Synthesis of Novel Thieno[3,2-*b*]thienobis(silolothiophene) Based Low Bandgap Polymers for Organic Photovoltaics

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Supporting Information

Experimental Details

All chemicals were purchased from commercial suppliers unless otherwise specified. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 spectrometer in $CDCl_3$ solution at 298 K unless, polymer ^{1}H NMR were recorded on a Bruker DRX400 in *o*-dichlorobenzene-d_4 at 313 K. 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. Electrospray and Electron Ionisation mass spectrometry were performed with a Micromass LCT Premier, respectively a Micromass AutoSpec Premier. 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. DSC experiments were carried out with a TA Instruments DSC Q20 and TGA plots were obtained with a Perkin Elmer Pyris 1 TGA.

All organic photovoltaic devices have a conventional device architecture, ITO/PEDOT:PSS/Polymer: $PC_{71}BM$/Ca/Al. The precoated ITO glass substrates were cleaned with acetone and isopropyl alcohol under sonification, followed by drying and oxygen plasma treatment. A 30 nm layer of PEDOT:PSS was spin-coated onto the plasma-treated ITO substrate and baked at 150°C for 20 minutes. An 80 nm active layer consisting of a 1:3.5 blend of polymer and $PC_{71}BM$ (optimized blend ratio) dissolved in *o*-dichlorobenzene (ODCB) was spin-coated on the PEDOT:PSS layer and then Ca (30 nm)/Al (120 nm) cathode was finally deposited by thermal evaporation under high vacuum (10^{-6} mbar) through a shadow mask. The pixel size, defined by the spatial overlap of the ITO anode and Ca/Al cathode, was 0.045 cm^2. The device characteristics were obtained using a Xenon lamp at AM1.5 solar illumination (Oriel Instruments). Incident photon conversion efficiency (IPCE) measurements were made using a 100 W tungsten halogen lamp (Bentham IL1 with Bentham 605 stabilized current power supply) coupled to a monochromator with computer-controlled stepper motor (Bentham M300, 300 mm focal length, slit width 3.7 nm, 1800 lines/m grating) The photon flux of light incident on the samples was calibrated using a UV-enhanced silicon photodiode. A 590 nm long-pass glass filter was inserted into the beam at illumination wavelengths longer than 620 nm to remove light from second-order diffraction. Photocurrent was measured using a Keithley 2400 source meter; Measurement duration for a given wavelength was sufficient to ensure the current had stabilized (up to around 5 s under low or zero bias light conditions).

3,6-dibromo-2,5-diiodothieno[3,2-*b*]thiophene (2). To a stirred solution of 3,6-dibromothieno[3,2-*b*]thiophene (20 g, 67.1 mmol) dissolved in a solvent mixture of chloroform (900 mL) and acetic acid (500 mL) was added *N*-iodosuccinimide (68 g, 302 mmol) in several portions at room temperature. The mixture was stirred during 7 days before the reaction was quenched with 1 L of water, leading to the formation of a white suspension. The white solid was filtered off and washed with water, to yield the title compound in excellent purity (35.2 g, 63.9 mmol, 95% yield). ^{13}C NMR (100 MHz, DMSO-d_6): δ 141.68, 111.70, 84.77. HRMS (EI): *m/z* calcd for $C_6Br_2I_2S_2$ (M^+) 549.5877 found 549.5872.

3,6-dibromo-2,5-bis(3-bromothiophen-2-yl)thieno[3,2-*b*]thiophene (3). To an oven dried microwave vessel was added compound **2** (2.3 g, 4.2 mmol) and tetrakis (triphenylphosphine) palladium (0.242 g, 0.2 mmol) under argon atmosphere. An 0.5 M THF solution of (3-bromothiophen-2-yl)zinc (II) bromide (17.6 mL, 8.8 mmol) was added before the sealed microwave vial was heated for 30 seconds at 80°C, followed by 7 minutes at 100°C in a microwave reactor. After completion of reaction, the mixture was cooled to room temperature and quenched with 20 mL of water. The precipitate was filtered off and washed with water, acetone and diethyl ether. The title compound was recovered as a yellow solid (1.89 g, 3.1 mmol, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, J = 5.4 Hz, 2H), 7.13 (d, J = 5.4 Hz, 2H). No ^{13}C NMR could be recorded due to the low solubility of compound 3. MS: *m/z* calcd for $C_{14}H_4Br_4S_4$ (M+) 619.6, 621.6, 617.6, 623.6 found 619.5, 621.5, 617.5, 623.5.

(5,5'-(3,6-dibromothieno [3,2-*b*] thiophene-2,5-diyl) bis (4-bromothiophene-5,2-diyl))bis (trimethylsilane) (4). To an oven dried three neck flask was added **3** (8.5 g, 13.7 mmol) and anhydrous THF (800 mL). The solution was cooled to -60°C, before a 1.8 M solution of lithium diisopropylamide (20.0 mL, 35.6 mmol) was added dropwise. After the complete addition, the solution was stirred during 2 hours and slowly warmed -40°C. The reaction was cooled down to -60°C, before trimethylsilyl chloride (7.0 mL, 54.8 mmol) was added quickly. After the reaction was warmed to room temperature overnight, it was quenched with methanol (200 mL) and water (500 mL). After extracting the reaction mixture with diethyl ether, the organic phase was washed with 0.1 M hydrochloric acid and water. The solution was dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using a mixture of *n*-hexane and ethyl acetate (9:1) as eluent. The title compound was recovered as an orange solid (8.0 g, 10.5 mmol, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (s, 2H), 0.37 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5, 139.8, 137.4, 133.5, 131.4, 114.1, 104.8, -0.24. HRMS (EI): *m/z* calcd for $C_{20}H_{20}Br_4S_4Si_2$ (M+) 763.6679 found 763.6676.

