Supporting information

Benzo[1,2-*b*:4,5-*b’*]bis[*b*]benzothiophene as Solution Processible Organic Semiconductor for Field-Effect Transistors

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I. Experimental section

1. General Methods:

Chemicals were obtained from Fluka, Aldrich, and Merck and used as received if not specified otherwise. ^{1}H NMR and ^{13}C NMR spectra were recorded in deuterated solvents such as CD_2Cl_2, $CDCl_3$, $C_2D_2Cl_4$ on a Bruker DPX 250 and Bruker DRX 500 spectrometer using the solvent proton or carbon signal as an internal standard. Field desorption (FD) mass spectra were obtained from a VG Instruments ZAB 2-SE-FPD. Melting points were measured on Büchi B-545 and not corrected. UV/Vis/NIR spectra were recorded at room temperature on a Perkin-Elmer Lambda 9 spectrophotometer. Fluorescence spectra were recorded on a SPEX-Fluorolog II (212) spectrometer. Elemental analysis was carried out on a Foss Heraeus Vario EL in the Institute for Organic Chemistry at the Johannes Gutenberg University, Mainz. The optical absorption measurements were performed at ambient temperature using an UV/Vis/NIR Perkin-Elmer Lambda 900 spectrometer. The PL measurements were performed on a J&M TIDAS spectrofluorometer. Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using gold working electrodes of 2 mm diameter, a platinum wire counter electrode, and a Ag/AgCl reference electrode on a computer-controlled PGSTAT12 at room temperature. Crystal structure determinations were carried out on a Nonius KCCD diffractometer with graphite monochromated MoK radiation. The structures were solved by direct methods (SHELXS-97). Refinement was done with anisotropic temperature factors for C and Cl, the hydrogen atoms were refined with fixed isotropic temperature factors in the riding mode. Some of the solvent molecules are disordered. These were refined with fixed isotropic temperature factors and occupancy factors which were fixed according to the geometry of disorder.

2. Synthetic Details:

Synthesis of 2-(4-butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)

1-Bromo-4-butyl-benzene (1.0 g, 4.7 mmol) was dissolved in absolute THF under argon. The solution was cooled to -78 ^{o}C before 3.1 ml (5.0 mmol) n-BuLi (1.6 M solution in hexane) was added dropwise. The reaction mixture was stirred for 10 min, before 1.0 ml (5.0 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added. The reaction mixture was allowed to warm up to room temperature and stirred for another 12 h before it was poured into ice water. The solution was extracted with diethyl ether, the organic phase washed with brine and dried with Na_2SO_4 before the solvent was removed. Purification by column chromatography on silica gel with hexane/THF (15:1) as an eluent yielded 1.0 g (85 %) of **3b** as a colorless oil. ^{1}H NMR (250 MHz, CD_2Cl_2): d (ppm): 0.86 (t, 3H, Me, J = 7.0 Hz), 1.18 ‑ 1.26 (m, 4H, 2 × CH_2), 1.33 (s, 12H, 4 × Me), 2.62 (t, 2H, CH2, J = 7.6 Hz), 7.20 (d, 2H, J = 7.6 Hz), 7.73 (d, 2H, J = 7.6 Hz). ^{13}C NMR (62.5 MHz, CD_2Cl_2): d (ppm): 14.12, 22.78, 25.04, 25.08, 33.96, 36.21, 83.97, 128.26, 135.07, 146.83; m/z = 260 (M+, 100 %).

Synthesis of 1,4-bisphenyl-2,5-bis(methylsulfinyl)benzene (4a)

