Supporting information for :

Controlling conjugated polymer morphology and charge carrier transport with a flexible-linker approach

By Andrea Gasperini, Sebastien Bivaud and Kevin Sivula*

Institut des Sciences et Ingénierie Chimiques
Ecole Polytechnique Fédérale de Lausanne
1015 Lausanne (Switzerland)
E-mail: kevin.sivula@epfl.ch
Homepage: limno.epfl.ch

1. Additional figures mentioned in the main text

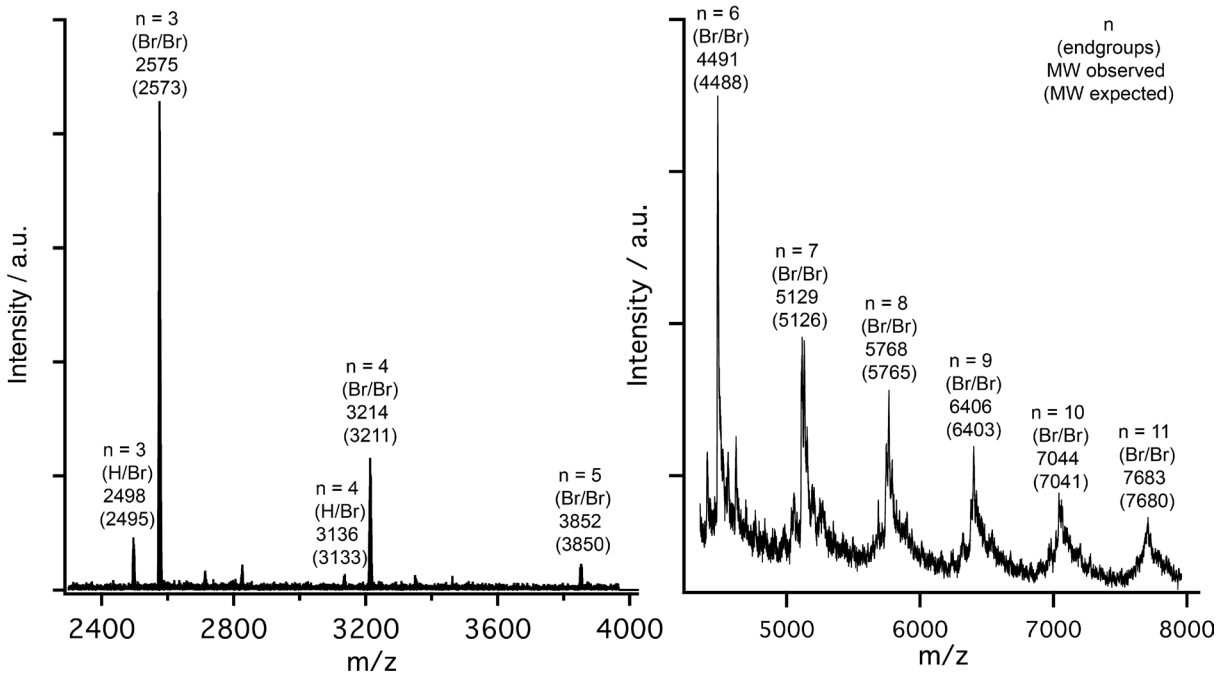

Figure S1: MALDI-TOF spectrum of compound **3** in reflection mode (left) and linear mode (right) using *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenyllidene]malononitrile as matrix

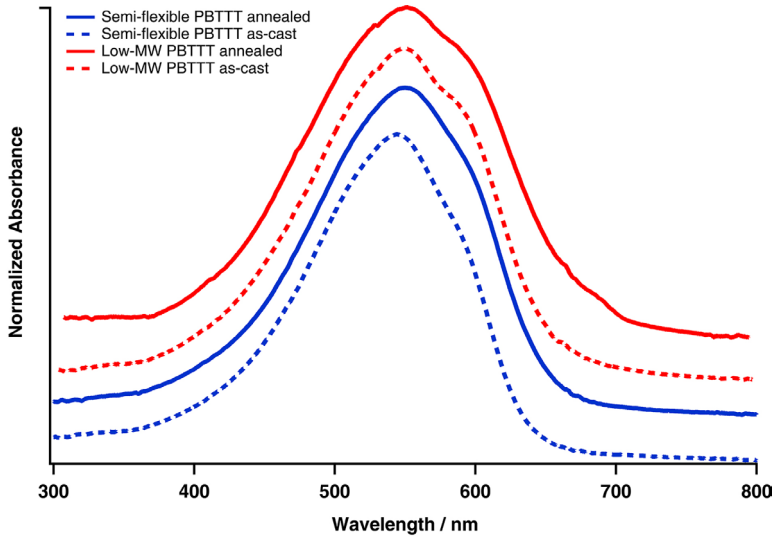

Figure S2: UV-Vis Absorption spectra of thin films of low MW-PBTTT **3** and the flexible linker polymer **7** in the "as cast state" (broken lines) and after thermal annealing at 180°C (solid lines). The spectra have been normalized and offset for clarity. The vibronic shoulder at ca. 600 nm is observable for both materials.