4,4,9,9 tetraoctyl (2,7-bis (trimethylsilyl)) bis-silolo[2',3'-*d'*:4'',5''-*b''*] thieno [4,5-*b'*:2'',3''-*d*] thieno[3,2-*b*]thiophene (5). To an oven dried round bottom flask, *tert*-butyllithium in pentane (1.7 M) (40.4 mL, 68.7 mmol) was added to 80 ml of anhydrous THF and cooled down to -90°C. In a second flask compound **4** (6.4 g, 8.4 mmol) was dissolved in

160 ml of anhydrous THF and cooled down to -90°C. This solution was added dropwise to the *t*-butyllithium solution, maintaining the temperature below -85°C. After complete addition, the resulting dark red solution was stirred during one hour at low temperature. Dichlorobis(2-octyl)silane (9.3 mL, 26.8 mmol) in dry THF (10.0 ml) was added dropwise. The reaction mixture was stirred at same temperature for additional 4 hours, and then the temperature was raised to room temperature overnight. The reaction mixture was diluted with *n*-hexane and quenched by addition of 200 ml of saturated ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted twice with *n*-hexane. The combined organic layers were washed with brine and dried over sodium sulfate. After solvent evaporation, the crude product was purified by column chromatography on silica using *n*-hexane as eluent. Compound **5** was recovered as a bright yellow solid (2.5 g, 2.6 mmol, 31% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (s, 2H), 1.51 (m, 8H), 1.29 (bm, 40H), 0.99 (m, 8H), 0.88 (t, 12H), 0.35 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 149.6, 144.3, 142.3, 140.8, 136.6, 133.9, 33.4, 32.0, 29.4, 29.3, 24.4, 22.9, 14.3, 11.9, 0.30. HRMS (EI): *m/z* calcd for $C_{52}H_{88}S_4Si_4$ (M+) 952.4846 found 952.4841.

4,4,9,9 tetraoctyl (2,7-dibromo) bis-silolo[2',3'-*d'*:4'',5''-*b''*] thieno [4,5-*b'*:2'',3''-*d*] thieno[3,2-*b*]thiophene (6). Compound **5** (0.450 g, 0.5 mmol) was dissolved in 8 mL of anhydrous THF and cooled to -20°C. Recrystallized NBS (0.172 g, 1.0 mmol) was dissolved in 8 mL of dry THF and slowly added to the reaction mixture. The reaction was slowly warmed to 0°C and quenched by the addition of water after one hour, followed by an extraction with diethyl ether. The organic phase was dried over sodium sulphate and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography with *n*-hexane to yield the title compound as a yellow solid (0.382 g, 0.4 mmol, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02 (s, 2H), 1.44 (m, 8H), 1.26 (bm, 40H), 0.96 (m, 8H), 0.86 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 149.1, 144.0, 140.9, 132.6, 132.4, 111.0, 33.3, 32.0, 29.3, 29.2, 24.3, 22.8, 14.3, 11.7. MS: *m/z* calcd for $C_{46}H_{70}Br_2S_4Si_2$ (M+) 966, 968, 967, 969, 964, 970, 965 found 966, 968, 967, 969, 964, 965, 970.

4,4,9,9 tetraoctyl (2,7-bis(trimethylstannyl)) bis-silolo[2',3'-*d'*:4'',5''-*b''*] thieno [4,5-*b'*:2'',3''-*d*] thieno[3,2-*b*]thiophene (7). Compound **6** (1.6 g, 1.7 mmol) was dissolved in 70 mL of anhydrous THF and cooled to -90°C before a 1.7 M *tert*-butyllithium solution in pentane (4.1 mL, 7.0 mmol) was added. After 30 minutes at low temperature, a 1 M THF solution of chlorotrimethylstannane (3.8 mL, 3.8 mmol) was added to the reaction. The reaction mixture was slowly warmed to room temperature. After two hours the reactive mixture was diluted with *n*-hexane and quenched by the addition of water. After separating the organic layer, the aqueous layer was extracted several times with *n*-hexane. The combined organic layers were dried over sodium sulphate and the solvent was removed by rotary evaporation. The crude product was further purified by means of recycling GPC and compound **7** was recovered as dark yellow solid (1.6 g, 1.4 mmol, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (s, 2H), 1.55 (m, 8H), 1.32 (bm, 40H), 1.01 (m, 8H), 0.91 (t, 12H), 0.44 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 149.6, 144.1, 142.0, 137.9, 137.7, 133.3, 33.5, 32.0, 29.4, 29.3, 24.4, 22.8, 14.3, 11.9, 7.9. MS: *m/z* calcd for $C_{52}H_{88}S_4Si_2Sn_2$ (M+) 1134, 1136, 1135, 1133, 1132, 1137, 1138 found 1134, 1136, 1135, 1133, 1132, 1137, 1138.

Polymerization A. A microwave vial was charged with monomer **7** (0.200 g, 0.18 mmol), 1.0 eq. of dibrominated monomer and 5 mol% of tetrakis(triphenylphosphine) palladium (0). The vial was sealed and 1 mL of *o*-xylene was added. The reaction mixture was degassed with argon during 30 minutes and submitted to the following temperature scheme in the microwave reactor: 5 minutes at 120°C, 5 minutes at 140°C, 5 minutes at 160°C and 40 minutes at 170°C. The reaction mixture was cooled down to room temperature and 0.1 eq. of bromobenzene was added in one portion by syringe. The mixture was resubmitted to the microwave reactor, 1 minute at 100°C, 1 minute at 120°C, 2 minutes at 140°C and 5 minutes at 160°C. Once the polymeric solution was cooled down, 0.1 eq. of trimethyl(phenyl) stannane was added by syringe. The reaction mixture was subjected on last time to the previously mentioned temperature scheme to finalize the end-capping reaction. After reaction, the crude polymer was precipitated in methanol and then further purified by Soxhlet extractions with acetone, *n*-hexane and chloroform, each for 24 hours. Remaining palladium residues were removed by treating a polymeric chloroform solution with an aqueous sodium diethyldithiocarbamate solution for 2 hours at 50°C under vigorous stirring. Afterwards the organic phase was separated from the aqueous phase and washed several times with water. The polymeric solution was concentrated under reduced pressure and precipitated into cold methanol. The recovered polymer was dried under high vacuum for at least 24 hours.