1,4-dibromo-2,5-bis(methylsulfinyl)benzene **2** (0.253 g, 0.70 mmol) and 0.316 g (1.55 mmol) of the borolane compound **3a** were dissolved in 25 ml of toluene. A 2 M K_2CO_3 solution (6 ml) and 0.1 g of trimethylbenzylammonium chloride were added. The reaction mixture was degassed by three freeze/thaw cycles before 16 mg (1.46×10^{-5} mol) of $Pd(PPh_3)_4$ was added under argon. The mixture was stirred for 24 h at 90 ^{o}C. The reaction mixture was extracted three times with CH_2Cl_2 and dried with $MgSO_4$. Compound **4a** (162 mg, 65 %, related to **2**) was obtained as white crystals from silica chromotography with hexane/THF (10:1 to 1:1) as an eluent and recrystalization from DMSO. ^{1}H NMR (250 MHz, CD_2Cl_2): d (ppm): 2.28 (s, 6H, 2 × (SO)Me), 7.17 (t, 2H, J = 8.1 Hz), 7.27 (m, 8H), 7.91 (s, 2H). ^{13}C NMR (62.5 MHz, CD_2Cl_2): d (ppm): 14.09, 22.73, 33.91, 35.69, 41.94, 125.87, 127.35, 127.6, 134.59, 139.92, 144.28, 147.90; m/z = 354.49 (M+, 100.0 %). Anal. Calcd. for $C_{20}H_{18}O_2S_2$: C, 67.76; H, 5.12. Found: C, 67.52; H, 5.33.

Synthesis of 1,4-bis(4-butylphenyl)-2,5-bis(methylsulfinyl)benzene (4b)

1,4-dibromo-2,5-bis(methylsulfinyl)benzene **2** (0.122 g, 0.34 mmol) and 0.182 g (0.70 mmol) of the borolane compound **3b** were dissolved in 25 ml of toluene. A 2 M K_2CO_3 solution (6 ml) and 0.1 g of trimethylbenzylammonium chloride were added. The reaction mixture was degassed by three freeze/thaw cycles before 8.4 mg (7.3×10^{-6} mol) of $Pd(PPh_3)_4$ was added under argon. The mixture was stirred for 24 h at 90 °C. The reaction mixture was extracted three times with CH_2Cl_2 and dried with $MgSO_4$. The product was purified by silica chomotography with hexane/THF (10:1) as an eluent. Compound **4b** (128 mg, 85 %, related to **2**) was obtained as a white solid. ^{1}H NMR (250 MHz, CD_2Cl_2): d (ppm): 0.88 (t, 6H, 2 × Me, J = 7.3 Hz), 1.32 (m, 4H, 2 × CH_2), 1.58 (m, 4H, 2 × CH_2), 2.28 (s, 6H, 2 × (SO)Me), 2.6 (t, 4H, 2 × CH_2, J = 7.3 Hz), 7.22 (d, 4H, J = 8.1 Hz), 7.30 (d, 4H, J = 8.1 Hz), 7.91 (s, 2H). ^{13}C NMR (62.5 MHz, CD_2Cl_2): d (ppm): 14.09, 22.73, 33.91, 35.69, 41.94, 125.87, 129.35, 129.36, 134.59, 139.92, 144.28, 147.70; m/z = 466.20 (M+, 100.0 %). Anal. Calcd. for $C_{28}H_{34}O_2S_2$: C, 72.06; H, 7.34. Found: C, 71.83; H, 7.52

Synthesis of Benzo[1,2-b:4,5-b']bis[b]benzothiophene (1a)

A 10 ml round bottomed flask was filled with 1,4-bisphenyl-2,5-bis(methylsulfinyl)benzene (**4a**) (100 mg, 0.282 mmol), Phosphorus pentoxide (14 mg, 0.1 mmol) and trifluoromethanesulfonic acid (4 ml). The mixture was stirred for 72 h at room temperature to give a dark brown solution, which was then poured into ice–water (100 ml). The yellow precipitate was collected by suction filtration and dried under vacuum. The structure of this compound, which was insoluble in apolar organic solvents, was assumed to be the sulfonium salt. Demethylation of the solid was achieved by refluxing in pyridine (30 ml) for 12 h. When the suspension was cooled to room temperature, a large volume of H_2O was added to precipitate the product. Colorless crystals were got after recrystallization from $C_2H_2Cl_4$. (61 mg, 75 %). ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 413 K): d (ppm): 7.47 (td, 2H), 7.48 (td, 2H), 7.85 (dd, 2H, J = 6.1, 3.1 Hz), 8.19 (dd, 2H, J = 6.1, 3.1 Hz), 8.56 (s, 2H). ^{13}C NMR (500 MHz, $C_2D_2Cl_4$, 413 K): d (ppm): 115.13, 121.45, 122.75, 124.41, 126.98, 134.80, 135.25, 136.68, 140.26; mp: 323 °C. FD-MS: m/z = 290.40 (M+, 100 %). Anal. Calcd. for $C_{18}H_{10}S_2$: C, 74.45; H, 3.47. Found: 74.18; H, 3.70

