

Supporting Information

Dithienosilole-Based All-Conjugated Block Copolymers Synthesized by a Combination of Quasi-Living Kumada and Negishi Catalyst-Transfer Polycondensations

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Instrumentation

¹H (500.13 MHz) and ¹³C (125.75 MHz) *NMR spectra* were recorded on a Bruker DRX 500 spectrometer at 303 K (unless otherwise noted) using CDCl₃ or C₂D₂Cl₄ as solvent. The ¹H spectra were referenced on the residual solvent peak (7.26 ppm or 5.98 ppm, respectively). The ¹³C spectra were measured in CDCl₃ referenced in the same way (residual solvent peak at 77.0 ppm).

GC/MS measurements were carried out on an Agilent system consisting of the gas chromatograph GC7890A (GC column HP-5MS) and the mass selective detector 5975C inert XL EI/CI (electron impact ionization at 70 eV). The GC oven temperature was set to 50 °C for 2 min and afterwards increased by 12 °C/min up to 280 °C. Helium was used as carrier gas with a flow rate of 1 ml/min and an inlet temperature of 300 °C was adjusted. 1 µl of the sample solution (3mg/ml in THF) was injected with a split of 1:100.

GPC measurements were carried out on a PL-GPC 50 Plus (Polymer Laboratories, USA) normal-temperature size exclusion chromatograph, equipped with refractive index detector and one column ResiPore (Agilent Technologies, USA) and on a second system GPC Series 1200 (Agilent Technologies, USA) with refractive index detector and one column PL MIXED-C (Agilent Technologies, USA). THF was used as eluent and the flow rate was 1 ml/min. Number average molecular weights (M_n) and dispersities ($D_M = M_w/M_n$) of obtained polymers were determined based on calibration with polystyrene standards obtained from Polymer Standards Service (PSS, Germany).

MALDI-TOF mass spectra were recorded on an Autoflex Speed MALDI-TOF-/TOF-TOF-System (Bruker, USA) in reflector mode with a Smartbeam laser (modified Nd:YAG laser). Solutions of the analyte were prepared in THF (1 mg/ml) and dithranol was used as the matrix (10 mg/ml in THF). Equal amounts of both solutions were mixed and spotted onto the MALDI plate.

All electrochemical measurements were performed under an argon atmosphere in a gas-tight three electrode cell with an Autolab PGSTAT101 potentiostat (Metrohm, Filderstadt, Germany) at room temperature. The counter electrode consisted of a platinum plate. As reference electrode a chlorinated silver wire was used (Ag/AgCl) and directly immersed into the electrolyte solution. Gold coated Si-wafer (with a 5nm thick Cr adhesion layer between Au and Si) were used as working electrodes. The gold layers were deposited by physical vapor deposition with a PVD system from Heraeus. The polymer films were deposited by a drop cast process from chlorobenzene solutions (1 mg·ml⁻¹). In all experiments an acetonitrile solution containing 0.1 M NBu₄PF₆ (Sigma-Aldrich, electrochemical grade) was used as the supporting electrolyte. Before each experiment the electrolyte was deaerated by argon bubbling.

Atomic force microscopy was conducted on a Bruker Dimension Icon in Tapping Mode using TESPA AFM probes (42 N/m).

Materials

Dichlorobis(2-ethylhexyl)silane¹, 3,3'-Dibromo-5,5'-bis(trimethylsilyl)-2,2'-bithiophene (**2**)², 2-Bromo-3-hexyl-5-iodothiophene (**6**)³ and the initiator phenyl-(1,2-bis(diphenylphosphino)ethane)nickel bromide PhNi(dppe)Br⁴ were synthesized according to literature procedures. Dry THF was prepared by refluxing over sodium / benzophenone. All other chemicals were ordered from Sigma-Aldrich and used as received.

Syntheses

2,6-Dibromo-4,4-bis(2-ethylhexyl)dithieno[3,2-*b*:2',3'-*d*]silole (**3**)

Under Nitrogen atmosphere and at -100 °C 14 ml (35.0 mmol, 2.06 eq.) of *n*-BuLi (2.5 M in hexanes) were added dropwise to a solution of 7.99 g (17.0 mmol, 1 eq.) **2** in 160 ml of dry THF. After 20 min a solution of 5.53 g (17.0 mmol, 1 eq.) dichlorobis(2-ethylhexyl)silane in 10 ml dry THF was added via syringe, the reaction mixture was warmed to room temperature in a water bath and was stirred for 2 h. At 0 °C 6.70 g (37.4 mmol, 2.2 eq.) of NBS was added in one portion. After stirring in the dark for 14 h the reaction mixture was poured into water and the organic phase was further washed with water and aqueous, saturated NaCl solution, dried over MgSO₄ and concentrated under reduced pressure. The crude material was purified by column chromatography (SiO₂/hexanes) and by Kugelrohr distillation (240 °C, 0.17 mbar), resulting in 7.32 g (74 %) of a yellow oil.