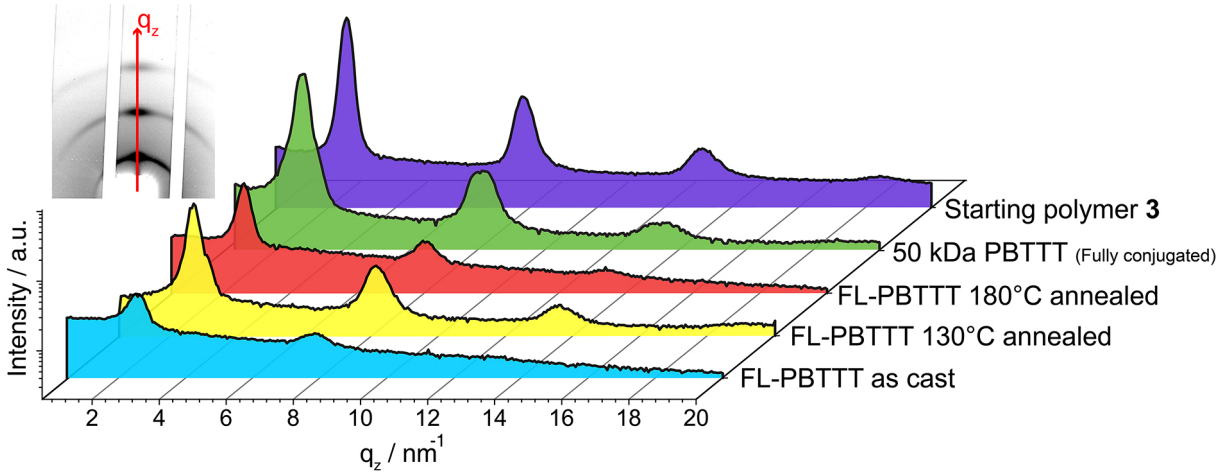

Figure S3: q_z cuts of the GIXD profiles extracted from the 2D data presented in Figure 2. The data represent the scattering intensity in the out of plane direction (i.e. $q_{xy} = 0$).

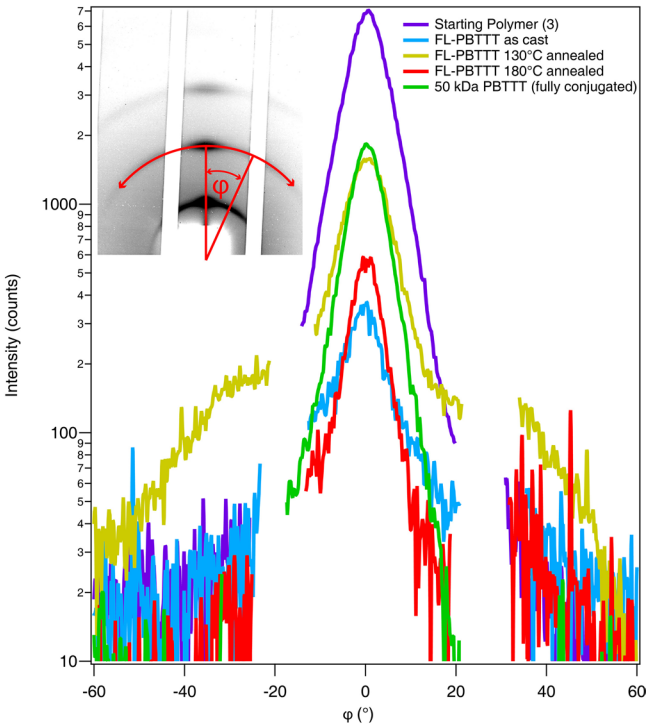

Figure S4: Azimuthal cuts of the 2D GIXD profiles presented Figures 2. The data were taken at the maximum value for qz = 0 for the (200) peak as indicated in the figure inset.

Table S1. Grazing incidence peak arching analysis for the (200) peak. The FWHM of the Azimuthal cut data (Figure S4) and the q_z cut data (Figure S3) are compared to quantify the shape of the peak. FWHM values were obtained via fitting the peaks with Voigt functions. Higher values of the FWHM ratio indicate more arched shape while lower values represent more cylindrically symmetric peaks.

Material	Film condition	2D GIXD Figure location	FWHM Azimuthal cut (°)	FWHM q_z cut ($Å^{-1}$)	FWHM ratio ($°Å^{-1}$)
Polymer **3**	as cast	Figure 2a	9.7	0.031	313
FL-PBTTT **7**	as cast	Figure 2b	9.7	0.052	187
	annealed 130°C	Figure 2c	10.5	0.041	256
	annealed 180°C	Figure 2d	7.6	0.040	190
56 kDa PBTTT	annealed 180°C	Figure 2e	8.5	0.053	160

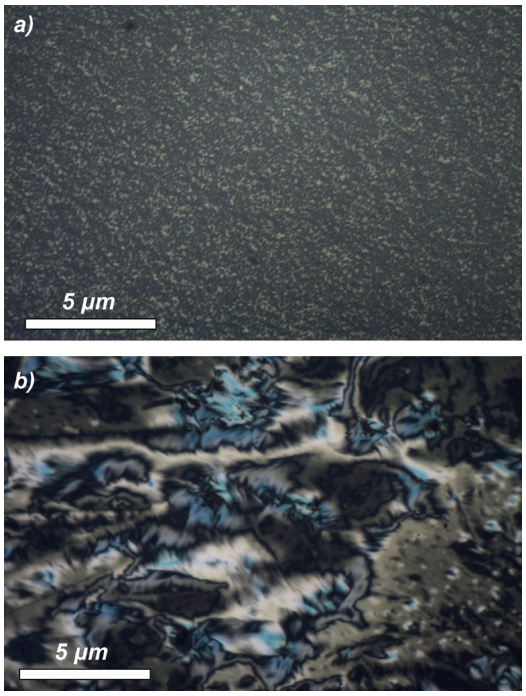

Figure S5; Polarized optical microscopy (epi-illumination) of a) the flexible linker polymer **7** and b) the starting polymer **3** and after annealing at 180°C on OTS-treated SiO_2 substrates.