Synthesis of Benzo[1,2-b:4,5-b']bis[b]benzothiophene-C_4 (1b)

A 10 ml round bottomed flask was filled with 1,4-bis(4-butylphenyl)-2,5-bis(methylsulfinyl)benzene (**4b**) (100 mg, 0.21 mmol), Phosphorus pentoxide (14 mg, 0.1 mmol) and trifluoromethanesulfonic acid (4 ml). The mixture was stirred for 72 h at room temperature to give a dark brown solution, which was then poured into ice–water (100 ml). The yellow precipitate was collected by suction filtration and dried under vacuum. The structure of this compound, which was insoluble in apolar organic solvents, was assumed to be the sulfonium salt. Demethylation of the solid was achieved by refluxing in pyridine (30 ml) for 12 h. When the suspension was cooled to room temperature, a large volume of CH_2Cl_2 was added to extract the product. BBBT-C4 (**1b**) was thus obtained as colorless plates by silica chromotography with hexane/CH_2Cl_2 (10:1) as an eluent (82 mg, 98 %). ^1H NMR (250 MHz, CD_2Cl_2): d (ppm): 0.88 (t, 6H, 2 × Me, J = 7.3 Hz), 1.34 (m, 4H, $2CH_2$), 1.63 (m, 4H, CH_2), 2.71 (t, 4H, 2 × CH_2, J = 7.3 Hz), 7.24 (d, 2H, J = 8.1 Hz), 7.60 (s, 2H), 8.03 (d, 2H, J = 8.1 Hz), 8.47 (s, 2H). ^{13}C NMR (62.5MHz, CD_2Cl_2): d (ppm): 14.10, 22.75, 30.07, 34.18, 36.16, 115.37, 121.64, 122.65, 125.92, 132.95, 135.20, 136.63, 140.49, 143.11; mp: 299.6 °C. FD-MS: m/z = 402.61 (M+, 100 %). Anal. Calcd. for $C_{26}H_{26}S_2$: C, 77.56; H, 6.51. Found: 77.23; H, 6.73

3. Single Crystal Structure:

Single crystals of **1a** suitable for the determination of X-ray crystal structure were grown by recrystallization from tetrachloroethane. The unit cell parameters of these white crystals are: monoclinic, space group $P2_1/n$, $a = 9.4941(5)$, $b = 5.9036(4)$, $c = 11.5824(5)$ and $\beta = 102.94(0)$ °, $V = 632.71(20)$ Å^3, $Z = 2$. The structure was refined to a final residual of $wR = 0.0387$.

Single crystals of **1b** suitable for the determination of X-ray crystal structure were grown by recrystallization from chloroform. **1b** was obtained as white needles with unit cell parameters: triclinic, space group $P\bar{1}$, $a = 4.5840(4)$, $b = 9.2230(5)$, $c = 12.4880(5)$, and $\alpha = 89.8540(12)$ °, $\beta = 79.5940(13)$ °, $\gamma = 79.1590(13)$ °, $V = 509.75(19)$ Å^3, $Z = 1$. The structure was refined to a final residual of $wR = 0.0565$.