Polymerization B. A 5 mL microwave vial was charged with monomer **7** (0.200 g, 0.18 mmol), 1.0 eq. of dibrominated monomer, 2 mol% of tris(dibenzylideneacetone)dipalladium (0) and 8 mol% of tri(*o*-tolyl) phosphine. The vial was sealed and chlorobenzene (0.7 mL) was added. The obtained solution was degassed with argon during 30 minutes. The vial was subjected to the following reaction conditions in the microwave reactor: 2 minutes at 100°C, 2 minutes at 120°C, 5 minutes at 140°C, 5 minutes at 160°C and 40 minutes at 170°C. The polymer was end-capped by addition of 0.1 eq. of bromobenzene before the reaction mixture was resubmitted to the microwave reactor, 1 minute at 100°C, 1 minute at 120°C, 2 minutes at 140°C and 5 minutes at 160°C. The polymeric solution was cooled down and 0.1 eq. of trimethyl(phenyl) stannane was added by syringe. The reaction vial was subjected to the previously mentioned temperature scheme to finalize the end-capping reaction. After reaction, the crude polymer was precipitated in methanol and then further purified by Soxhlet extractions with acetone, *n*-hexane and chloroform during 24 hours each. Remaining palladium residues were removed by treating a polymeric chloroform solution with an aqueous sodium diethyldithiocarbamate solution for 2 hours at 50°C under vigorous stirring. Afterwards the organic phase was separated from the aqueous phase and washed several times with water. The polymeric solution was concentrated under reduced pressure and precipitated into cold methanol. The polymer was filtered off and dried under high vacuum for at least 24 hours.

Si4T-BT. Polymerization A. Dark-blue solid (0.126 g, 0.14 mmol). $M_n = 19.0$ kg mol^{-1}, $M_w = 53.0$ kg mol^{-1}, PDI = 2.8. ^{1}H NMR (*o*-DCB-d_4, 400 MHz, 313 K, δ): 8.63 (s, 2H), 8.14-

7.79 (s, 2H), 2.00-1.78 (bm, 8H), 1.66-1.54 (bm, 8H), 1.50-1.33 (bm, 40H), 1.06 (t, J = 6 Hz, 12H).

Si4T-TPD. Polymerization B. Dark-blue solid (0.143 g, 0.14 mmol). M_n = 21.0 kg mol^{-1}, M_w = 26.0 kg mol^{-1}, PDI = 1.2. ^{1}H NMR (*o*-DCB-d_4, 400 MHz, 313 K, δ): 8.52 (s, 2H), 4.13-3.74 (bm, 2H), 2.09-1.93 (bm, 2H), 1.90-1.70 (bm, 8H), 1.64-1.28 (bm, 58H), 1.07 (m, 15H).

Si4T-2FBT. Polymerization A. Dark-blue solid (0.114 g, 0.12 mmol). M_n = 40.0 kg mol^{-1}, M_w = 58.0 kg mol^{-1}, PDI = 1.5. ^{1}H NMR (*o*-DCB-d_4, 400 MHz, 313 K, δ): 8.84 (s, 2H), 1.98-1.80 (bm, 8H), 1.68-1.54 (bm, 8H), 1.50-1.30 (bm, 40H), 1.06 (t, J = 6 Hz, 12H).

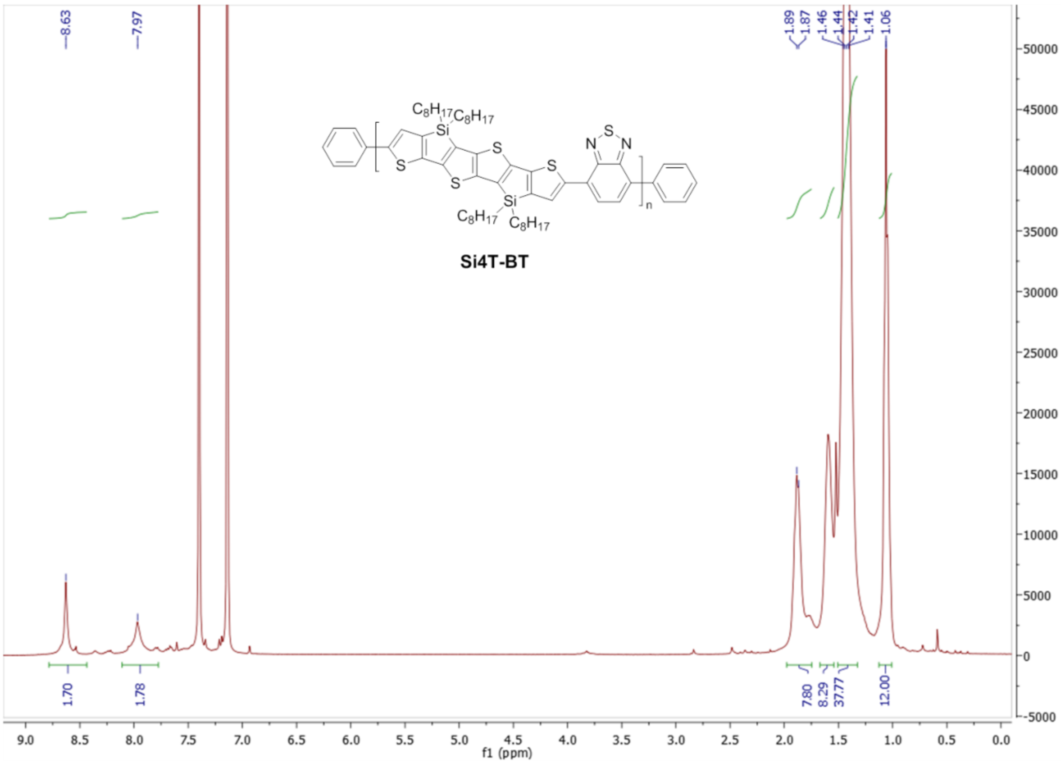

Figure S1. ^{1}H NMR spectrum of **Si4T-BT** in d$_4$-1,2-dichlorobenzene at 313K.