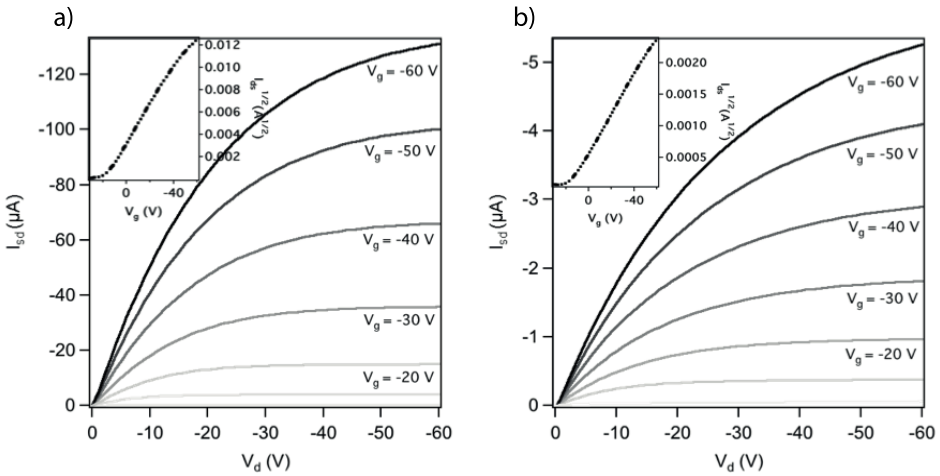

Figure S6: I-V curves and respective transfer curves for low MW PBTTT **3,** a) as-cast b) annealed at 180°C.

2. Synthetic methods and standard characterization

All reagents were of commercial reagent grade (Sigma-Aldrich, Acros and Fluorochem) and were used without further purification. Tetrahydrofuran (Fisher Chemical, HPLC grade) and chlorobenzene (Alfa Aesar, HPLC grade) were purified and dried on a Pure Solv-MD Solvent Purification System (Innovative Technology, Amesbury, United States) apparatus. Normal phase silica gel chromatography was performed with an Acros Organic silicon dioxide (pore size 60 Å, 40–50 µm technical grades) and reverse phase silica gel chromatography was performed with a Material Harvest C18 reverse phase silica gel (pore size 60 Å, 40-63 µm). The (^{1}H) and (^{13}C) NMR spectra were recorded at room temperature using per-deuterated solvents as internal standards on a NMR Bruker Advance III-400 spectrometer (Bruker, Rheinstetten, Germany). Chemical shifts are given in parts per million (ppm) referenced to residual ^{1}H or ^{13}C signals in CDCl3 (^{1}H: 7.26, 13C: 77.0) and o-dichlorobenzene-d4 (^{1}H: 6.94). EI-MS spectrum was recorded on an EI/CI-1200L GC-MS (Varian) instrument and APPI-MS spectrum was recorded on an ESI/APCI LC-MS Autopurification System with a ZQ Mass detector (Waters, Milford, United States) instrument using a positive mode. Infrared (IR) spectra were recorded on a FTS 7000(e) Series from Portman Instruments AG (Biel-Benken, Germany).

5,5'-trimethyltin thieno[3,2b]thiophene (**1**) and **2,5-dibromo-3-dodecylbithiophene** (**2**) were prepared as described in our previous work[1] following the procedure from McCulloch et al.[2]

Poly[2,5-bis(3-dodecylthiophen-2-yl)thieno[3,2-b]thiophene], ***PBTTT Br terminated, (3)***: PBTTT polymerization conditions were optimized in order to preferentially synthetize short chains that exclusively resulted to be end-functionalized with bromine. A ratio of 1.6-1.8 to 1 of 2,5-dibromo-3-dodecylbithiophene to 5,5'-trimethyltin thieno[3,2b]thiophene was thus chosen. Typical number-average molecular weight (M_n) of 5.5-7 kDa (PDI 1.4) against Polystyrene standards were calculated by analytical size exclusion chromatography using Chlorobenzene as eluent at 80°C. Successive fractionation by preparative SEC (in 80°C, chlorobenzene, 6 mL min^{-1}, 40.0 x 250 mm column, linear M packing, Polymer Standards Service GmbH) allowed the selection of a narrow distribution of chains at 11.7 kDa with PDI 1.19 (continuous grey line Figure 1). The sample solution in chlorobenzene was passed through a polytetrafluoroethylene filter (5 µm pore size) before injection. Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS) was carried on a Axima-CFRTM plus using trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenyllidene] malononitrile as matrix and THF as solvent (see Figure S1). From the comparison between the calculated and recorded MALDI-TOF spectrum of the bromine end-groups appeared that the conditions chosen successfully favoured the end-functionalization of the rigid PBTTT segment with only a 10% of mono-brominated chains. Taking into account a stoichiometric imbalance of 0.1, the maximum monomer conversion rate was thus fixed at 90% whereas, as predicted by the Carothers equation, the maximum degree of polymerization achievable calculated was 7.