¹H NMR (CDCl₃, 500 MHz)

δ [ppm] = 6.98 (s, 2 H), 1.37 (m, 2 H), 1.30-1.05 (m, 16 H), 0.91 (m, 4 H), 0.84 (t, 6 H), 0.77 (t, 6 H).

¹³C NMR (CDCl₃, 125 MHz)

δ [ppm] = 148.59, 141.95, 132.27, 111.35, 35.81, 35.60, 28.88, 28.83, 22.93, 17.52, 14.08, 10.76.

(6-Bromo-4,4-bis(2-ethylhexyl)dithieno[3,2-*b*:2',3'-*d*]silol-2-yl)zinc(II) chloride (**5**)

To a solution of 0.54 g (0.93 mmol, 1 eq.) **3** in 20 ml dry THF were added 0.34-0.36 ml (0.84-0.89 mmol, 0.9-0.95 eq.) of *n*-BuLi (2.5 M in hexanes) under Nitrogen atmosphere at -100 °C.

After 30 min 0.20 g (1.5 mmol, 1.6 eq.) of dry zinc(II) chloride dissolved in 10 ml dry THF were added via syringe and the mixture was stirred for 15 min in the cold, warmed up to room temperature with a water bath and stirred for additional 1 h. The monomer solution was immediately used for the polymerization.

To investigate the percentage of monometalation via GC/MS a little amount (about 1 ml) was quenched in 2 ml MeOH, diluted with CHCl₃, washed with water and dried over MgSO₄. Finally, the solvents were removed under reduced pressure.

In another experiment it was determined that the conversion from **3** to **5** is nearly 100 %.

Poly(4,4-bis(2-ethylhexyl)dithieno[3,2-*b*:2',3'-*d*]silole (PDTS)

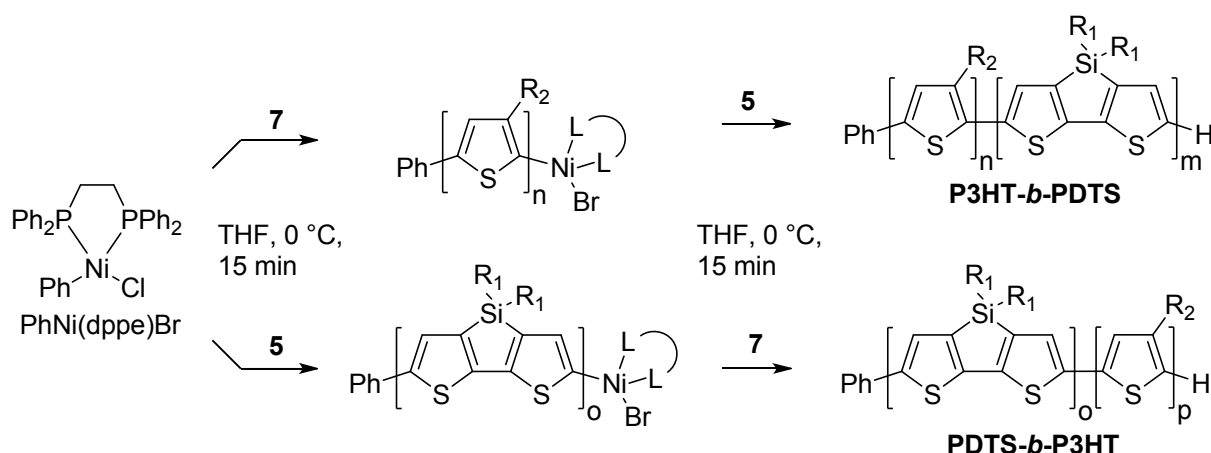
Different feed molar ratios of the initiator phenyl-(1,2-bis(diphenylphosphino)ethane)nickel bromide PhNi(dppe)Br and of the monomer **5** were set (1:20, 1:30, 1:50). The typical synthesis procedure (feed molar ratio 1:50) was as follows:

3.2 mg (5.2 μmol, 1 eq.) PhNi(dppe)Br were dissolved in 3 ml dry THF and transferred into a dried flask with Nitrogen atmosphere. The freshly prepared solution of monomer **5** (synthesized from 0.15 g (0.26 mmol, 50 eq.) **3**) was added via syringe at the desired temperature (in general at room temperature) and the colour changed immediately to dark violet. After 30 min the polymerization was quenched by adding 1 ml HCl (5 M) and the reaction mixture was poured into water. The organic phase was washed with water, dried over MgSO₄ and solvents were removed under reduced pressure. The raw polymers were purified via Soxhlett extraction with methanol, acetone and hexane. The residual was collected with dichloromethane, resulting in 40 mg (37 %) of a dark violet to blueish solid (GPC: $M_n = 25000 \text{ g}\cdot\text{mol}^{-1}$, $M_w = 40000 \text{ g}\cdot\text{mol}^{-1}$, $D_M = 1.60$).

