

## Supporting Information

### A regioregular terpolymer comprising two electron-deficient and one electron-rich unit for ultra small band gap solar cells

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The supporting information contains the experimental part, synthesis route for monomers and polymers (Scheme S1), TGA and DSC of the polymers (Fig. S1), absorption spectra of the polymers in chloroform solution (Fig. S2).

#### Materials and Measurements

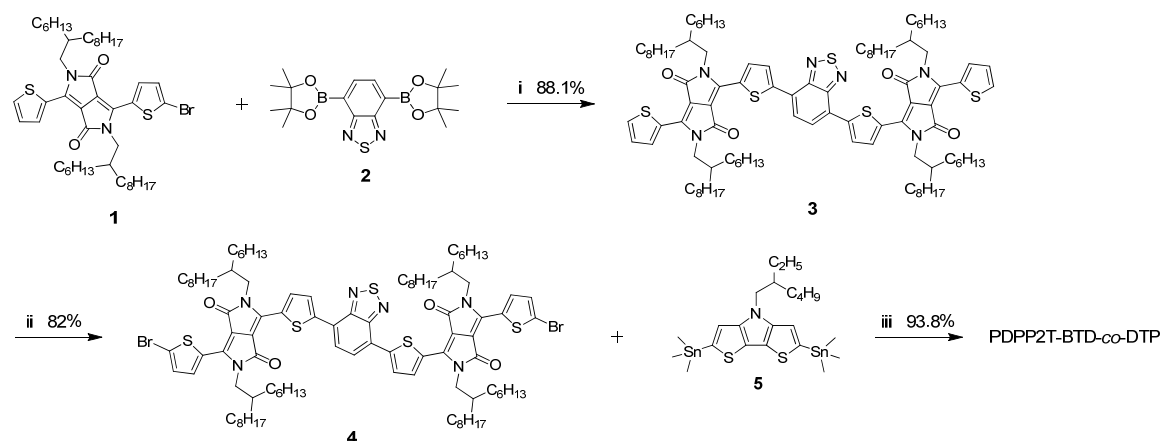
All synthetic procedures were performed under argon atmosphere. Commercial chemicals were used as received. Dry solvents were distilled over 4 Å molecular sieves. [70]PCBM (purity ~95%) was purchased from Solenne BV. 3-(5-Bromothiophen-2-yl)-2,5-bis(2-hexyldecyl)-6-(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**1**),<sup>1</sup> polymer PDPP2T-BT<sup>2</sup> and PDPP2T-DTP<sup>3</sup> were synthesized according to literature procedures. 4,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*c*][1,2,5]thiadiazole (**2**) was purchased from Aldrich Chemical Co. and recrystallized from heptanes before use in the reactions.

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded at 400 MHz and 100 MHz on a VARIAN mercury spectrometer with CDCl<sub>3</sub> as the solvent and tetramethylsilane (TMS) as the internal standard. Molecular weight of PDPP2T-BT was determined

with GPC at 140 °C on a PL-GPC 220 system using a PL-GEL 10 $\mu$ m MIXED-B column and *o*-DCB as the eluent against polystyrene standards. Low concentration of 0.06 mg mL<sup>-1</sup> polymer in *o*-DCB was applied to reduce aggregation. Electronic spectra were recorded on a Perkin Elmer Lambda 900 UV/vis/nearIR spectrophotometer. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on TA2100 and Perkin-Elmer Diamond DSC instrument, respectively, under a nitrogen atmosphere at a heating rate of 10 °C/min to record TGA and DSC curves. TEM was performed on a Tecnai G<sup>2</sup> Sphera TEM (FEI) operated at 200 kV.