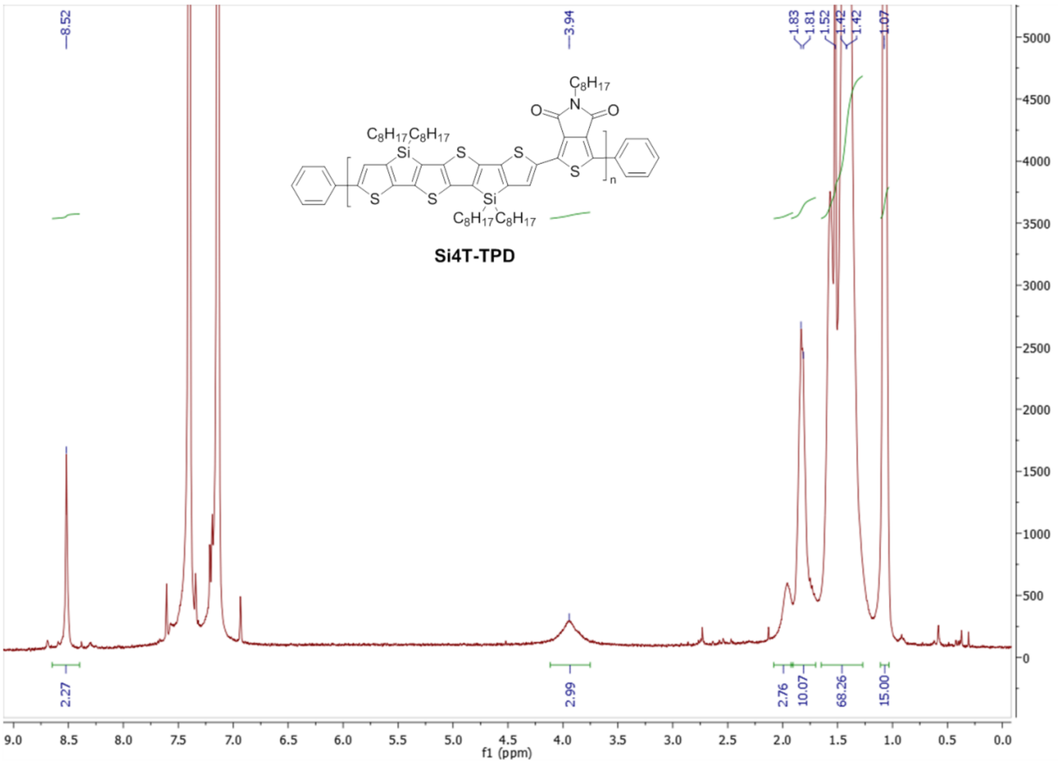

Figure S2. ^{1}H NMR spectrum of **Si4T-TPD** in d_4-1,2-dichlorobenzene at 313K.

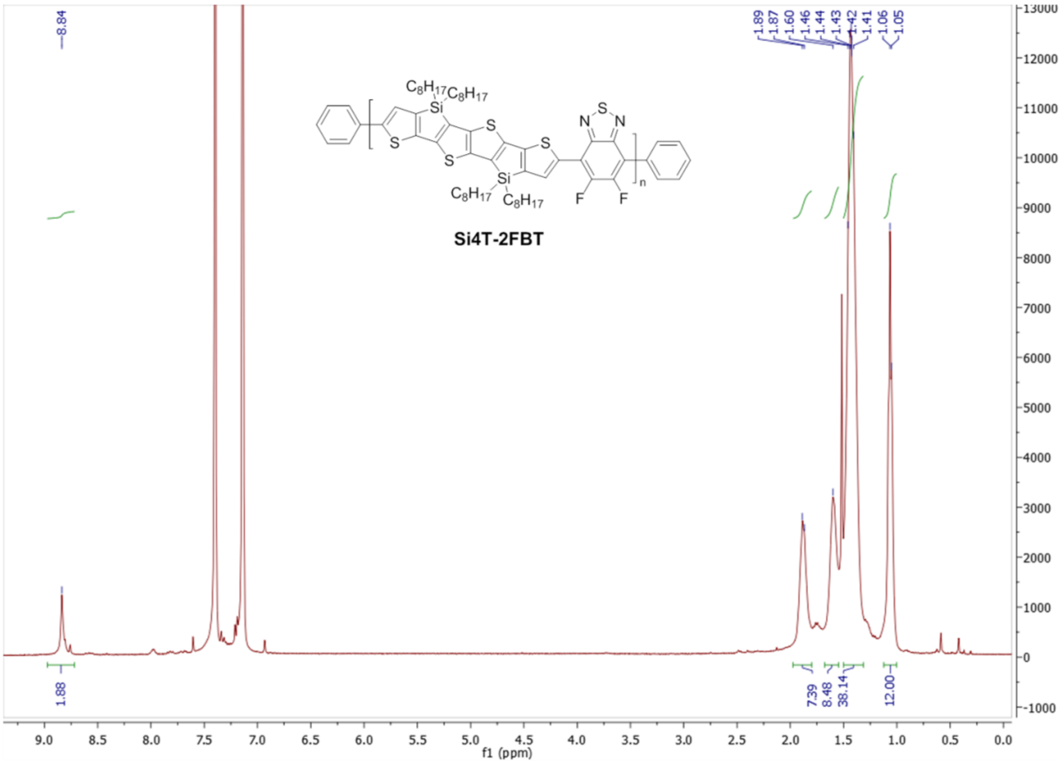

Figure S3. ^{1}H NMR spectrum of **Si4T-2FBT** in d_4-1,2-dichlorobenzene at 313K.

