Electronic Supplementary Information

Direct visualization of microphase separation in block copoly(3-alkylthiophene)s

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Experimental details

Reagents and Instrumentation

All reagents were purchased from Sigma-Aldrich, Acros Organics, Merck, TCI and Alfa Aesar. Tetrahydrofuran (THF) was dried by a solvent purification system MBRAUN SPS 800 (columns with activated alumina). Compounds **3** and **5** were synthesized according to literature procedures.[1] ^{1}H NMR measurements were carried out with a Bruker Avance 300 MHz or 600 MHz. Gel permeation chromatography (GPC) measurements were done with a Shimadzu 10A apparatus with an absorbance detector and a differential refractometer in THF toward polystyrene standards. Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Q 2000 apparatus in Tzero Aluminium Hermatic pans. Indium was used as a calibration reference. Samples were heated from 0°C up to 300°C. Heating and cooling rates of 5°C/min were maintained. The second heating/cooling cycle is used in the analysis. The morphological AFM characterisation was carried out in ambient conditions, with a Bruker Multimode microscope equipped with a Nanoscope V controller. The measurements were carried out in intermittent-contact (‘tapping’) mode, using commercially available silicon probe-tips (PPP-NCHR, Nanosensors GmbH) with a spring constant of 42 N/m, a resonance frequency of about 330 kHz and a typical radius of curvature of the tip apex below 7 nm. The deposits of the polymer for AFM measurements were prepared from solutions in chlorobenzene with a concentration of 0.2 mg/mL. The deposits were generated by dropcasting (±25μL/cm^2) of the solution on ITO-coated glass substrates and allowing the solvent to evaporate overnight in a solvent-saturated atmosphere.

The STM-images have been recorded *in situ* at the interface between a graphite surface and a solution of the polymer in 1,2,4-trichlorobenzene (TCB). The substrate is a freshly cleaved Highly Ordered Pyrolytic Graphite (HOPG). Imaging started 1 minute after sample preparation. Images were acquired using either a PicoLE-III SPM (Agilent) or a Multimode Nanoscope III-d STM (Bruker), both in constant current mode. Platinum/Iridium (80/20%) tips were prepared by mechanical cutting and immersed in the solution at room temperature. Concentrations of the solution range from 1/200 000 and 1/1000 in weight, *i.e.* from 7.31 x 10^{-3} mg/mL to 1.46 mg/mL. For analysis, images of the graphite substrate underneath the monolayer were recorded immediately after recording images of the polymer layer to ensure a good calibration of the distance measurements. For STM imaging parameters, typical bias voltage and set-point current were respectively in the range -700/-1300 mV and 30–400 pA for the polymer, and -100/-400 mV and 100−200 pA in the case of the HOPG. STM data were analyzed with the free WsXM software (Nanotec Electronica, Spain).

Synthesis of P3OT-*b*-P3BT

*i*PrMgCl.LiCl (0.95 mL, 1.316 M) is added dropwise to an argon purged solution of 2-bromo-5-iodo-3-octylthiophene (1.25 mmol, 0.501 g) in dry THF (11.6 mL) and this mixture is allowed to react. After one hour, a small aliquot (0.5 mL) of the reaction mixture is quenched in D_2O to analyze the monomer conversion. The rest of the GRIM mixture (12.0 mL) is cannulated to a flask in which bromo(o-tolyl)bis(triphenylphosphine)nickel (30.0 µmol, 22.6 mg) has been combined with 1,3-bis(diphenylphosphino)propane (60.0 µmol, 24.7 mg) in dry THF (3 mL) and stirred for 10 minutes. At the same time, *i*PrMgCl.LiCl (0.80 mL, 1.316 M) is added dropwise to an argon purged solution of 2-bromo-5-iodo-3-butylthiophene (1.05 mmol, 0.362 g) in dry THF (20.2 mL) and reacted for 1 hour. After a polymerization time of 1 hour, part of the polymerization mixture (2.50 mL) is quenched by cannulating it to a flask containing acidified THF. Subsequently, 20 ml of the 3-butylthiophene monomer solution is added to the rest of the polymerization mixture. The remainder of the 3-butylthiophene monomer mixture (1 mL) is quenched in D_2O to analyze monomer conversion. After an additional block copolymerization time of 2 hours, the polymerization mixture is quenched by the addition of acidified THF. Both the **P3OT** homopolymer and the **P3OT-*b*-P3BT** block copolymer are subsequently precipitated in methanol and filtered off. These polymers are further purified by Soxhlet extraction with methanol and chloroform. The chloroform fraction was concentrated and precipitated in methanol and used for further analysis.