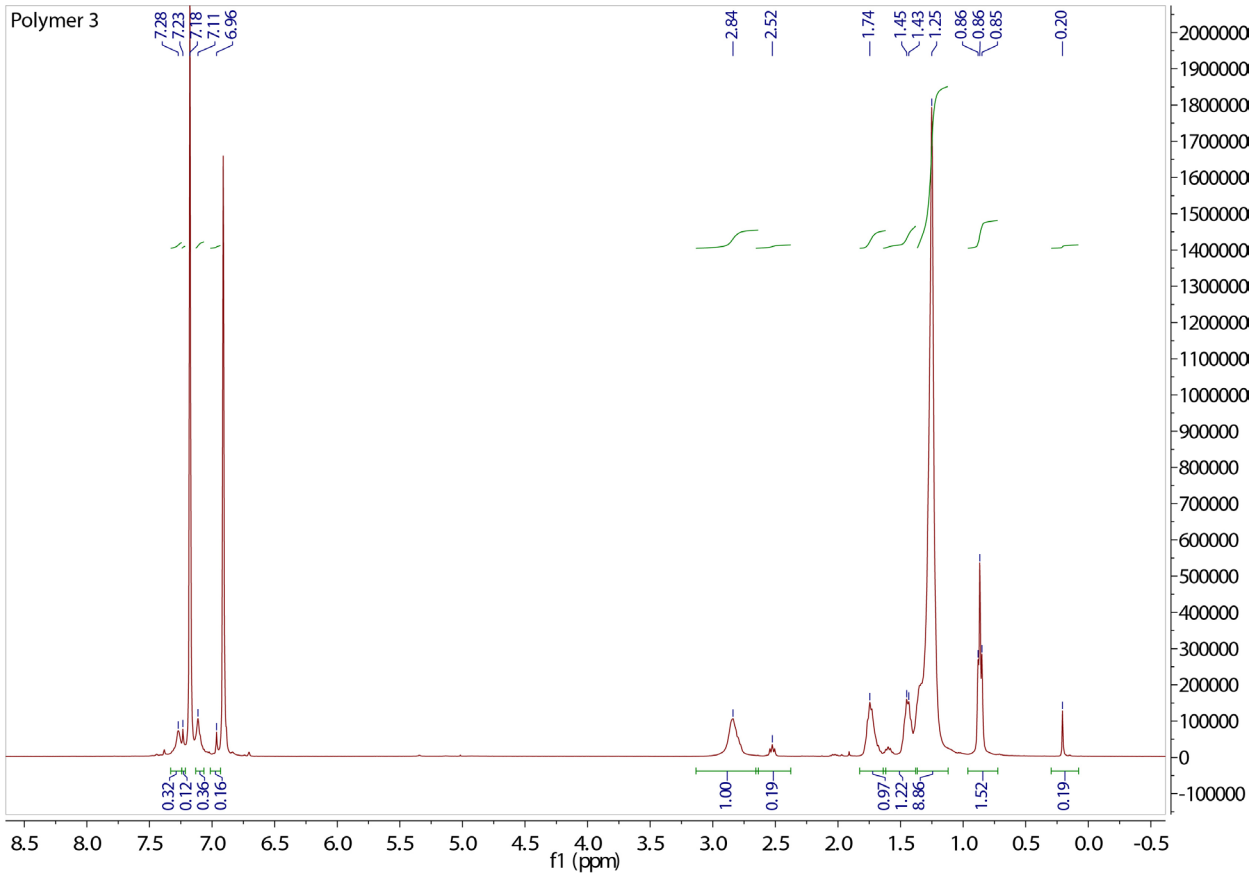

Figure S7. ^{1}H NMR spectrum of compound 3 the 11.7 kDa PBTTT with Br end-groups (in o-dichlorobenzene D_4). NB: Integration of the aromatic region is complicated by solvent peaks.

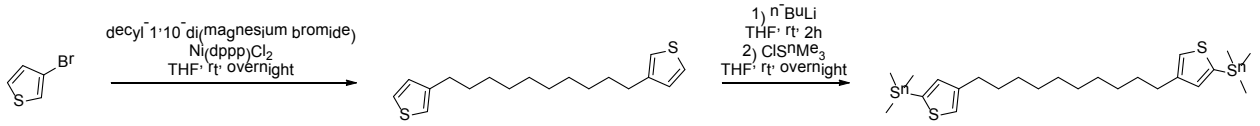

Figure S9. Synthetic route to compounds 5 and 6.

1,10-di(thiophen-3-yl)decane (5), **following the procedure described by S. Saito *et al*:**[3] To a solution of 1,10-dibromodecane (**4**, 9.14 g, 30.40 mmol) in dried tetrahydrofuran (80 mL), magnesium turnings (1.54 mg, 64.0 mmol) was added portion wised at 0°C in 1h under argon. The mixture was stirred for 4h at room temperature. Then, 3-bromothiophene (10 g, 61.3 mmol) followed by dichloro[1,3-bis(diphenylphosphino)propane]nickel (670 mg, 1.23 mmol) were added quickly at –30°C under argon. The mixture was warmed to room temperature and stirred overnight. Afterward, a saturated solution of ammonium chloride was added (20 mL). The aqueous layer was extracted with diethyl ether (50 mL) and

the organic layer was washed with brine (2 x 20 mL), dried over anhydrous magnesium sulfate, filtered and concentrated under vacuum. The residue was subjected to silica gel chromatography using hexane as eluent or by distillation under vacuum (T_{eb} = 190°C at 1.7 mbar) to afford 5.21 g (56%, 16.96 mmol) of a white solid.

Mp: 43.5-46 °C; ^{1}H NMR (400 MHz, $CDCl_3$-d_3): δ=7.25 (dd, ^{3}J = 4.9 & ^{4}J = 3.0 Hz, 2H), 6.95 (d, ^{3}J = 4.9 Hz 2H), 6.93 (d, ^{4}J = 3.0 Hz, 2H), 2.64 (t, ^{3}J = 7.7 Hz, 4H), 1.67-1.59 (m, 4H), 1.36–1.29 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$-d_3): δ=143.31 (2C), 128.38 (2C), 125.14 (2C), 119.87 (2C), 30.68 (2C), 30.41 (2C), 29.70 (2C), 29.58 (2C), 29.45 (2C); IR: 2918, 2845, 1466, 1431, 1078, 937, 864, 833, 791, 754, 727, 696, 679, 592 ; MS: 306 (EI): Calcd. [$C_{18}H_{26}S_2$]: 306.15; Elmt. Anal. Calcd [$C_{18}H_{26}S_2$]: C, 70.53; H, 8.55; Found : C, 70.72 ; H, 8.15