¹H-NMR (C₂D₂Cl₄, 500 MHz, 393 K)

δ [ppm] = 7.64, 7.41, 7.29, 7.26-7.10, 1.55, 1.48-1.17, 1.16-1.03, 1.01-0.80.

Synthesis of the block copolymers



Scheme S1 Preparation of DTS-based block copolymers with different monomer addition order.

A series of BCP was synthesized based on different feed molar ratios of the initiator PhNi(dppe)Br, the 3-hexylthiophene (3HT) monomer **7** and the DTS monomer **5**. A typical procedure with the feed molar ratio 1:50:15 is described below. Additionally, the reverse monomer addition order was also used for the synthesis of PDTS-*b*-P3HT.

The 3HT monomer solution was prepared by dissolving 100 mg (0.27 mmol, 50 eq.) 3-bromo-5-iodo-3-hexylthiophene in 4 ml dry THF, adding 0.27 ml (0.27 mmol, 50 eq.) tert-butylmagnesium chloride solution (1.0 M in THF) at 0 °C and stirring it for 2 h (solution A). The solution of DTS monomer **5** was synthesized as already described using 46 mg (0.08 mmol, 15 eq.) **3** (solution B).

Under Nitrogen atmosphere a solution of 3.3 mg (5.4 μmol, 1 eq.) PhNi(dppe)Br in 1 ml dry THF was cooled to 0 °C and solution A was added in one portion. After stirring for 15 (up to 45) min a little probe was taken to investigate the P3HT block and quenched with 0.1 ml HCl (5 M). Afterwards solution B was added in one portion via syringe and the resulting solution was stirred for 15 (up to 45) min. The reaction was quenched by adding 1 ml HCl (5 M) to the solution followed by the addition of water. The organic phase was washed with water and dried over MgSO₄. After removing the solvents the sample was purified using Soxhlett extraction with methanol, acetone and hexane. The residual was collected with dichloromethane.

The P3HT homopolymer sample was diluted with chloroform and the organic phase was washed with water. After drying with MgSO_4 the solvents were removed under reduced pressure, yielding a dark red solid.

$^1\text{H-NMR}$ ($\text{C}_2\text{D}_2\text{Cl}_4$, 500 MHz, 393 K)

δ [ppm] = 7.60, 7.38, 7.29, 7.16, 7.20 - 7.07, 6.98, 2.81, 1.71, 1.50 - 1.07, 1.00, 0.92, 0.88-0.70.