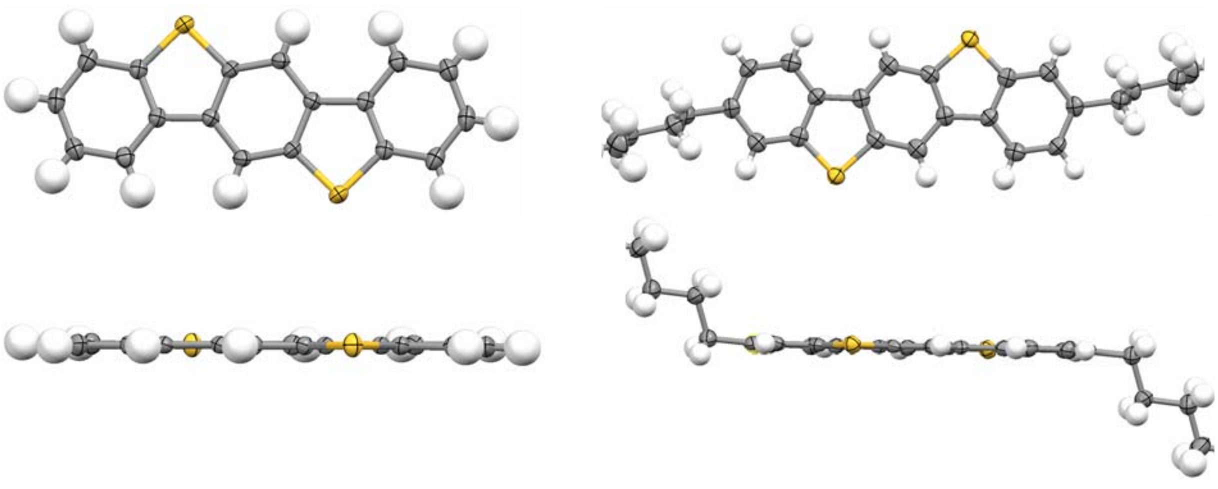

Figure S1. Molecular structure of **1a** (left) and **1b** (right).

4. Cyclic voltammetry (CV) measurements:

CV measurements were performed on a computer-controlled PGSTAT12 with a three-electrode cell in a solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) dissolved in dichloromethane at a scan rate of 50 mV/s. The solution in the three-electrode cell was purged with ultrahigh-purity N_2 for 10-15 minutes before each experiment and a blanket of N_2 was used during the experiment. A Pt wire was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. HOMO energies was estimated by the empirical equation HOMO = - (4.4 + E^{onset}_{oxd}) eV.

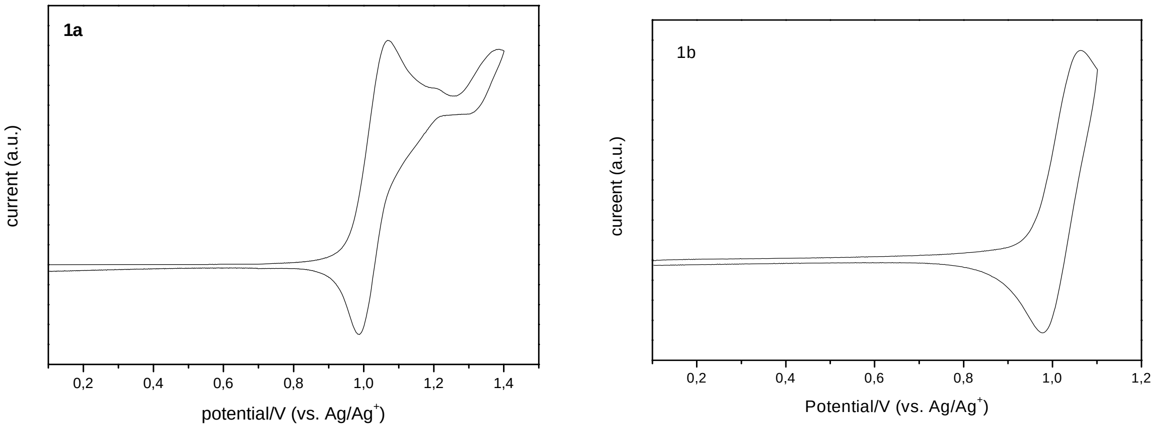

Figure S2. Cyclic voltamograms of **1a** (left) and **1b** (right) in dry CH_2Cl_2.