Mass= 248 mg (70%)

^{1}H NMR analysis of the polymers

P3OT homopolymer

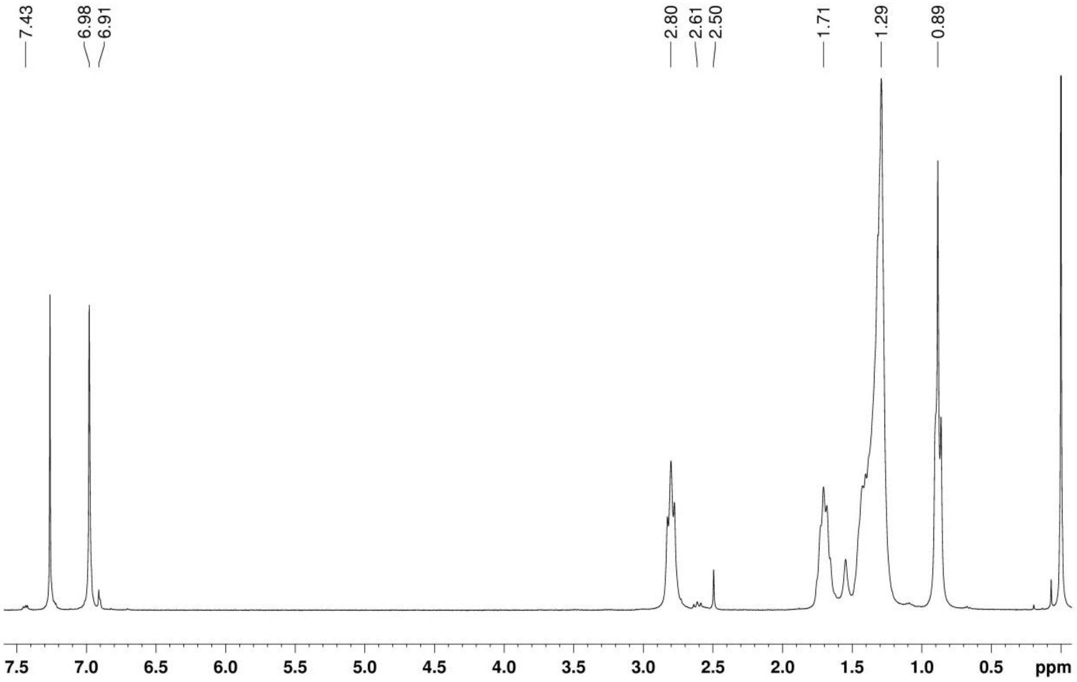

Figure S1. ^{1}H NMR spectrum of **P3OT**.