NMR spectra

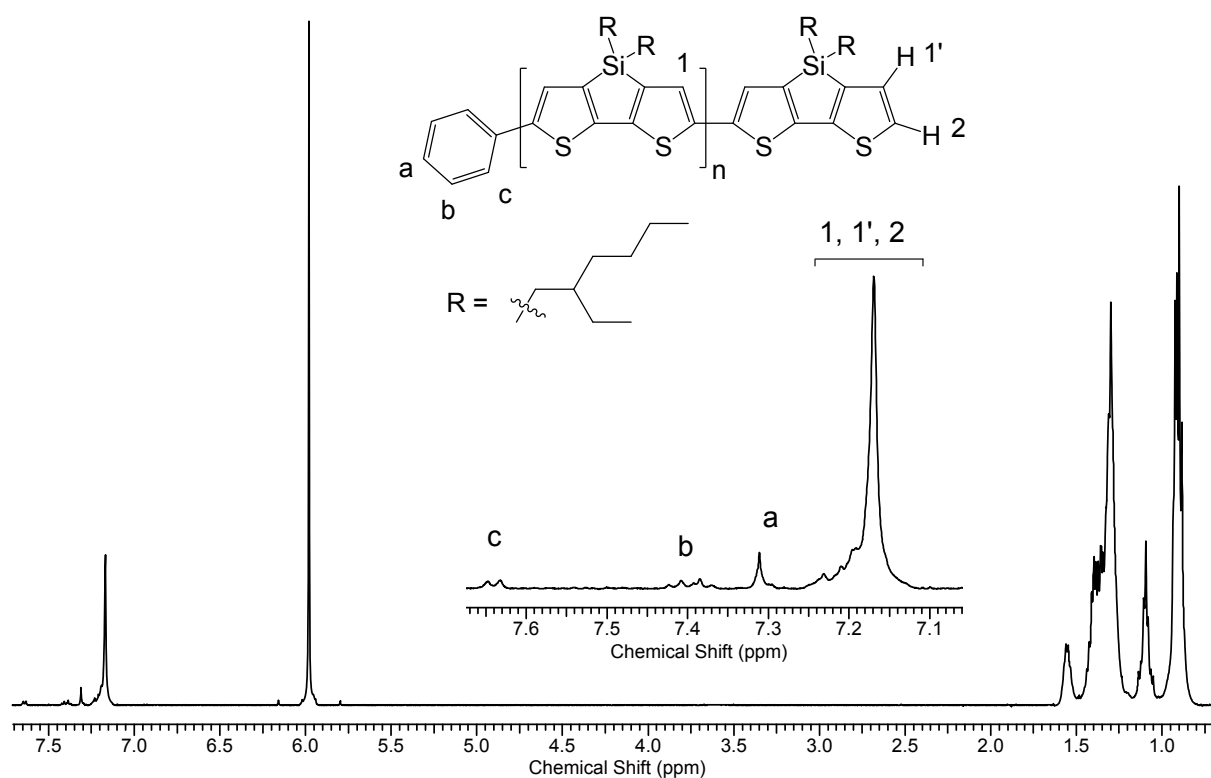


Fig. S1 $^1\text{H-NMR}$ spectra of PDTS (feed ratio $\text{PhNi}(\text{dppe})\text{Br}:\mathbf{5} = 1:50$, $M_n = 25000$ g/mol, $M_w/M_n = 1.60$) in $\text{C}_2\text{D}_2\text{Cl}_4$ at 393 K showing signals of terminal Ph groups (a is overlaid) and signals of the aromatic DTS protons.

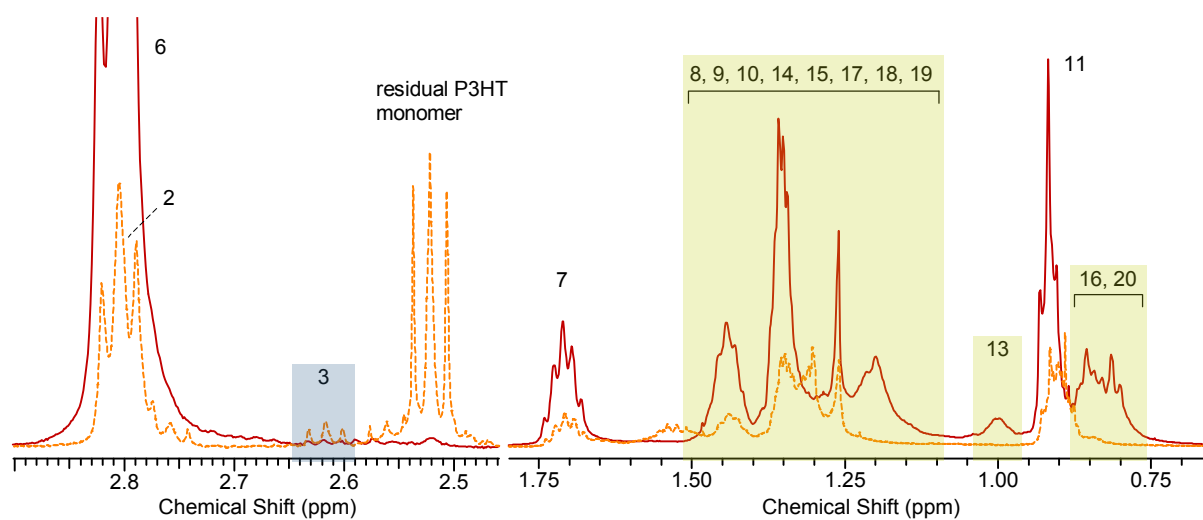
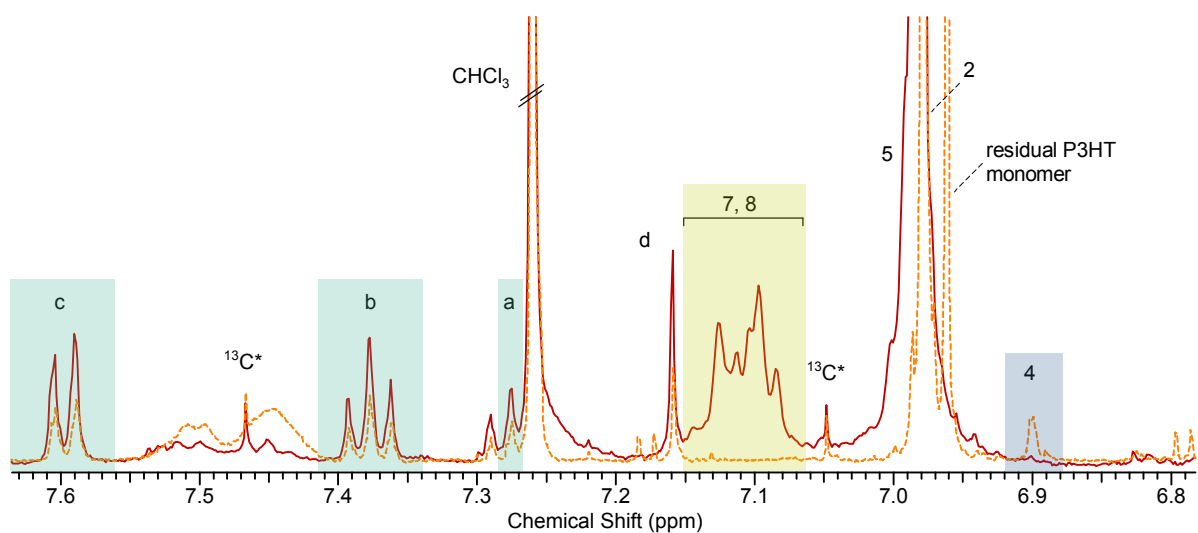
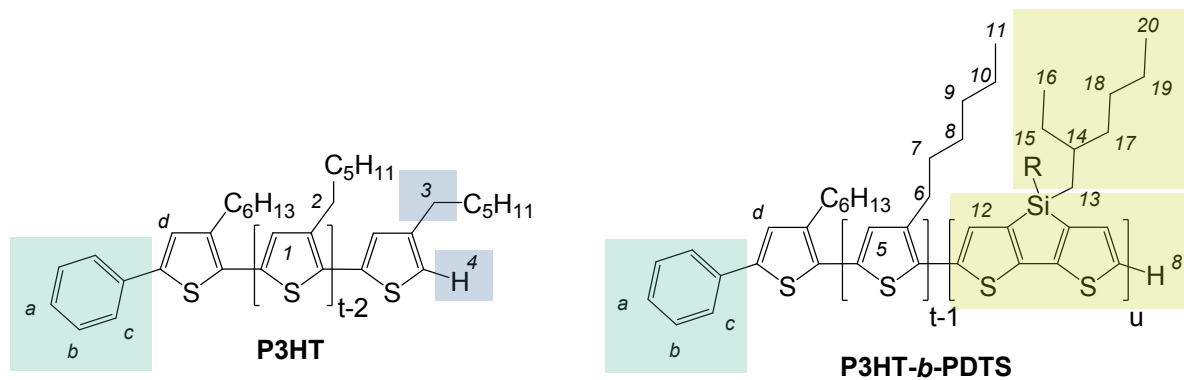