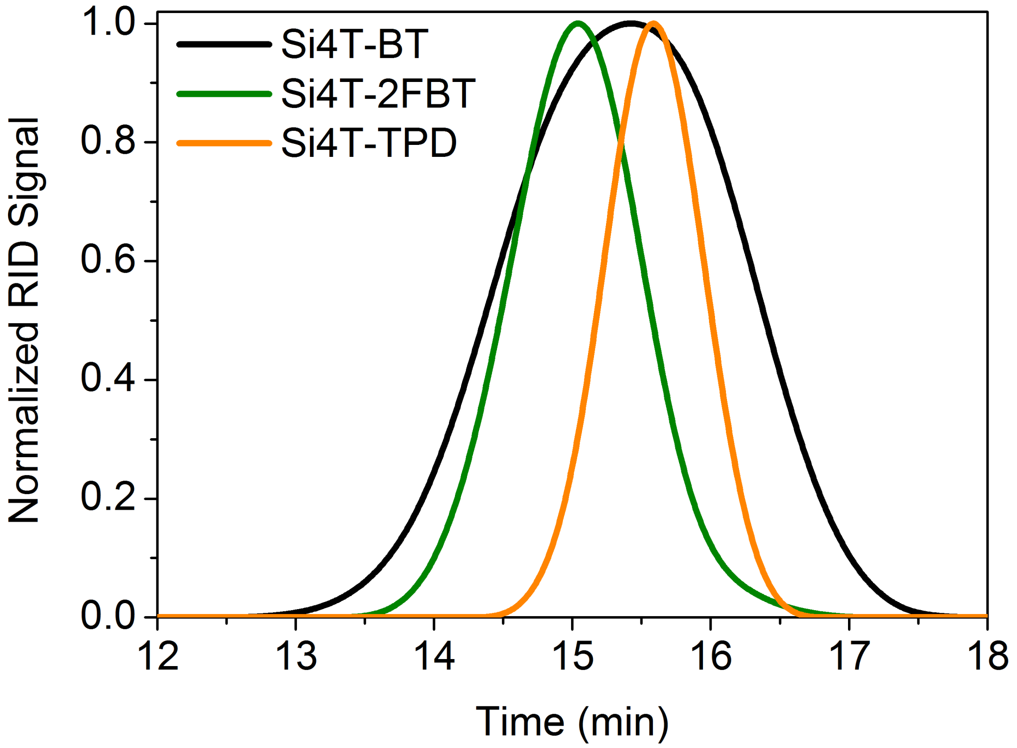

Figure S4. GPC traces of **Si4T** polymers.

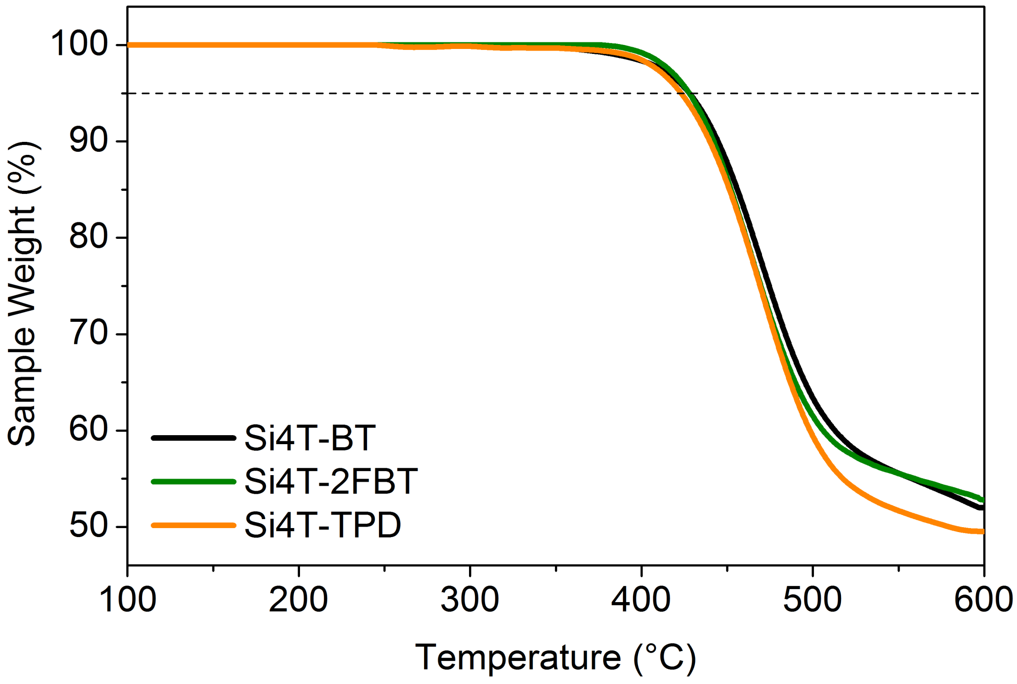

Figure S5. TGA thermograms of the **Si4T** polymers with a heating rate of 10°Cmin $^{-1}$ under nitrogen atmosphere.

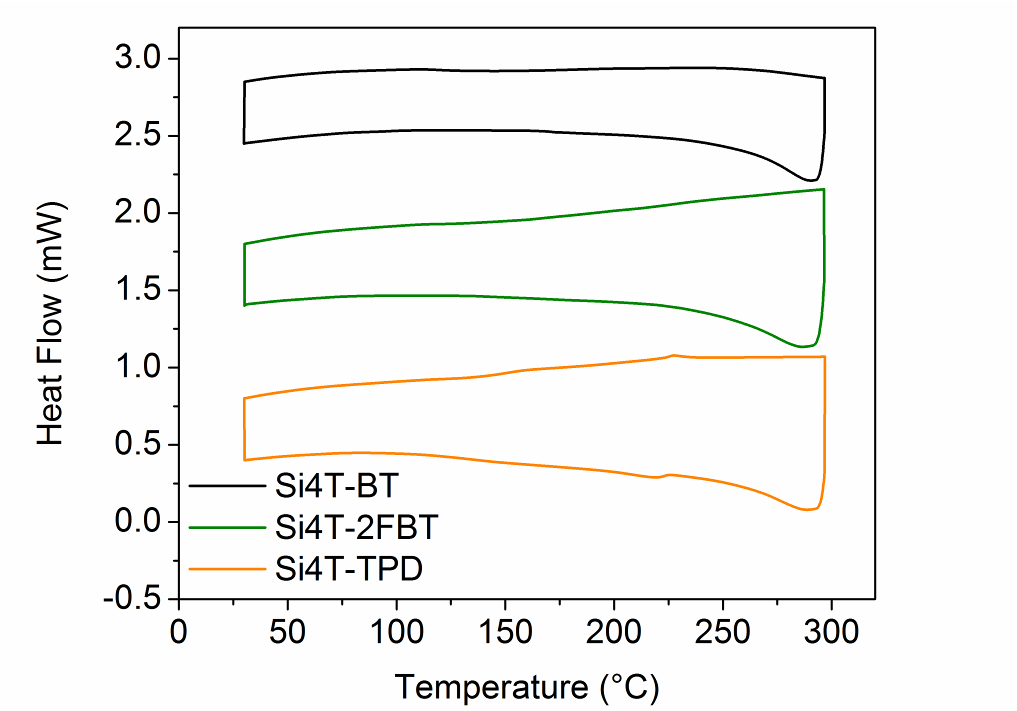

Figure S6. DSC traces (endo UP) of **Si4T** polymers recorded at a heating, respectively cooling rate of 20°C/min. **DTBT**.