5. Photoluminescence emission spectra of compound 1a and 1b:

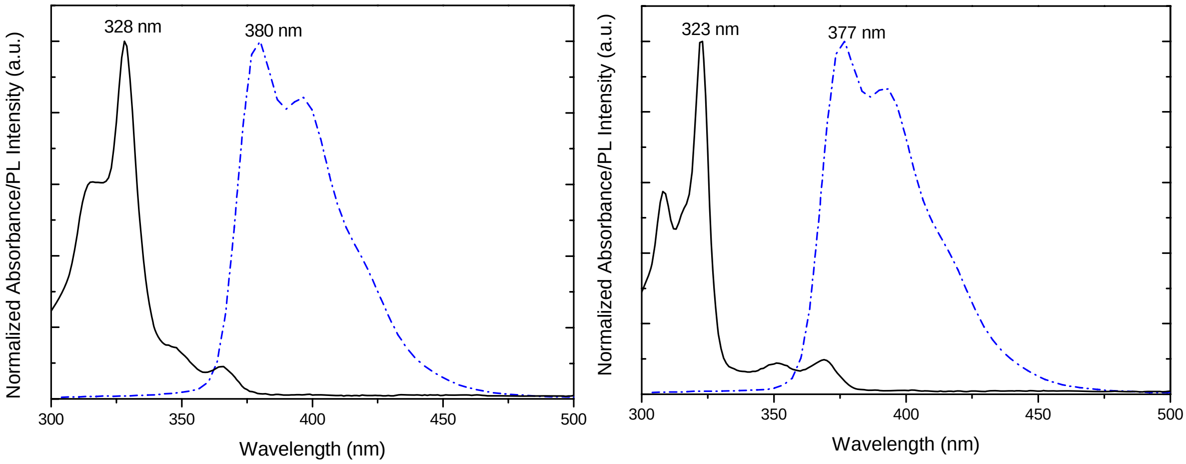

Figure S3. Absorption (solid) and photoluminescence (PL) (dash-dotted) spectra of **1a** (left) and **1b** (right) in THF (1.0×10^{-6}M).

6. FET Device Fabrication:

For all devices, heavily doped silicon wafers with a 150 nm thick thermally grown silicon dioxide layer were used as substrates. Source and drain electrodes with channel lengths of 10 µm and widths of 5 mm were defined on top of SiO_2 by conventional photolithography, followed by Cr/Au evaporation to a height of 2/50 nm.

Phenyltriethoxysilane was deposited via immersing the substrates in a 0.1 vol.% THF solution for two hours, followed by a thermal treatment at 120 °C for two hours. To improve the charge carrier injection from the electrodes into the semiconductor different thiols like 1-propanethiol, 1-octanethiol and 1-hexadecanethiol were used like described elsewhere[1].

All preparations and electrical measurements were performed in nitrogen atmosphere. Electrical characteristics of the devices were measured using a Keithley 4200 semiconductor parameter analyzer.

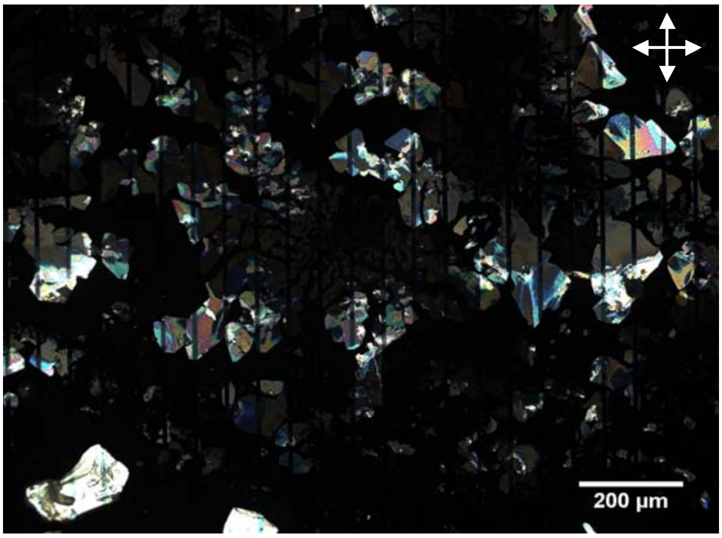

Figure S4. Spotlike film formation of BBBT (**1a**)on a PTES treated bottom contact device (polarized optical microscopy).