Fig. S2 ¹H-NMR spectra of P3HT macroinitiator (orange, dashed) and resulting block copolymer P3HT-*b*-PDTS (red, solid) in CD₃Cl at 303 K. Disappearing signals of P3HT end groups (3 and 4, grey area) point out the conversion of living P3HT chain ends by the addition of the second monomer 5 as well as the absence of P3HT homopolymer contaminations in the P3HT-*b*-PDTS block copolymer.

GPC measurements

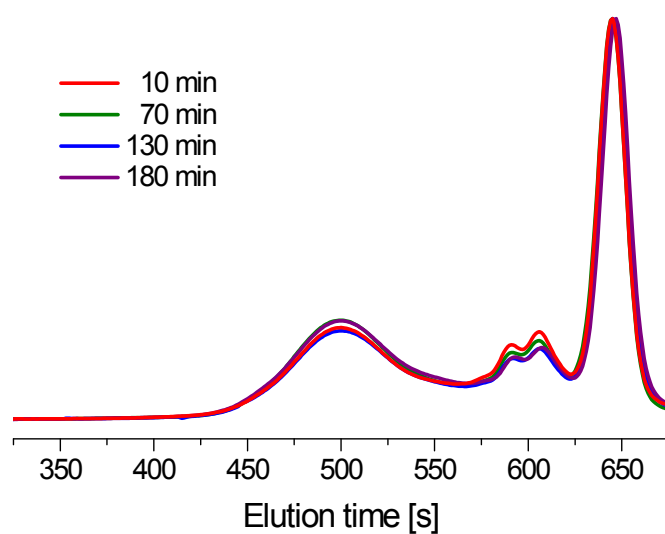


Fig. S3 GPC profiles of samples taken from the PDTS polymerization at room temperature.

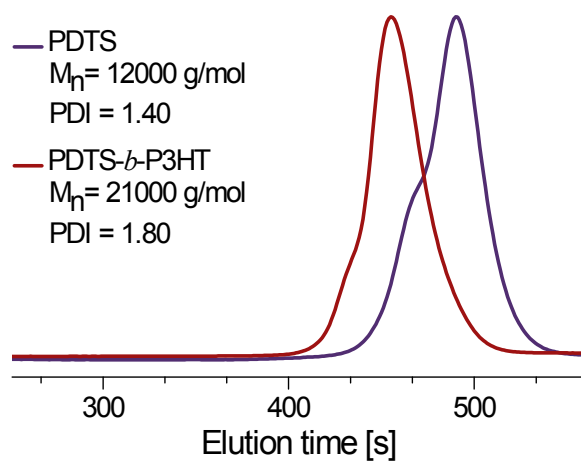


Fig. S4 GPC profiles of samples taken from the block copolymerization of PDTS-*b*-P3HT using the reverse monomer addition order.