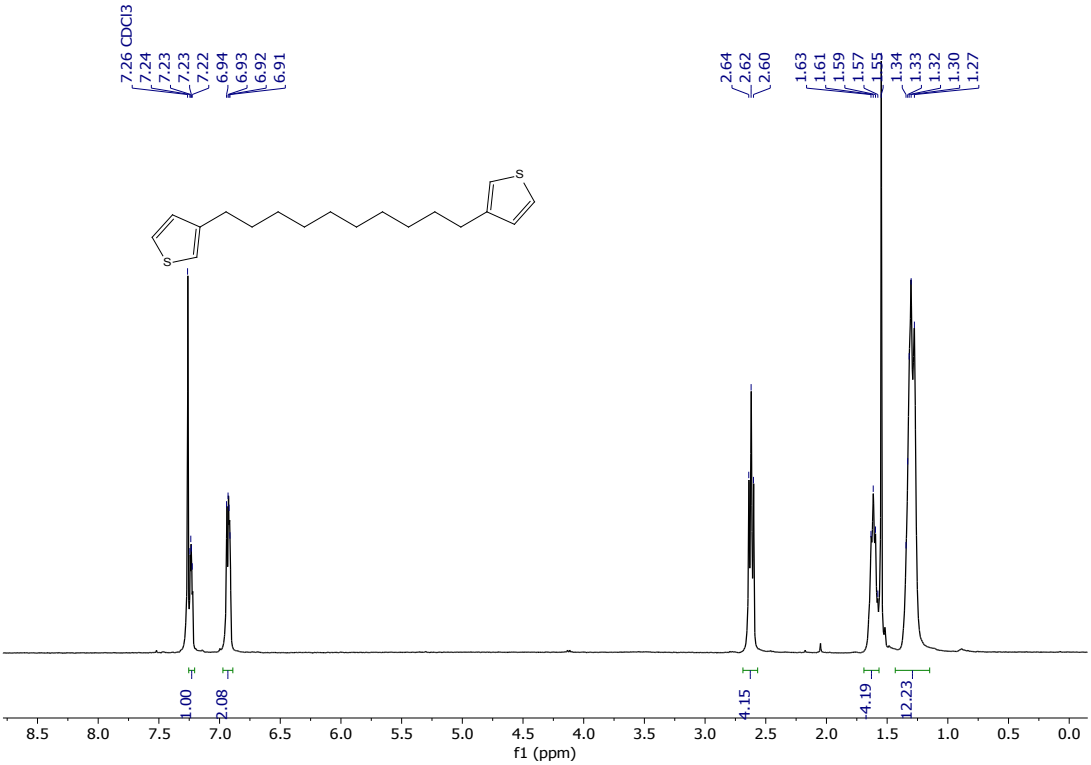

Figure S8: ^{1}H NMR spectrum of compound **5** ($CDCl_3$).

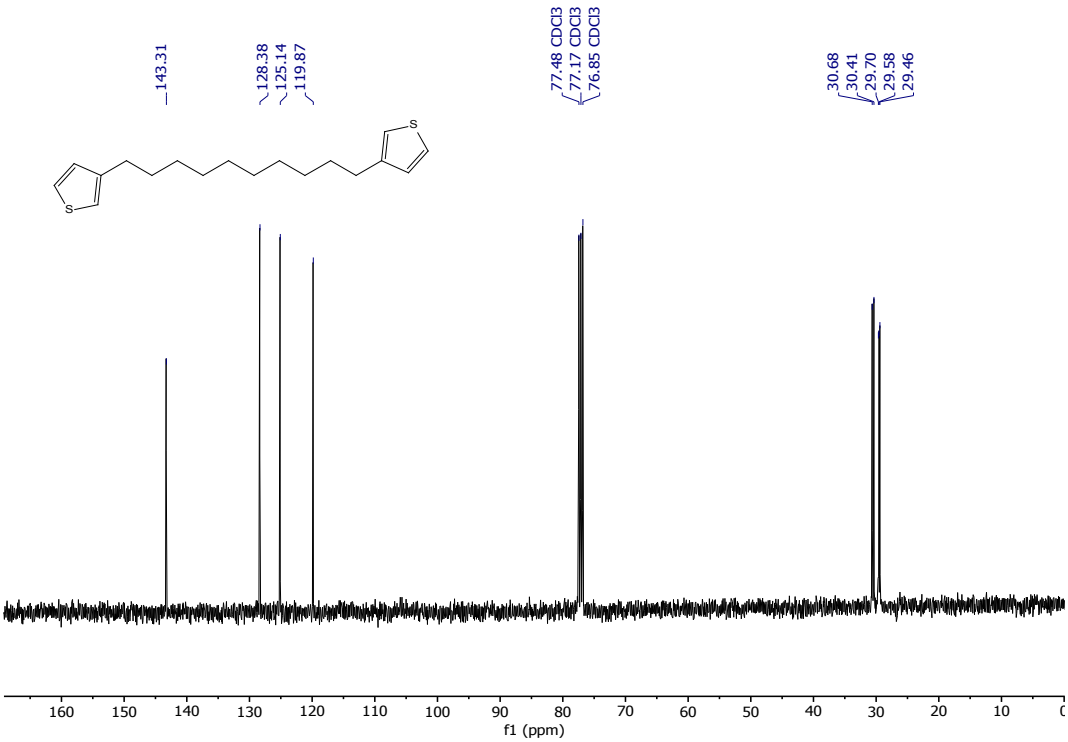

Figure S9: ^{13}C NMR spectrum of compound **5** ($CDCl_3$).

1,10-bis(5-(trimethylstannyl)thiophen-3-yl)decane (6) : To a solution of compound **5** (5.21 g, 16.99 mmol) in dried tetrahydrofuran (50 mL) and tetramethylethylenediamine (5.91 g, 7.62 mL, 50.88 mmol), a 2.5 M solution of n-butyllithium in hexane (14.25 mL, 35.62 mmol) was added dropwise at -78°C under argon over a period of 15 min. Then the reaction mixture was stirred at -78°C for 30 min and warmed to room temperature. After stirring for 1h30 at room temperature, trimethyltin chloride (7.10g, 35.62 mmol) in dried tetrahydrofuran (5 mL) was added at -78°C. Then, the solution was stirred overnight at room temperature. Aqueous ammonium chloride (20 mL) and aqueous potassium fluoride (10 mL) were added. The aqueous layer was extracted with diethyl ether (30 mL) and the organic layer was washed twice with brine (20 mL), dried over anhydrous magnesium sulfate, filtered and concentrated under vacuum. The residue was subjected to reverse phase silica gel chromatography using hexane as eluent to afford a pale yellow oil. Finally, 7.2 g (67%, 11.39 mmol) of a white solid were obtained after recrystallization in isopropanol at –30°C.