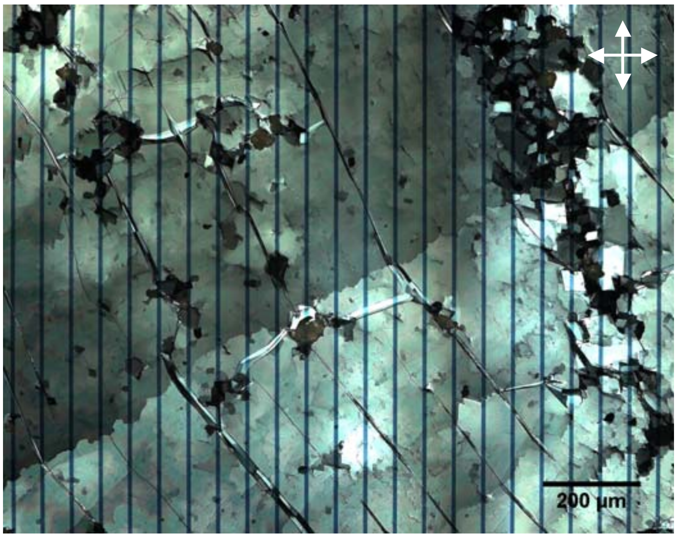

Figure S5. Film formation of BBBT-C4 (**1b**) on a 1-octanethiol treated bottom contact device (polarized optical microscopy).

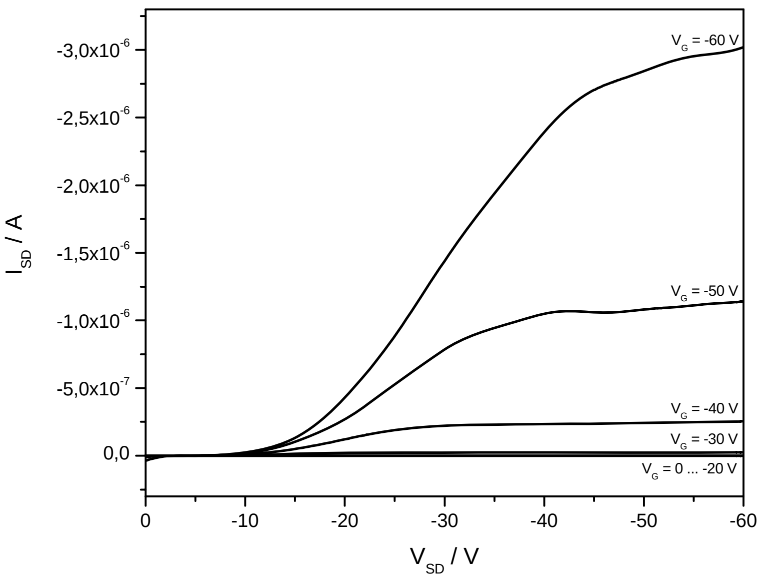

Figure S6. Transistor output curves of BBBT (**1a**)-based FETs.