Thermal analysis

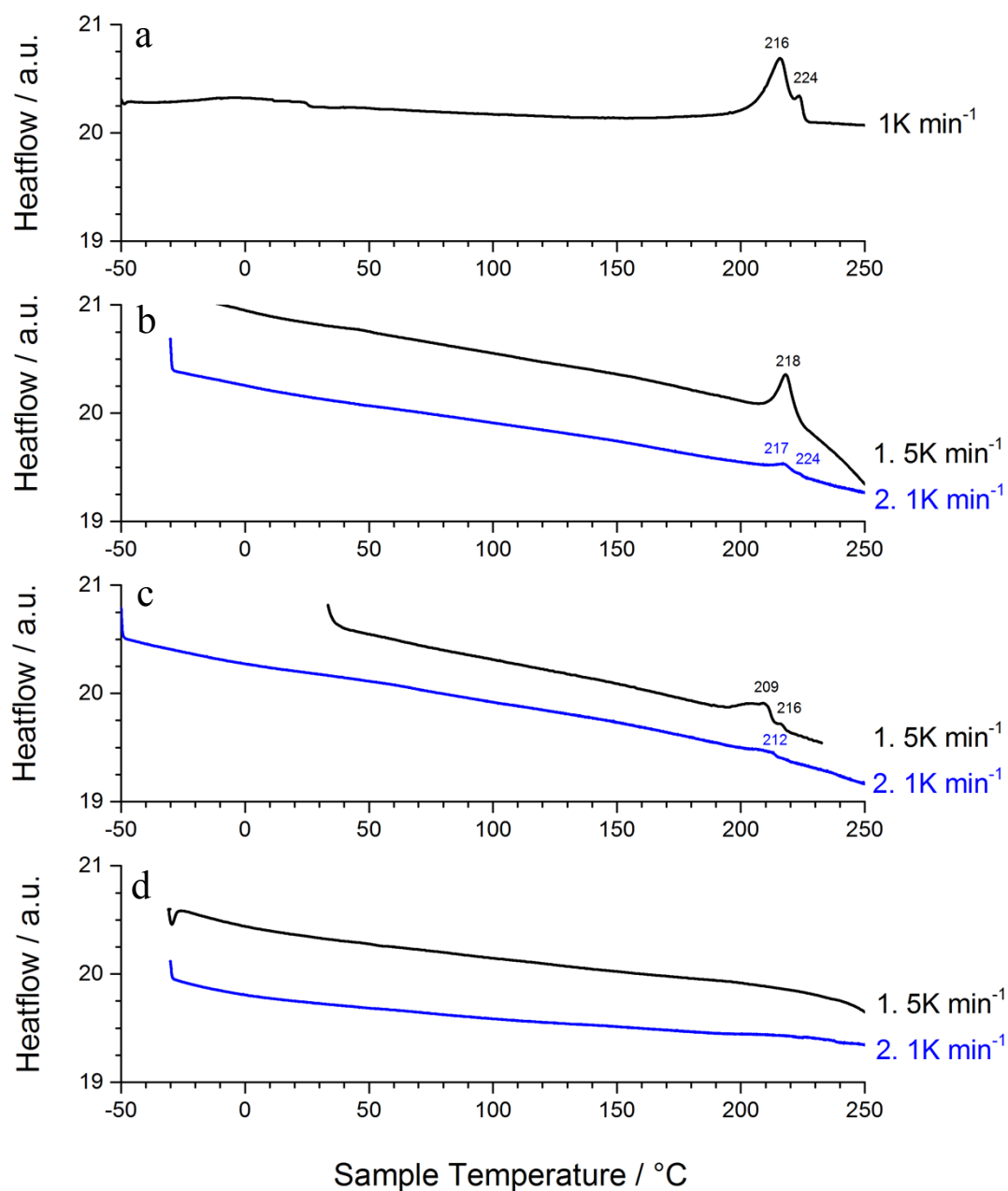


Fig. S5 Differential Scanning Calorimetry (DSC) heating cycles of P3HT-*b*-PDTS (a, b), P3HT macroinitiator (c) and PDTS homopolymer (d). Samples b-d were precrystallized in the DSC vials from a chloroform solution at 70 °C.