^{1}H NMR (400 MHz, $CDCl_3$-d_3): δ=7.19 (s, 2H), 7.00 (s, 2H), 2.64 (t, ^{3}J = 7.9 Hz, 4H), 1.69-1.55 (m, 4H), 1.37-1.19 (m, 12H), 0.35 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$-d_3): δ=144.64 (2C), 137.28 (2C), 136.74 (2C), 125.79 (2C), 30.89 (2C), 30.12 (2C), 29.73 (2C), 29.62 (4C) -8.13 (6C); IR: 2922, 2899, 2847, 1464, 1177, 972, 912, 858, 833, 764, 741, 723, 534, 524, 511 ; MS: 634.07 (APPI): Calcd. [$C_{24}H_{42}S_2Sn_2$]: 634.08; Elmt. Anal. Calcd. [$C_{24}H_{42}S_2Sn_2$]: C, 45.60; H, 6.70; Found: C, 45.82; H, 6.09

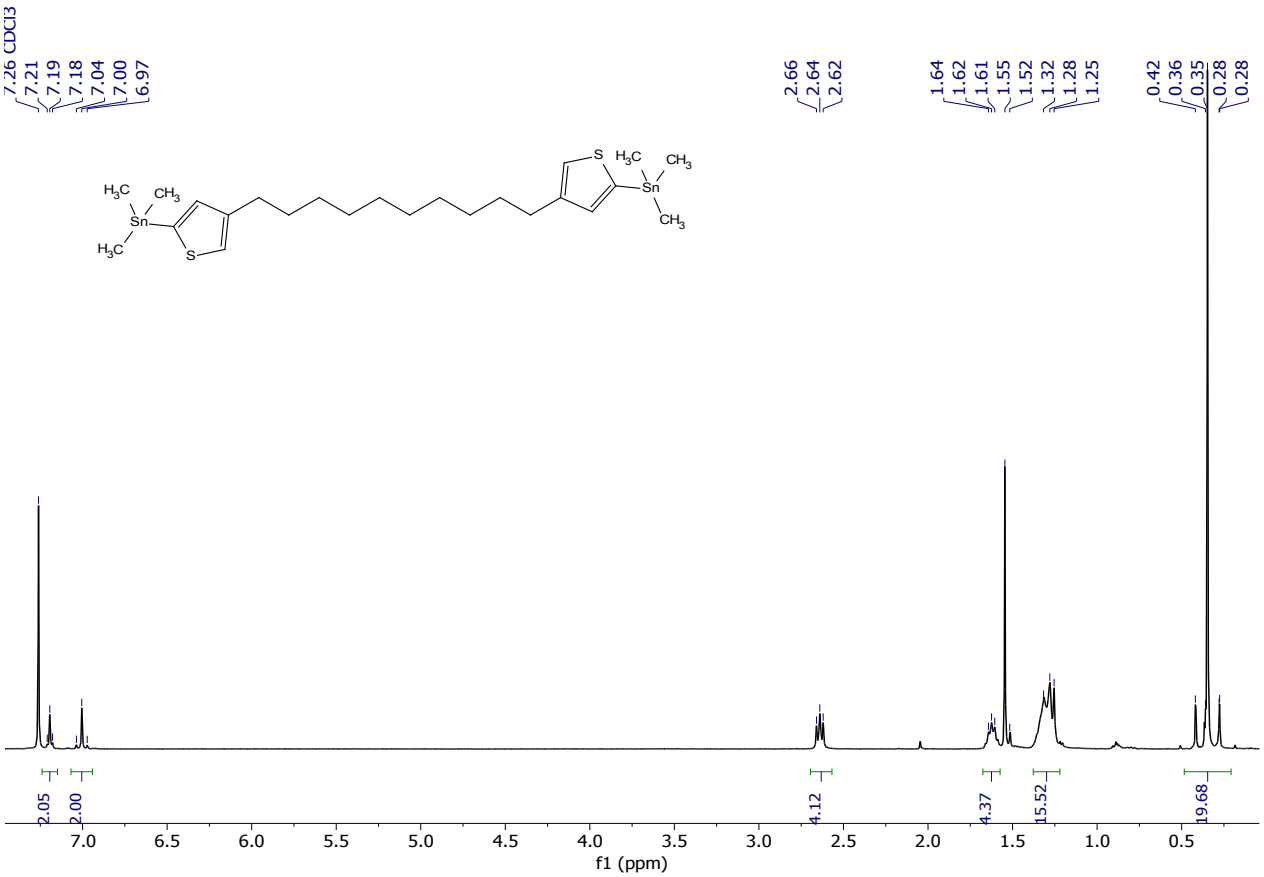

Figure S10: ^{1}H NMR spectrum of compound **6** ($CDCl_3$).