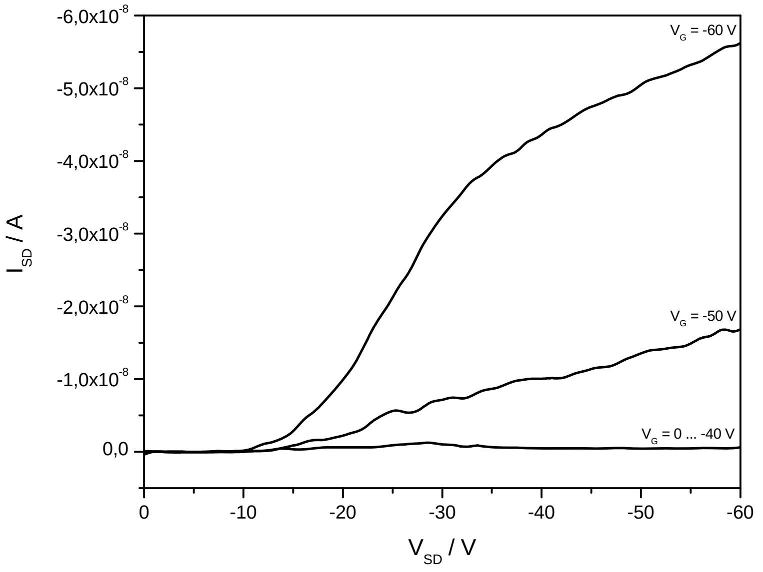

Figure S7. Transistor output curves of BBBT-C4 (**1b**)-based FETs.

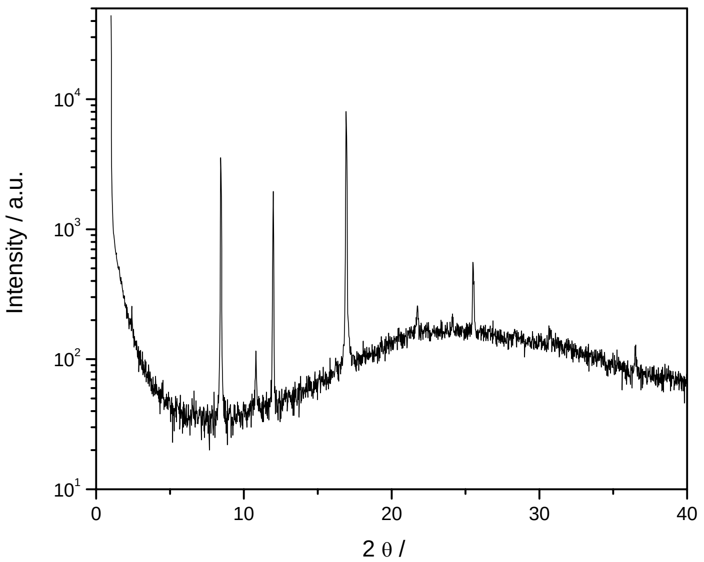

Figure S8. X-ray scattering in reflection of the BBBT (**1a**) film on a PTES treated glass plate.

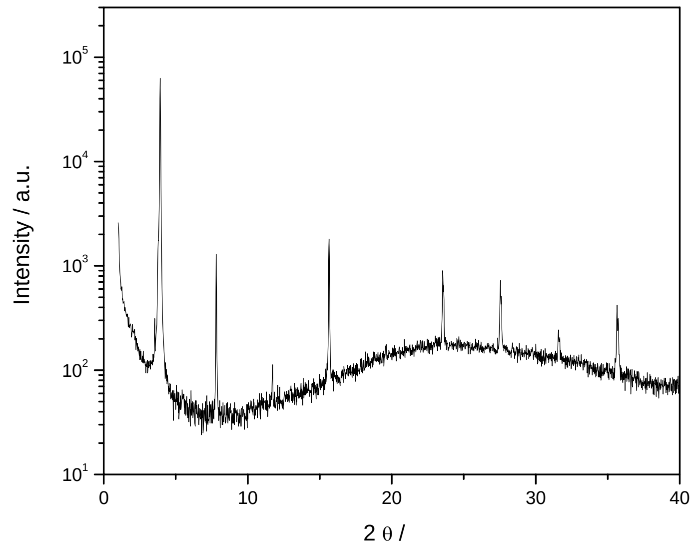

Figure S9. X-ray scattering in reflection of the BBBT-C4 (**1b**) film on a PTES treated glass plate.

7. X-ray Diffraction Studies:

X-ray diffraction (XRD) measurements were recorded on a Siemens D-500 powder diffractometer (Cu-Ka: 1.541 Å) with scan rate of 0.1°/20 s.

(1) W. Wang, T. Lee, M. A. Reed, *Phys. Rev. B*, 2003, **68**, 035416.