Optical properties

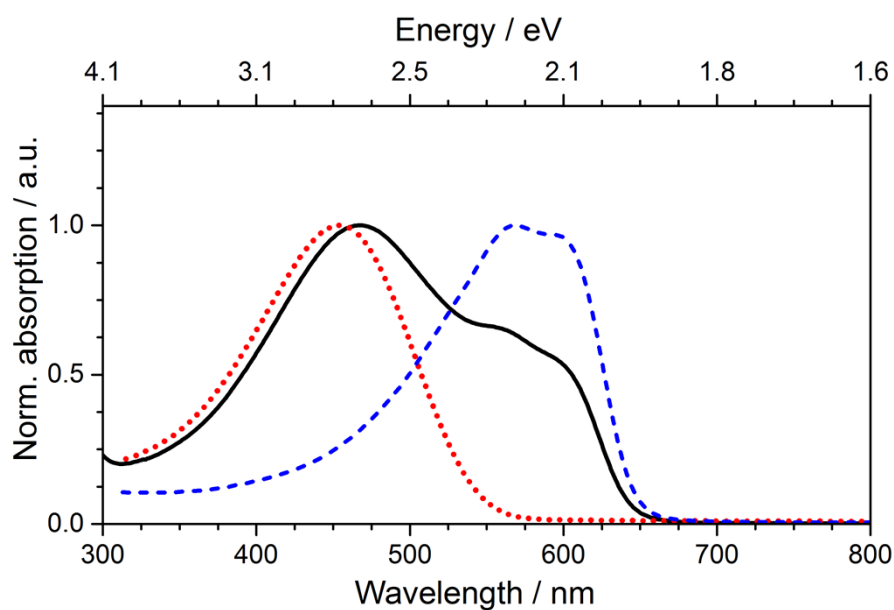


Fig. S6 UV-VIS absorption spectra in chlorobenzene solution ($c = 0.01 \text{ g}\cdot\text{l}^{-1}$): P3HT-*b*-PDTS block copolymer (black, solid line), P3HT macroinitiator (red, dotted line) and PDTS homopolymer (blue, dashed line).

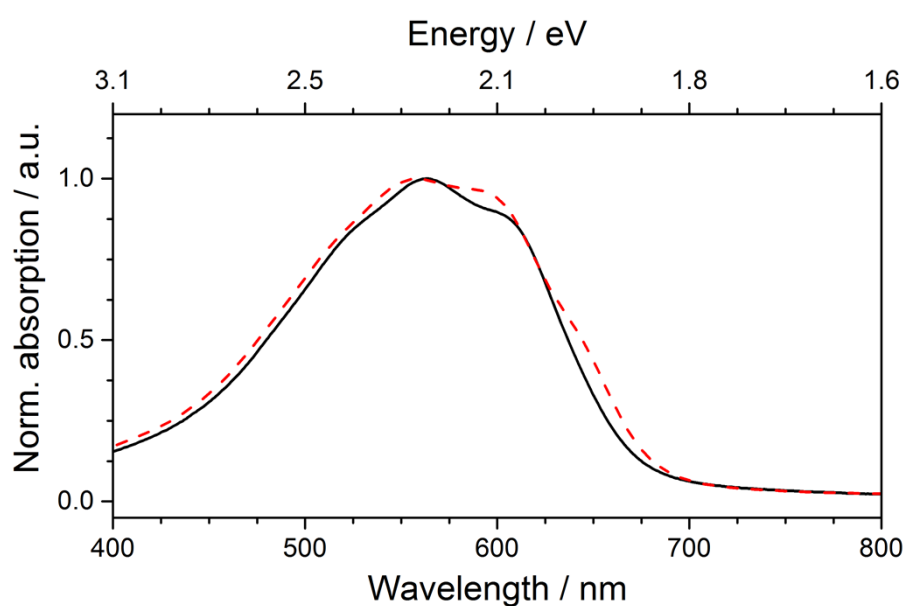


Fig. S7 UV-VIS absorption spectra of P3HT-*b*-PDTS block copolymer (black, solid line) and a film of a P3HT:PDTS blend with weight fractions 57:43 (red, dashed line). Both films were spin-coated from chlorobenzene solution ($c=3 \text{ g}\cdot\text{l}^{-1}$) at 1000 rpm for 20 seconds.