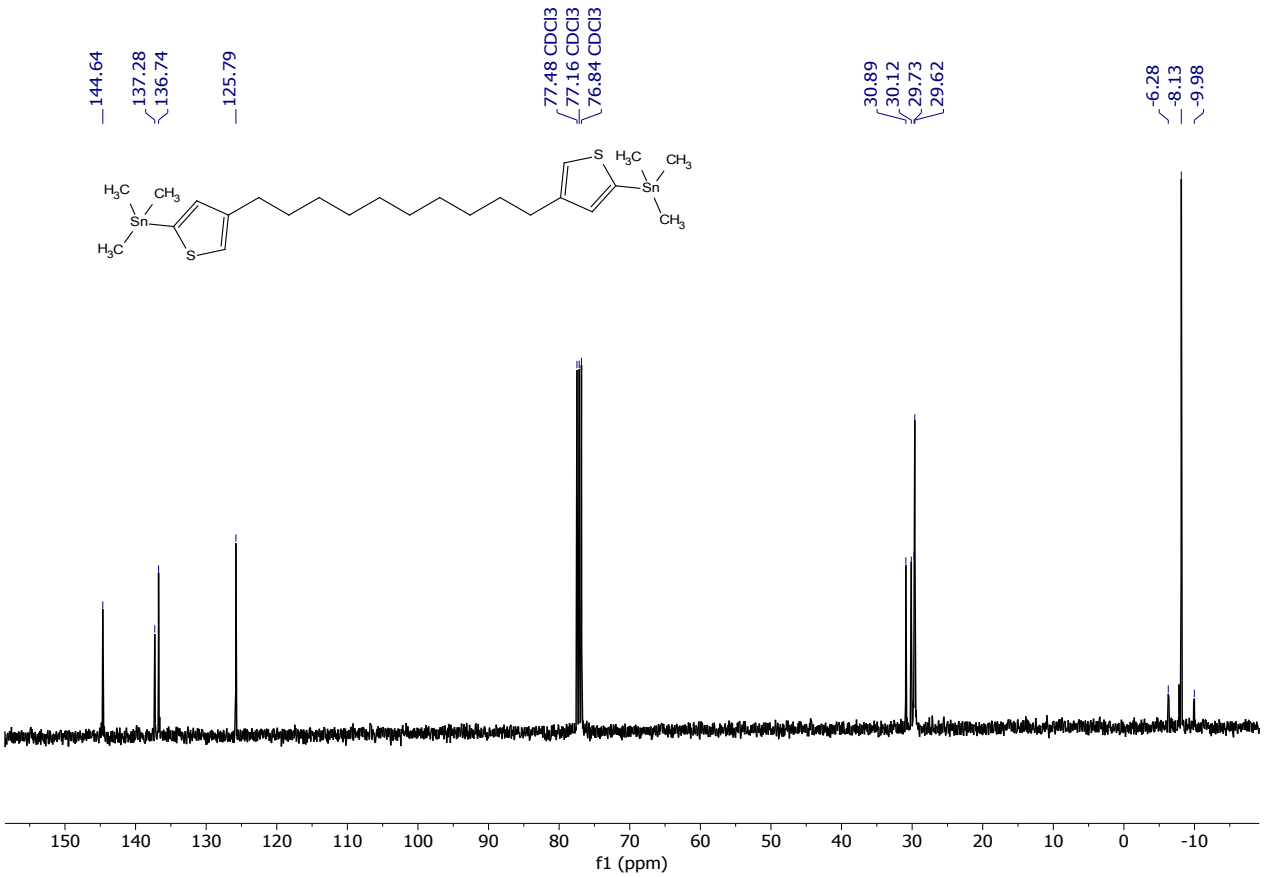

Figure S11: ^{13}C NMR spectrum of compound **6** ($CDCl_3$).

***Flexibly-link PBTTT Compound 7*;** In a 25ml round bottom flask 100 mg of compound **3** (8.4 µmol) and **6** (8.4 µmol) were added in 5 ml of anhydrous chlorobenzene under Argon atmosphere using 2% mol of tris(dibenzylideneacetone)dipalladium and tri(o-tolyl)-phosphine as a catalyst. At the end of the polymerization time (36 h) the polymer was isolated by precipitation in methanol for 2 h. The crude polymer fraction was analyzed through an analytical size exclusion chromatography column (SEC) at 80°C using chlorobenzene as mobile phase at 1 mL min^{-1}. Successive fractionation by preparative SEC (in 80°C, chlorobenzene, 6 mL min^{-1}, 40.0 x 250 mm column, linear M packing, Polymer Standards Service GmbH) afforded to selective isolate the high molecular weight fraction (black solid curve, Figure 1 main text) with a M_n of 56.0 kDa and a PDI of 1.1.