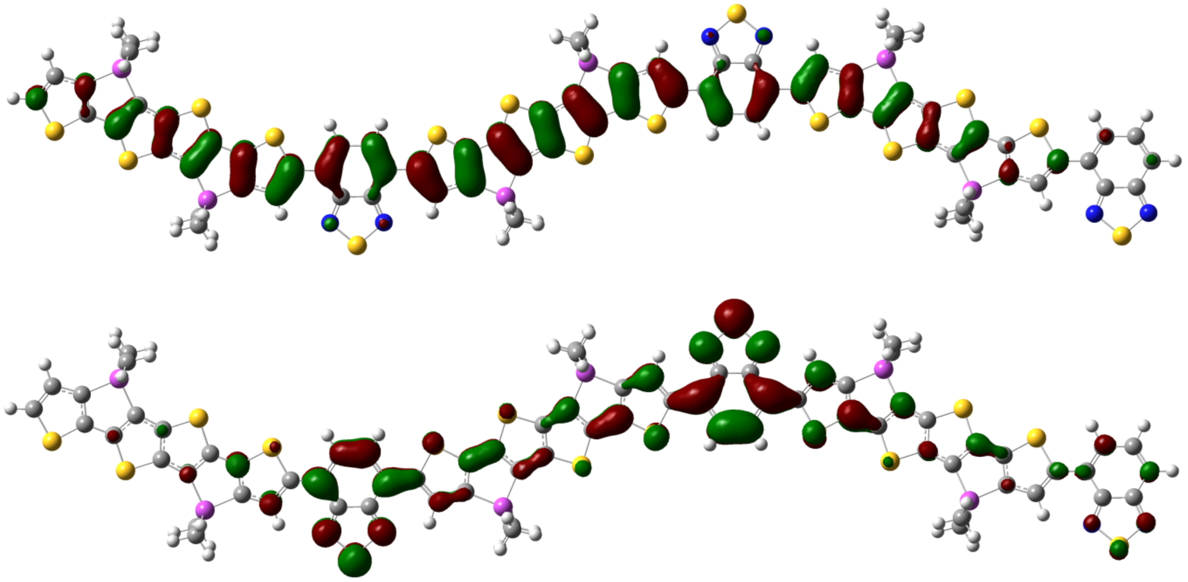

Figure S7. Energy-minimized structure (B3LYP/6-31G*) of a methyl-substituted **Si4T-BT** trimer with a visualisation of the HOMO (top) and LUMO (bottom) energy distributions.

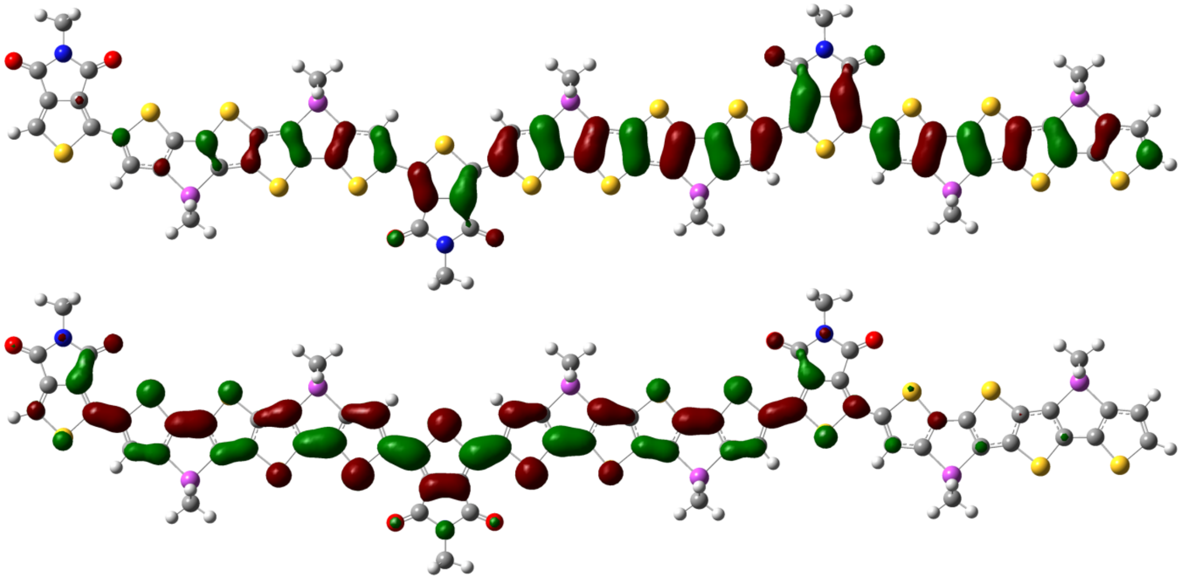

Figure S8. Energy-minimized structure (B3LYP/6-31G*) of a methyl-substituted **Si4T-TPD** trimer with a visualisation of the HOMO (top) and LUMO (bottom) energy distributions.