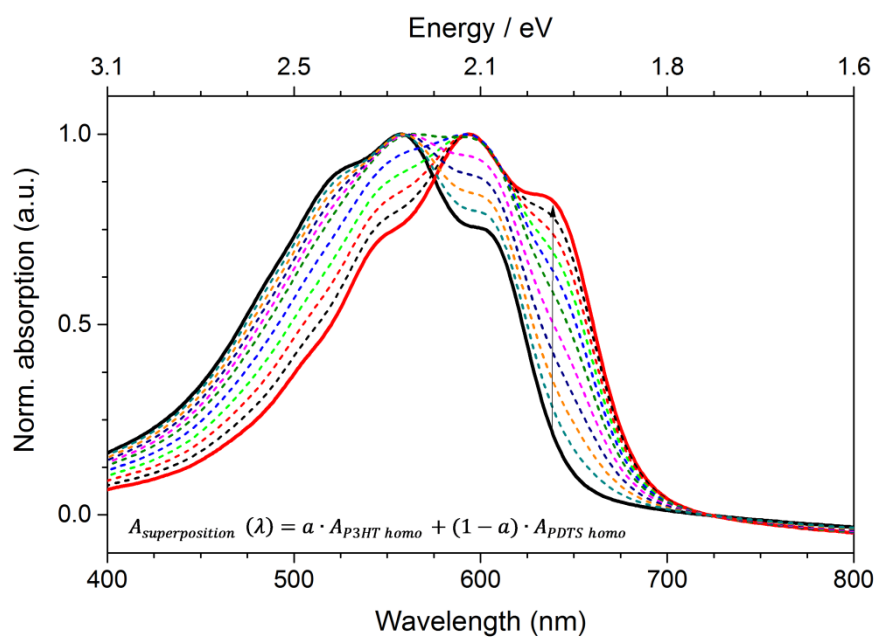


Fig. S8 Normalized UV-VIS absorption spectra of P3HT (black, solid line) and PDTS (red, solid line) thin films spin-coated from chlorobenzene solution ($c = 3 \text{ g}\cdot\text{l}^{-1}$) at 1000 rpm for 20 seconds. Dashed spectra are calculated by addition of the two homopolymer spectra of P3HT and PDTS by changing the weight factor a of P3HT: $a=0.1$ (cyan), $a=0.2$ (orange), $a=0.3$ (navy blue), $a=0.4$ (pink), $a=0.5$ (dark green), $a=0.6$ (blue), $a=0.7$ (light green), $a=0.8$ (red) and $a=0.9$ (black). The formula is shown in the graph.

Cyclic voltammetry measurements

Table S4 Characteristic potential values (E_{CV}^{ox} and E_{CV}^{red}), electrochemical and optical HOMO-LUMO gap of the **P3HT**, **PDTS**, **BCP** and the **P3HT:PDTS** blend. All E are vs. Fc/Fc⁺.

	E_{CV}^{ox} / V	E_{CV}^{red} / V	HOMO / eV	LUMO / eV	band gap / eV ^b	opt. band gap / eV ^c
P3HT	+0.1	-2.3	-5.2	-2.8	2.4	1.9
PDTS	+0.2	-2.1	-5.3	-3.0	2.3	1.7
BCP	+0.1	-2.3	-5.2	-2.8	2.4	1.8
P3HT:PDTS blend	0.0	-2.1 ^a	-5.1	-3.0	2.1	1.8

^a determined from the first cycle of a freshly prepared electrode; chemically irreversible signal.

^b determined according to HOMO = $-(E_{CV}^{ox} + 5.1)$ [eV] and LUMO = $-(E_{CV}^{red} + 5.1)$ [eV].⁵

^c determined from absorption onset of the film spectra.

Atomic force microscopy (AFM)

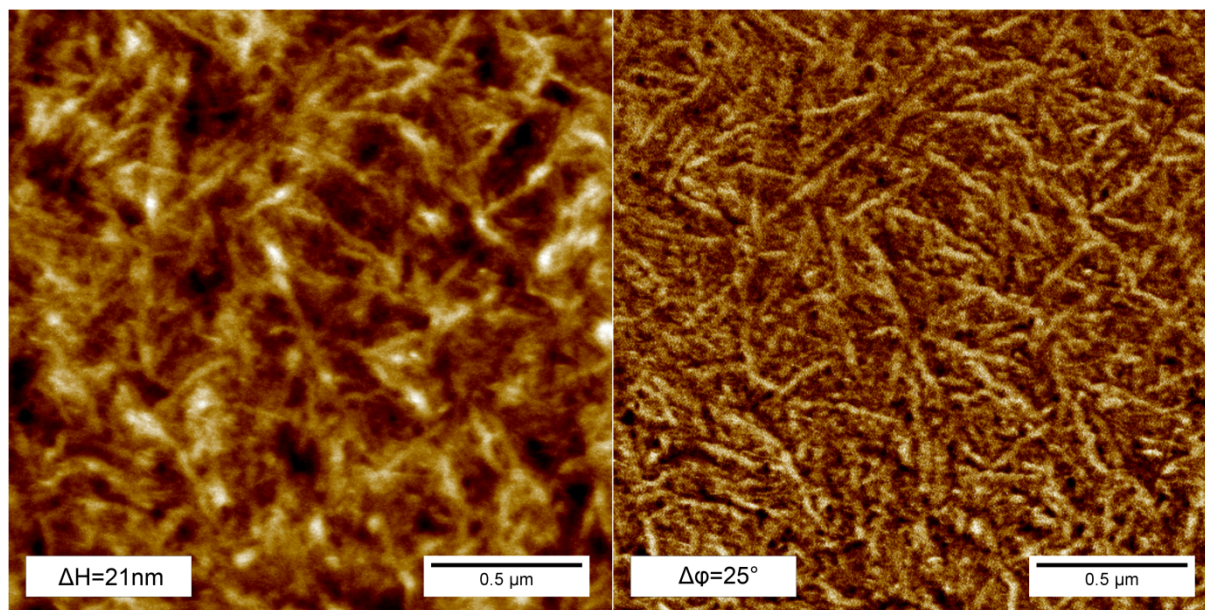


Fig. S9 AFM height and phase image of a 14 nm thin BCP film spincoated on a silicon substrate and post-treated by thermal annealing. Spincoating was performed from chlorobenzene solution (3 gL^{-1}) at 1000 rpm for 20 seconds (acceleration 2 sec.); thermal annealing was performed by heating the film to 235 °C and holding it for 1 minute at this temperature, followed by cooling to 200°C within 2 Kmin^{-1} and holding for another 120 min. The last step included cooling to 30°C with 2 Kmin^{-1} .

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