Random Benzotrithiophene-Based Donor-Acceptor Copolymers for Efficient Organic Photovoltaic Devices

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Supporting Information

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Experimental Section

All chemicals were purchased from commercial suppliers unless otherwise specified. ¹H NMR spectra were recorded on a BRUKER DRX400 spectrometer in CDCl₃ solution at 323 K unless otherwise noted. Number-average (M_n) and weight-average (M_w) molecular weights were determined with an Agilent Technologies 1200 series GPC in chlorobenzene at 80 °C, using two PL mixed B columns in series, and calibrated against narrow polydispersity polystyrene standards. UV-Vis absorption spectra were recorded on a UV-1601 Shimadzu UV-Vis spectrometer. Photo Electron Spectroscopy in Air (PESA) measurements were recorded with a Riken Keiki AC-2 PESA spectrometer with a power setting of 5 nW and a

power number of 0.5. AFM images were obtained with a Picoscan PicoSPM LE scanning probe in tapping mode.

BHJ solar cells were fabricated with a conventional device configuration (ITO/PEDOT:PSS/polymer:PC₇₁BM/LiF/Al) and tested under simulated 100 mW/cm² AM1.5G illumination (all data summarized in Table 3). Devices were in all cases prepared with a polymer : $PC_{71}BM$ blend ratio of 1 : 2 and solution processed from a chloroform : *o*-dichlorobenzene (4 : 1) solvent mixture.

2,8-Bis(trimethylstannyl)-5-hexadecylbenzo[1,2-b:3,4-b':5,6-d'']trithiophene (C16-BTTditin). 5-Hexadecylbenzo[1,2-b:3,4-b':5,6-d'']trithiophene (1.3 g, 2.8 mmol) was dissolved in 200 mL of anhydrous THF and cooled to -78° C. A 2.5 M solution of n-butyl lithium in hexanes (2.8 mL, 7.0 mmol) was added slowly to the reaction mixture. After two hours of stirring at low temperature, trimethyltin chloride (7.2 mL, 7.2 mmol) in a 1 M THF solution was added and the reaction mixture was allowed to warm slowly to room temperature over night. The bright yellow solution was diluted with hexane and quenched with water. The organic layer was separated and dried with sodium sulphate. After solvent evaporation, a pale yellow oil was obtained, which was further purified by recycling gel permeation chromatography to yield pure 2,8-bis(trimethylstannyl)-5-hexadecylbenzo[1,2-b:3,4-b':5,6d'']trithiophene as a colourless oil (842 mg, 1.06 mmol, 38% yield). ¹H NMR (400 MHz, 298 K, (CD₃)₂CO): δ 7.99 (s, 1H), 7.73 (s, 1 H), 7.67 (s, 1H), 3.02 (t, 2H), 1.81 (quint, 2H), 1.47 – 1.21 (m, 26H), 0.87 (t, 3H), 0.49 (s, 1H), 0.48 (s, 1H). ¹³C NMR (100 MHz, 298 K, (CD₃)₂CO): δ 145.90, 140.64, 139.40, 134.67, 133.62, 133.49, 132.17, 131.18, 131.07, 121.14, 206.26, 32.80, 32.42, 31.36, 30.54, 30.48, 29.88, 23.50, 15.77, 14.54, -8.01.

BTT-DPP. A degassed solution of C16-BTT-ditin (141.60 mg, 0.17780 mmol), C8C12-DPPdibromide (181.19 mg, 0.17778 mmol), Pd₂(dba)₃ (3.51 mg, 0.004 mmol) and P(o-tol)₃ (4.42 mg, 0.015 mmol) in anhydrous chlorobenzene (2.5 mL) was stirred at 180°C for 30 minutes in a microwave reactor. The crude polymer was end-capped with bromobenzene (1.2 μ L) and trimethyl(phenyl)tin (0.7 μ L) and subsequently precipitated into methanol. Using a Soxhlet extractor, the crude polymer was washed with acetone and hexane and subsequently extracted with chloroform and precipitated into methanol to afford the title compound (126 mg, 53% yield) as a black solid. GPC: M_n = 25.8 kDa, M_w = 65.7 kDa, PDI = 2.55. ¹H NMR: δ (ppm) 9.0 (br s, 2H), 7.3 (br s, 5H), 4.0 (br s, 4H), 3.2 (br s, 2H), 1.3 (br m, 109H). **P1**. Following the procedure for **BTT-DPP** using C16-BTT-ditin (65.07 mg, 0.08170 mmol), C8C12-DPP-dibromide (62.46 mg, 0.06128 mmol) and BT-dibromide (6.02 mg, 0.02048 mmol) to afford **P1** (54 mg, 57% yield) as a black solid. GPC: $M_n = 108$ kDa, $M_w = 173$ kDa, PDI = 1.60. ¹H NMR: δ (ppm) 9.0 (br s), 7.3 (br s), 3.2 (br s), 1.3 (br m).

P2. Following the procedure for **BTT-DPP** using C16-BTT-ditin (66.30 mg, 0.08325 mmol), C8C12-DPP-dibromide (63.63 mg, 0.06243 mmol) and C8-TPD-dibromide (8.81 mg, 0.02082 mmol) to afford **P2** (86 mg, 88% yield) as a black solid. GPC: $M_n = 71$ kDa, $M_w = 100$ kDa, PDI = 1.41. ¹H NMR: δ (ppm) 9.0 (br s), 7.3 (br s), 3.2 (br s), 1.3 (br m).

P3. Following the procedure for **BTT-DPP** using C16-BTT-ditin (94.87 mg, 0.1191 mmol), C8C12-DPP-dibromide (91.09 mg, 0.08937 mmol) and C8C8-BTT-dibromide (19.17 mg, 0.02983 mmol) to afford **P3** (63 mg, 43% yield) as a black solid. GPC: $M_n = 148$ kDa, $M_w = 279$ kDa, PDI = 1.89. ¹H NMR: δ (ppm) 9.0 (br s), 7.3 (br s), 3.2 (br s), 1.3 (br m).

P4. Following the procedure for **BTT-DPP** using C16-BTT-ditin (73.37 mg, 0.09213 mmol), C8C12-DPP-dibromide (46.96 mg, 0.04608 mmol) and C8C8-BTT-dibromide (29.58 mg, 0.04603 mmol) to afford **P4** (65 mg, 62% yield) as a black solid. GPC: $M_n = 134$ kDa, $M_w = 243$ kDa, PDI = 1.81. ¹H NMR: δ (ppm) 9.0 (br s), 7.3 (br s), 3.2 (br s), 1.3 (br m).



Figure S1 Thermal Gravimetric Analysis (TGA) traces recorded on a Pyris 1 Thermogravimetric Analyzer from Perkin Elmer at a rate of 10°C/min under nitrogen.



Figure S2 Differential Scanning Calorimetry (DSC) traces for the second heating and cooling cycle recorded on a Q20 Differential Scanning Calorimeter from TA Instruments with a heating/cooling rate of 20°C/min.



Figure S3 Optical absorption spectra of all polymer:PC₇₁BM blends (1:2) spin-cast from chloroform:*o*-dichlorobenzene (4:1).



Figure S4 AFM (tapping-mode, 2×2 μm) of polymer:PC₇₁BM (1:2) blends spin-cast from chloroform:*o*-DCB (4:1). RMS surface roughnesses are 1.26 nm (BTT-DPP), 1.05 nm (P1), 2.56 nm (P2), 0.67 nm (P3), and 0.85 nm (P4).