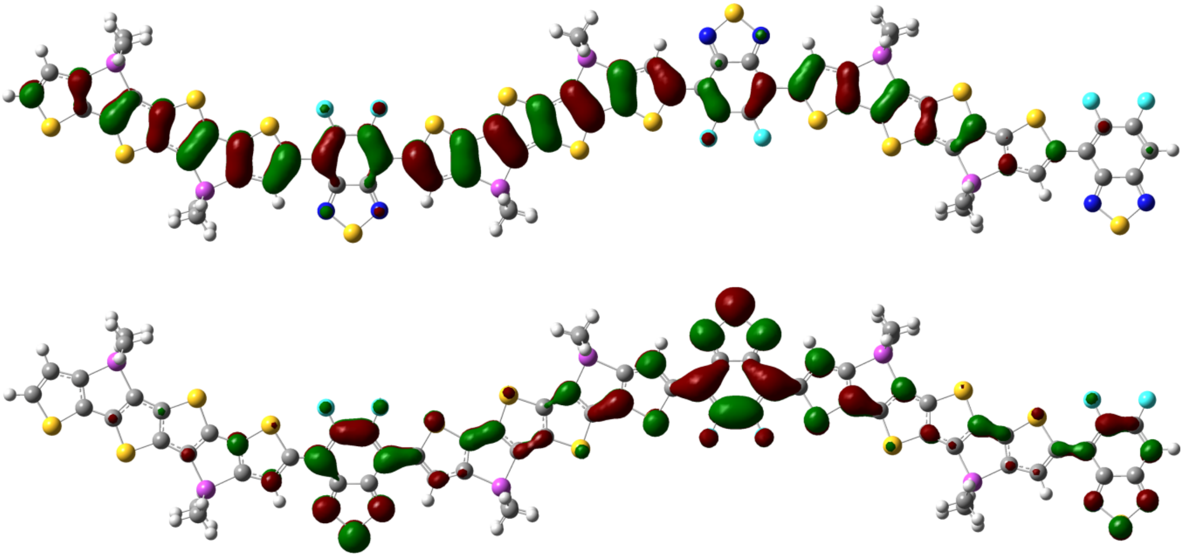

Figure S9. Energy-minimized structure (B3LYP/6-31G*) of a methyl-substituted **Si4T-2FBT** trimer with a visualisation of the HOMO (top) and LUMO (bottom) energy distributions.

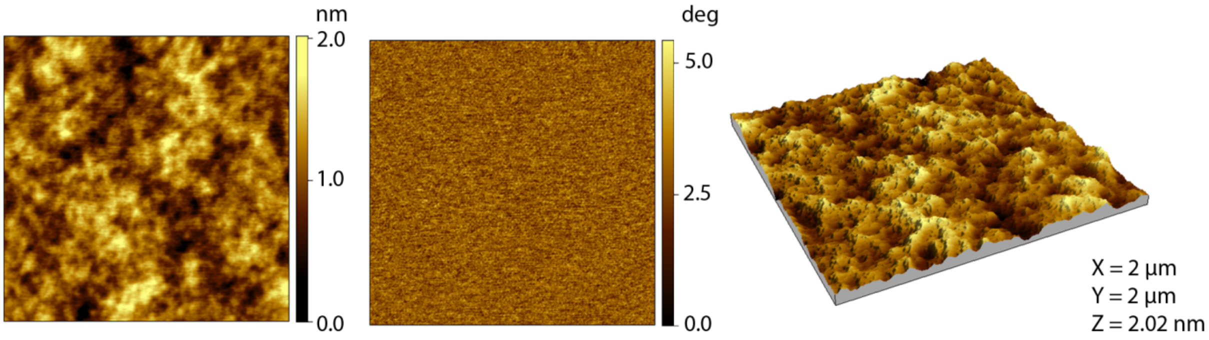

Figure S10. AFM topography (left), phase (middle) and 3D topography (right) images (tapping-mode, 2 × 2 µm) of **Si4T-BT**:PC$_{71}$BM (1:3.5) blend spin-cast from *o*-dichlorobenzene.

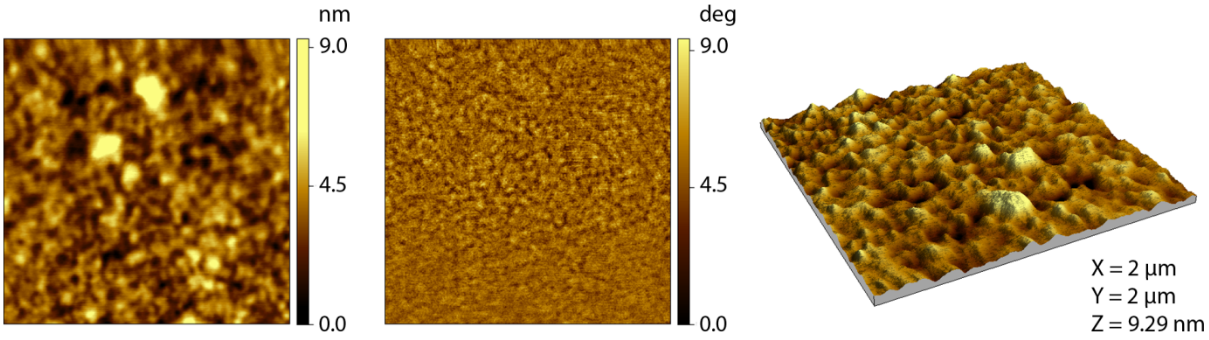

Figure S11. AFM topography (left), phase (middle) and 3D topography (right) images (tapping-mode, 2 × 2 µm) of **Si4T-2FBT**:PC$_{71}$BM (1:3.5) blend spin-cast from *o*-dichlorobenzene.