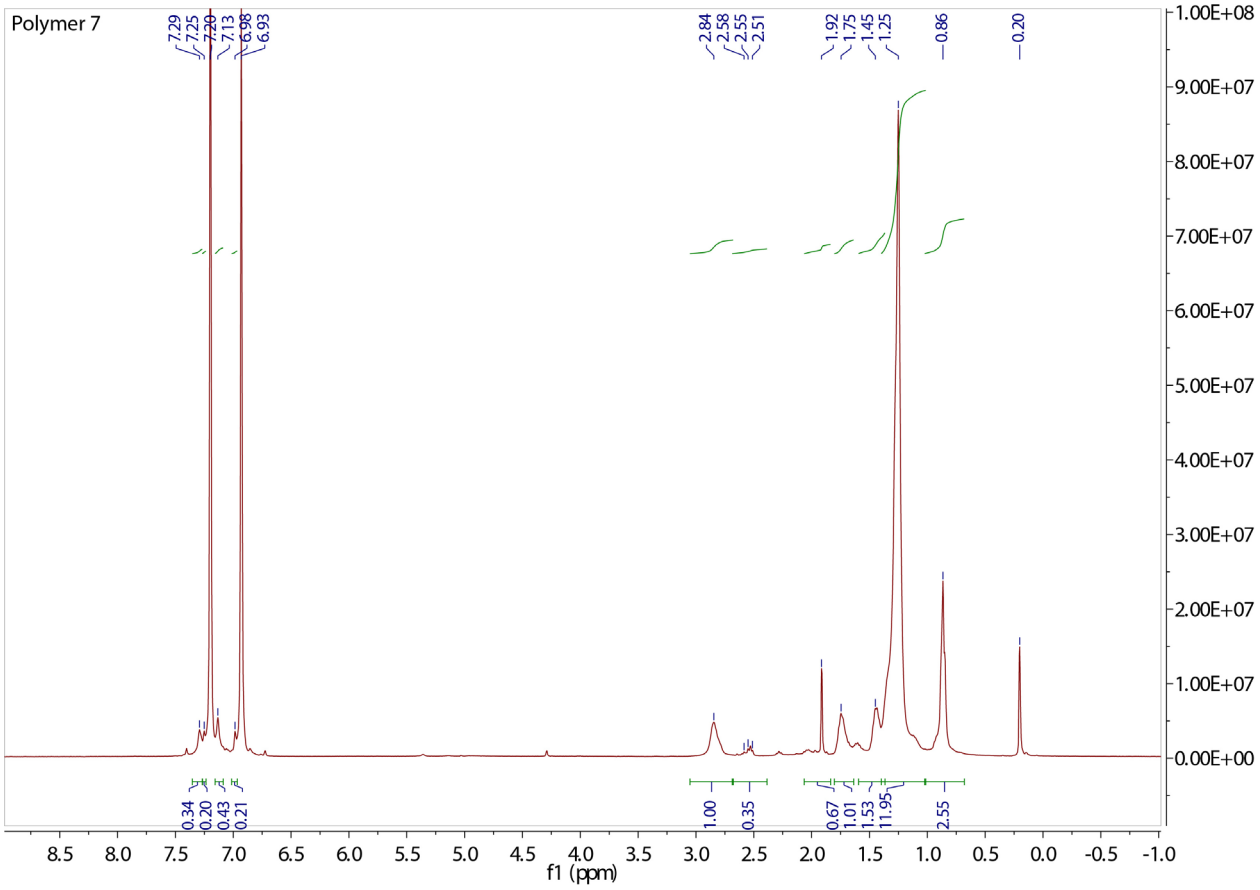

Figure S12. ^{1}H NMR spectrum of compound 7 the FL-PBTTT (in o-dichlorobenzene D_4). NB: Integration of the aromatic region is complicated by solvent peaks.

3. Additional experimental and characterization details

Thermal characterization

Melting temperatures, T_m, and enthalpies of fusion, ΔH_f, were measured with a PerkinElmer DSC8000 differential scanning calorimeter calibrated with indium and zinc, using a scanning rate of 20 °C/min. ΔH_f were calculated from the surface area underneath both melting endotherms. The material was deposited by drop-casting, and once the solvent evaporated, it was directly annealed in the pan at 180 °C for 10 min.

Transistor fabrication

Bottom contact field-effect transistors (FETs) were fabricated on pre-patterned test substrates (purchased from Fraunhofer Institute for Photonic Microsystems IPMS) whose source and drain contacts were composed of a 30 nm thick gold layer on top of a 10 nm thick titanium layer. A 230 nm thick silicon oxide was used as gate dielectric and n-doped silicon crystal as gate electrode. The channel length (L) was 10 or 20 µm and channel width (W) was 10 mm. The transistor substrates were cleaned by

sonication in acetone and isopropanol at RT for 15 min in each solvent. After drying under nitrogen, the substrates were subsequently exposed to a nitrogen plasma for 30 min. All substrates were submerged in 10 mM solution of octadecyltrichlorosilane (OTS) in toluene for 15 min at 75 °C under argon atmosphere to afford the self- assembled monolayer with a measured contact angle of 105°. Polymer films of ~60 nm thickness were spin-coated from 20 mg mL^{-1} solutions in o-DCB at 500 rpm (for 1 min). The polymer solutions were prepared by dissolution at 80 °C for 1h under continuous stirring. All polymer solutions and films were prepared in an argon atmosphere. Annealed films were heated on a hot plate at 180 °C for 20 min and left to cool down slowly to RT. Unannealed films were left overnight under vacuum before testing. Characterization of the OFETs was carried out in a nitrogen atmosphere using a custom-built probe station and a Keithley 2612A dual-channel source measure unit. Field effect mobilities (μ_{sat}) were determined from the current−voltage transfer characteristics in the saturation regime using the following equation:

$$\mu_{sat} = \frac{2L}{WC_i}\left(\frac{\partial\sqrt{I_d}}{\partial V_g}\right)^2 \qquad \text{Eq. 1}$$

Here I_d is the source-drain current, V_g is the gate voltage, C_i is the capacitance per unit area of the gate dielectric (18 nF cm^{-2}). At minimum six transistors were tested for each condition (two substrates and three transistors on each substrate), and the average values are reported with errors corresponding to ±1 standard deviation. The contact resistances in the FET devices were estimated by using a previously published method[4] by using the data obtained from a transistors with a channel length of 10 and 20 µm and extracting the contact resistance for V_g = –60 V.

Morphological characterization

Measurements of X-ray scattering were carried out at the European Synchrotron Radiation Facility on beam line BM02. The incident energy was 11 keV. For grazing incidence X-ray scattering (GIXS), the films were illuminated at a constant incidence angle of 0.15° using a 2D-area detector. AFM characterization was performed with an Asylum Research Cypher in AC mode using Atomic Force AC240TS tips directly on measured transistors surface.

References

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(2) McCulloch, I.; Heeney, M.; Bailey, C.; Genevicius, K.; MacDonald, I.; Shkunov, M.; Sparrowe, D.; Tierney, S.; Wagner, R.; Zhang, W.; Chabinyc, M. L.; Kline, R. J.; McGehee, M. D.; Toney, M. F. *Nat. Mater.* **2006**, *5*, 328.

(3) Saito, S.; Nakakura, K.; Yamaguchi, S. *Angew. Chem. Int. Ed.* **2012**, *51*, 714.

(4) Singh, K. A.; Sauve, G.; Zhang, R.; Kowalewski, T.; McCullough, R. D.; Porter, L. M. *Appl. Phys. Lett.* **2008**, *92*, 263303.