Photovoltaic devices were made by spin coating poly(ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Clevios P, VP AI 4083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates (14  $\Omega$  per square) (Naranjo Substrates). The photoactive layer were deposited by spin coating a chloroform solution containing the polymers and [70]PCBM with 1:2 (w/w) ratio and the appropriate amount of *o*-DCB or 1-chloronaphthalene (1-CN). LiF (1 nm) and Al (100 nm) were deposited by vacuum evaporation at  $\sim 2 \times 10^{-7}$  mbar as the back electrode. The active area of the cells was 0.09 or 0.16 cm<sup>2</sup> and no size dependence was found between these two dimensions.  $J-V$  characteristics were measured under  $\sim 100$  mW cm<sup>-2</sup> white light from a tungsten-halogen lamp filtered by a Schott GG385 UV filter and a Hoya LB 120 daylight filter, using a Keithley 2400 source meter. Short circuit currents under AM1.5G conditions were estimated from the spectral response and convolution with the solar spectrum. The spectral response was measured under simulated 1 sun operation conditions using bias light from a 532 nm solid state laser (Edmund Optics). Light from a 50 W tungsten halogen lamp (Osram64610) was used as probe light and modulated with a mechanical chopper before passing the monochromator (Oriel, Cornerstone 130) to select the wavelength. The response was recorded as the voltage over a 50  $\Omega$  resistance, using a lock-in amplifier (Stanford Research Systems SR 830). A calibrated Si cell was used as reference. The device was kept behind a quartz window in a nitrogen filled container. The thickness of the active layers in the photovoltaic devices was measured on a Veeco Dektak 150 profilometer.

## Synthesis

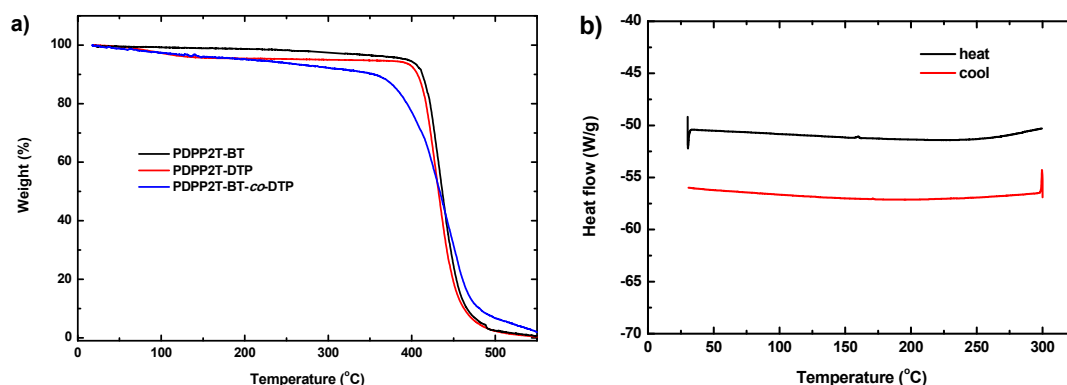


**Scheme S1** Synthesis route of DPP based monomers and polymerization for these polymers. (i) Pd(PPh<sub>3</sub>)<sub>4</sub>/K<sub>2</sub>CO<sub>3</sub> (aq)/Aliquat 336 in toluene at 80 °C. (ii) NBS in CHCl<sub>3</sub>. (iii) Stille polymerization by using Pd<sub>2</sub>(dba)<sub>3</sub>/PPh<sub>3</sub> in toluene/DMF (10:1, v/v) at 115 °C.