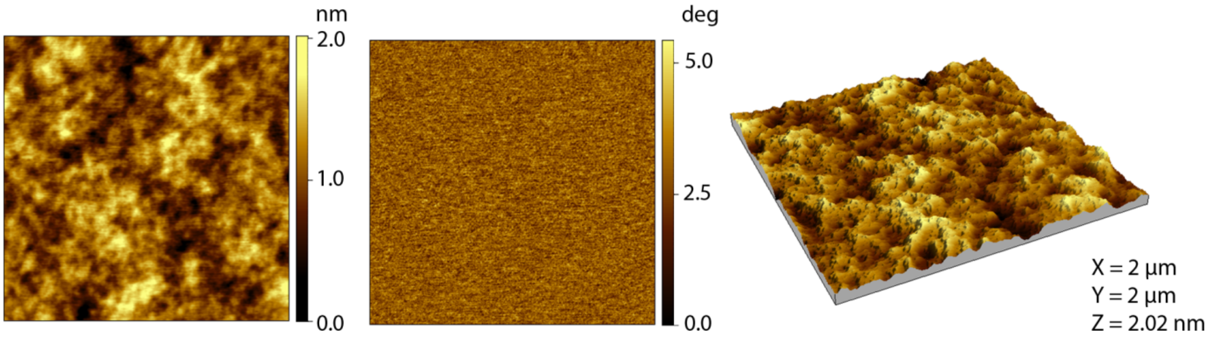

Figure S12. AFM topography (left), phase (middle) and 3D topography (right) images (tapping-mode, 2 × 2 µm) of **Si4T-TPD**:PC$_{71}$BM (1:3.5) blend spin-cast from *o*-dichlorobenzene.

The X-ray crystal structure of **4,4,9,9 tetraoctyl (2,7-bis (trimethylsilyl)) bis-silolo[2',3'-*d'*:4'',5''-*b''*] thieno [4,5-*b'*:2'',3''-*d*] thieno[3,2-*b*]thiophene** (**5**).

Crystal data for **5**: $C_{52}H_{88}S_4Si_4$, M = 953.82, triclinic, P-1 (no. 2), a = 11.9054(4), b = 11.9347(4), c = 12.3649(4) Å, α = 64.485(3), β = 64.935(3), γ = 85.259(3)°, V = 1425.49(10) Å^3, Z = 1 [C_i symmetry], D_c = 1.111 g cm^{-3}, μ(Mo-Kα) = 0.282 mm^{-1}, T = 173 K, yellow blocks, Oxford Diffraction Xcalibur 3 diffractometer; 9276 independent measured reflections (R_{int} = 0.0192), F^2 refinement,[1] R_1(obs) = 0.0484, wR_2(all) = 0.1404, 6934 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{\text{max}}$ = 65°], 327 parameters. CCDC 881354.

The crystal structure of **5** was found to have a centre of symmetry in the middle of the C(9)–C(9A) bond. The ends of both unique octyl chains were found to be disordered. For the C(15)-based chain, three orientations of ca. 49, 32 and 19% occupancy were found for the C(18) to C(22) portion, whilst for the C(23)-based chain two orientations of ca. 59 and 41% occupancy were found for the C(28) to C(30) portion. In both cases the geometries of the partial occupancy orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the atoms of the major occupancy orientation were refined anisotropically (the remainder were refined isotropically).

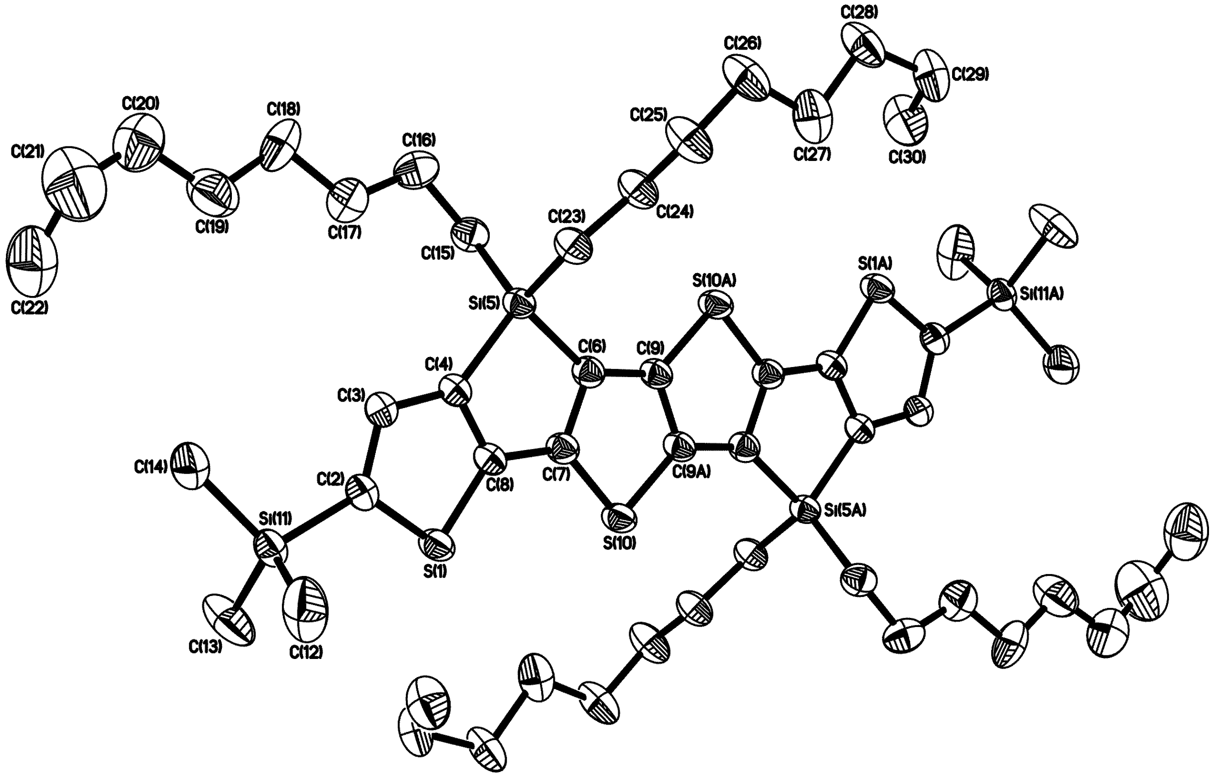

Figure S13. The crystal structure of 5 (50% probability ellipsoids). Atom labels with an "A" after the number are related to their counterparts without the letter by a centre of symmetry situated at the middle of the C(9)–C(9A) bond.

[1] G.M. Sheldrick, *Acta Cryst.*, **2008**, *A64*, 112-122.