N, 2.96.

Synthesis of 3,6-Di(2-bromothien-5-yl)-2,5-di(2-decyltetradecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione

N-Bromosuccinimide (NBS) (1.26 g, 7.08 mmol) was added slowly to a solution of **DTDPP** (3g, 3.08 mmol) in CHCl₃ (100 mL). The solution was protected from light and stirred at room temperature for 48 h. The reaction mixture was poured into water (100 mL) and extracted into CHCl₃. The organic layer was dried over MgSO₄ and the solvent was evaporated under reduced pressure. The crude product was purified by chromatography on silica with 0-50% dichloromethane in hexane as eluent. Isolated yield = 1.8 g (53%) as a

thick viscous dark purplish oil. ^1H NMR(CDCl_3 , 600 MHz): δ ppm 8.62 (d, $J = 4.18$, 2H), 7.21 (d, $J = 4.17$, 2H), 3.91 (d, $J = 7.71$, 4H), 1.87 (m, 2H), 1.29-1.21 (m, 80H), 0.89-0.86 (m, 12H). ^{13}C NMR (CDCl_3 , 150 MHz): δ ppm 161.38, 139.39, 135.31, 131.42, 131.17, 118.95, 108.01, 46.36, 37.77, 31.94, 30.00, 29.70, 29.68, 29.66, 29.57, 29.39, 26.20, 22.70, 14.13. MALDI-TOF MS(m/z) 1131.45(M^+). Anal. Calcd for $\text{C}_{62}\text{H}_{102}\text{Br}_2\text{N}_2\text{O}_2\text{S}_2$: C, 65.82; H, 9.09; N, 2.48. Found: C, 68.14; H, 9.36; N, 2.43.

Synthesis of poly[triphenylamine-4,4'-diyl-co-3,6-dithien-2-yl-2,5-di(2-decyltetradecanyl)-pyrrolo[3,4-c]pyrrole-1,4-dione-5',5''-diyl] (PTPA-co-DTDPP)

N-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (86 mg, 0.17 mmol), dibromide **1** (200 mg, 0.17 mmol), Aliquat[®] 336 (8 mg, 13 mol %), 2.0 M aqueous K_2CO_3 (7 mL), and toluene (10 mL) were taken together in a Schlenk flask and purged with argon for 15 minutes. To this solution, tetrakis(triphenylphosphine)palladium (10 mg, 8.6 μmol) was added and the reaction mixture was heated at 95 °C under vigorous stirring for 72 h. The reaction was poured into a mixture of methanol and 2.0 M HCl (1:1, 300 mL) and filtered. The collected dark solid was redissolved in chlorobenzene (10 mL) and added dropwise to methanol (200 mL). The resulting solid was filtered off and subjected to sequential Soxhlet extraction with methanol (1 d), acetone (1 d) and hexane (1 d) to remove low molecular weight fraction of the materials. The residue was extracted with chlorobenzene to give dark purplish product after precipitating again from methanol and drying *in vacuo*. Isolated yield of polymer **PTPA-co-DTDPP** = 150 mg (75%). GPC analysis $M_n = 14.94$ kg/mol, $M_w = 20.76$ kg/mol, and PDI = 1.39 (against PS standard). ^1H NMR(CDCl_3 , 600 MHz): δ ppm 8.97 (br, 2H), 7.56-7.58 (br, 4H), 7.4-7.39 (br, 2H), 7.35-7.32 (br, 2H), 7.19-7.17 (br, 2H), 7.13-7.14 (br, 4H), 4.07 (br, 4H), 2.00 (br, 2H), 1.34-1.21 (br, 80H), 0.88-0.83 (12H). Anal. Calcd for $\text{C}_{68}\text{H}_{105}\text{BrN}_4\text{O}_2\text{S}_3$: C, 68.82; H, 8.92; N, 4.72. Found: C, 68.61; H, 9.19; N, 5.01.

References

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