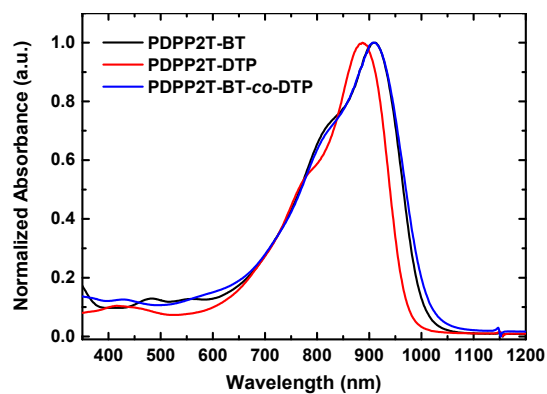
**Compound 3.** To a degassed mixture of 3-(5-bromothiophen-2-yl)-2,5-bis(2-hexyldecyl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (**1**) (0.66 g, 0.8 mmol), 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*c*][1,2,5]thiadiazole (**2**) (0.15 g, 0.39 mmol), 2 M K<sub>2</sub>CO<sub>3</sub> in H<sub>2</sub>O (2 mL), toluene (10 mL) and Aliquat 336 (0.2 mL), was added tetrakis(triphenylphosphine)palladium(0) (46.26 mg, 40 μmol). The mixture was stirred at 80 °C for 24 h. The resulting mixture was cooled to room temperature after which it was poured out in chloroform, washed by water and brine, and dried by evaporation. The resulting solid was subjected to column chromatography (silica, eluent heptane/CHCl<sub>3</sub>, 25%/75%) and then crystallized from Acetone/Toluene (20 mL/2 mL) at 0 °C to afford **3** (0.56 g, 88.1%). <sup>1</sup>H NMR δ (ppm): 9.09 (d, 2H), 8.92 (m, 2H), 8.18 (m, 2H), 8.0 (m, 2H), 7.62 (m, 2H), 7.26 (m, 2H), 4.10 (m, 8H), 2.0 (m, 4H), 1.45 – 1.1 (m, 96H), 0.86 (m, 24H). <sup>13</sup>C NMR δ (ppm): 161.71, 161.64, 152.28, 143.85, 140.35, 139.91, 136.25, 135.41, 131.62, 130.58, 129.85, 128.45, 128.12, 125.85, 125.71, 108.69, 108.27, 46.42, 46.28, 38.15, 37.76, 31.87, 31.86, 31.83, 31.76, 31.18, 30.02, 29.80, 29.68, 29.57, 29.50, 29.31, 29.29, 26.32, 26.30, 26.20, 26.17, 22.65, 22.64, 22.62, 14.10, 14.08. MS (MALDI): Calcd, 1630.55; found, 1630.03 (M<sup>+</sup>).

**Compound 4.** To a degassed solution of **3** (0.24 g, 0.15 mmol), in chloroform (15 mL) at 0 °C, *N*-bromosuccinimide (53.14 mg, 0.30 mmol) was added in portions in 10 min, and the reaction mixture was stirred in another 2 hours at room temperature. After this the mixture was poured out in chloroform, washed with water and brine, and evaporated. The resulting solid was subjected to column chromatography (silica, eluent heptane/CHCl<sub>3</sub>, 25%/75%) and then crystallized from Acetone/Toluene (20 mL/4 mL) at 0 °C to afford **4** (0.22 g, 82%). <sup>1</sup>H NMR  $\delta$  (ppm): 9.05 (m, 2H), 8.65 (m, 2H), 8.08 (m, 2H), 7.87 (m, 2H), 7.16 (m, 2H), 4.08 (m, 4H), 3.92 (m, 4H), 2.0 (m, 2H), 1.9 (m, 2H), 1.45 – 1.1 (m, 96H), 0.86 (m, 24H). MS (MALDI): Calcd, 1788.35; found, 1788.85 (M<sup>+</sup>).

**PDPP2T-BT-co-DTP.** To a degassed solution of monomer **4** (107.42 mg, 0.060 mmol), 4-(2-ethylhexyl)-2,6-bis(trimethylstannyl)-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrole (**5**) (37.07 mg, 0.060 mmol) in toluene (2 mL) and DMF (0.2 mL), tris(dibenzylideneacetone)dipalladium (0) (1.65 mg, 1.8  $\mu$ mol) and triphenylphosphine (1.89 mg, 7.2  $\mu$ mol) were added. The mixture was stirred at 115 °C for 16 h, after which it was precipitated in methanol and filter through a Soxhlet thimble. The polymer was extracted with acetone, hexane, dichloromethane and then dissolved in 1,1,2,2-tetrachloroethane (TCE) (80 mL) at 140 °C, which was then precipitated into acetone. Finally the resulting polymer can be solubilized in chloroform for device fabrication. Yield: 108 mg (93.8%) as a dark solid.



**Fig. S1** (a) TGA curves of the DPP-polymers. 5% weight loss occurs at 395 °C for PDPP2T-BT, 300 °C for PDPP2T-DTP, and 207 °C for PDPP2T-BT-*co*-DTP. 10% weight loss occurs at 413 °C for PDPP2T-BT, 406 °C for PDPP2T-DTP, and 354 °C for PDPP2T-BT-*co*-DTP (b) DSC curve of PDPP2T-BT-*co*-DTP.



**Fig. S2** Electronic absorption spectra of the DPP polymers in CHCl<sub>3</sub> solution.

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