P3OT-*b*-P3BT block copolymer

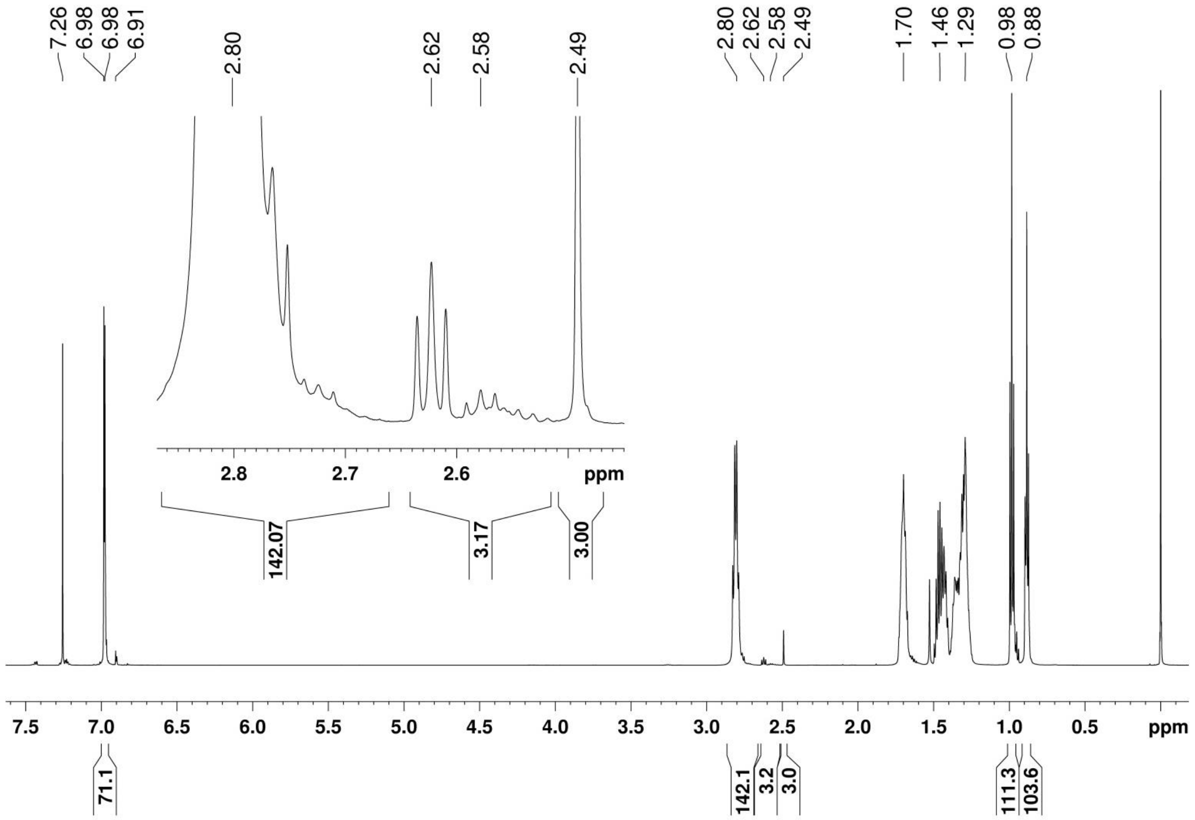

Figure S2. ^{1}H NMR spectrum of **P3OT-*b*-P3BT**.

The inset in the ^{1}H NMR spectrum in Figure S2 contains the α-methylene signals of all end groups of the block copolymer . The singlet at 2.49 ppm accounts for the *o*-tolyl group of the initiator, this signal is calibrated as 3 (as it accounts for 3 H-atoms). In this way, the relative value of all polymer chains initiated with the *o*-tolyl entity corresponds to 1. The total integration value of the other chain end of the block copolymers which are initiated by the *o*-tolyl entity must integrate for 2 (as they account for 2 H-atoms). However, the total integration value of the other chain ends integrate for 3.17. This means that there are chain ends which correspond to block copolymer chains which are not initiated with the *o*-tolyl entity and they account for an integration value of 1.17. This integration value concerns 2 chain ends with 2 H-atoms per chain end, therefore the relative value corresponding to the amount of chains which are not initiated by the *o*-tolyl entity is obtained by dividing the integration value by 4, resulting in a value of 0.2925. From these values, the relative amounts of the different initiated block copolymers can be calculated:

Chains initiated with the *o*-tolyl entity:

$$\frac{1}{1+0.2925} \times 100 = 77.4\%$$

Chains not initiated with the *o*-tolyl entity:

$$\frac{0.2925}{1+0.2925} \times 100 = 22.6\%$$

The 77.4% of the block copolymer chains with the *o*-tolyl entity is exclusively composed of A-B diblock copolymers. A fraction of the other 22.6% of the block copolymers, however consists out of B-A-B triblock copolymer contaminants. The percentage hereof can be readily calculated based on the 'nickel chain walking' theory developed by Kiriy and applied by us.[1,2] This theory states that a polymer chain has a certain probability to grow unidirectional or bidirectional, depending on the chain length (N for the 1st block and M for the 2nd block) and the type of monomer used, through the 'stickiness' parameter (δ) which is equal to 0.73 in the case of 3-octylthiophene.[1] In the block copolymer chains without *o*-tolyl entity, there are four possible ways in which the polymers can be formed (Table S1)

Table S1. The four different possibilities in which a block copolymer without the *o*-tolyl function can grow.

Case	1st block (octyl)	2nd block (butyl)	A-B or B-A-B?
a	uni	uni	A-B
b	bi	uni	A-B
c	bi	bi	B-A-B
d	uni	bi	B-A-B

P(N) is defined as the probability that the 1st block grows in a unidirectional manner.

$$P(N) = N^{\delta-1} = 27^{0.73-1} = 0.41$$

P(N+M) is defined as the probability that the 1st and the 2nd block grow in a unidirectional manner.

$$P(N+M) = (N+M)^{\delta-1} = 56^{0.73-1} = 0.34$$

Combining these parameters, four equations can be constructed:

$$P(N) = a + d$$

$$1 - P(N) = b + c$$

$$P(N + M) = a$$

$$\frac{P(N + M)}{P(N)} = a + b$$

From these equations, the probabilities of the four cases a-d can be calculated:

$$a = P(N + M) = 0.34$$

$$b = \frac{P(N + M)}{P(N)} - a = \frac{0.34}{0.41} - 0.34 = 0.49$$

$$c = 1 - P(N) - b = 1 - 0.41 - 0.49 = 0.10$$

$$d = P(N) - P(N + M) = 0.07$$

The sum of cases A-D account for 22.6%, rescaling these probabilities results in the following total percentages:

$$a = 0.34 \times 22.6\% = 7.68\%$$

$$b = 0.49 \times 22.6\% = 11.1\%$$

$$c = 0.10 \times 22.6\% = 2.26\%$$

$$d = 0.07 \times 22.6\% = 1.58\%$$

Finally, from these total percentages the amount of A-B and B-A-B block copolymers can be calculated:

$$\%_{A-B} = \%_{o-tolyl} + \%_{a} + \%_{b} = 77.4\% + 7.68\% + 11.1\% = 96.2\%$$

$$\%_{B-A-B} = \%_{c} + \%_{d} = 2.26\% + 1.58\% = 3.8\%$$

DSC measurements

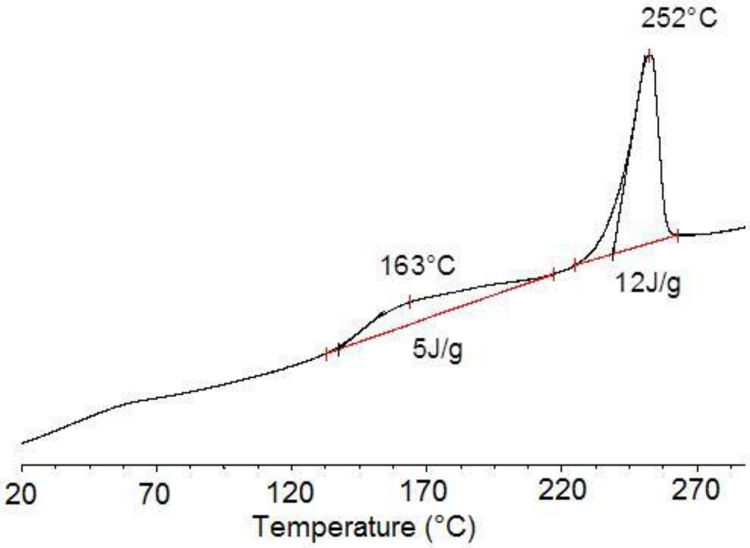

Figure S3 DSC melting transitions observed of **P3OT-*b*-P3BT**.

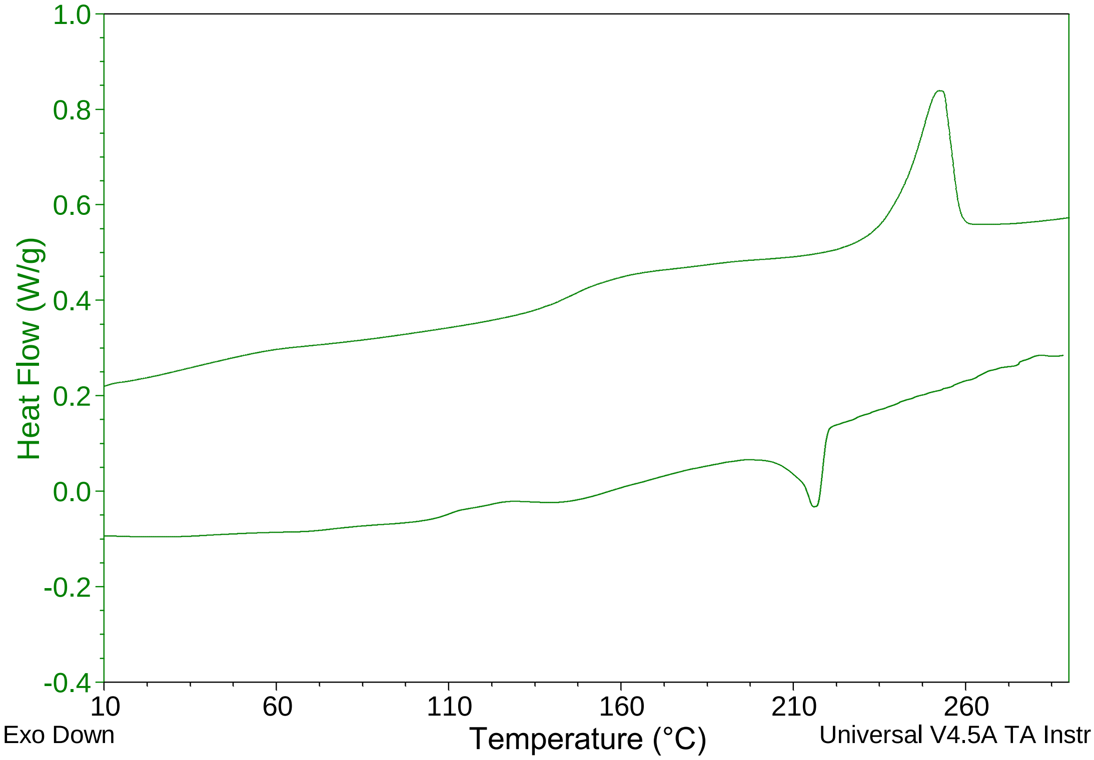

Figure S4. DSC spectrum of **P3OT-*b*-P3BT**

AFM measurements

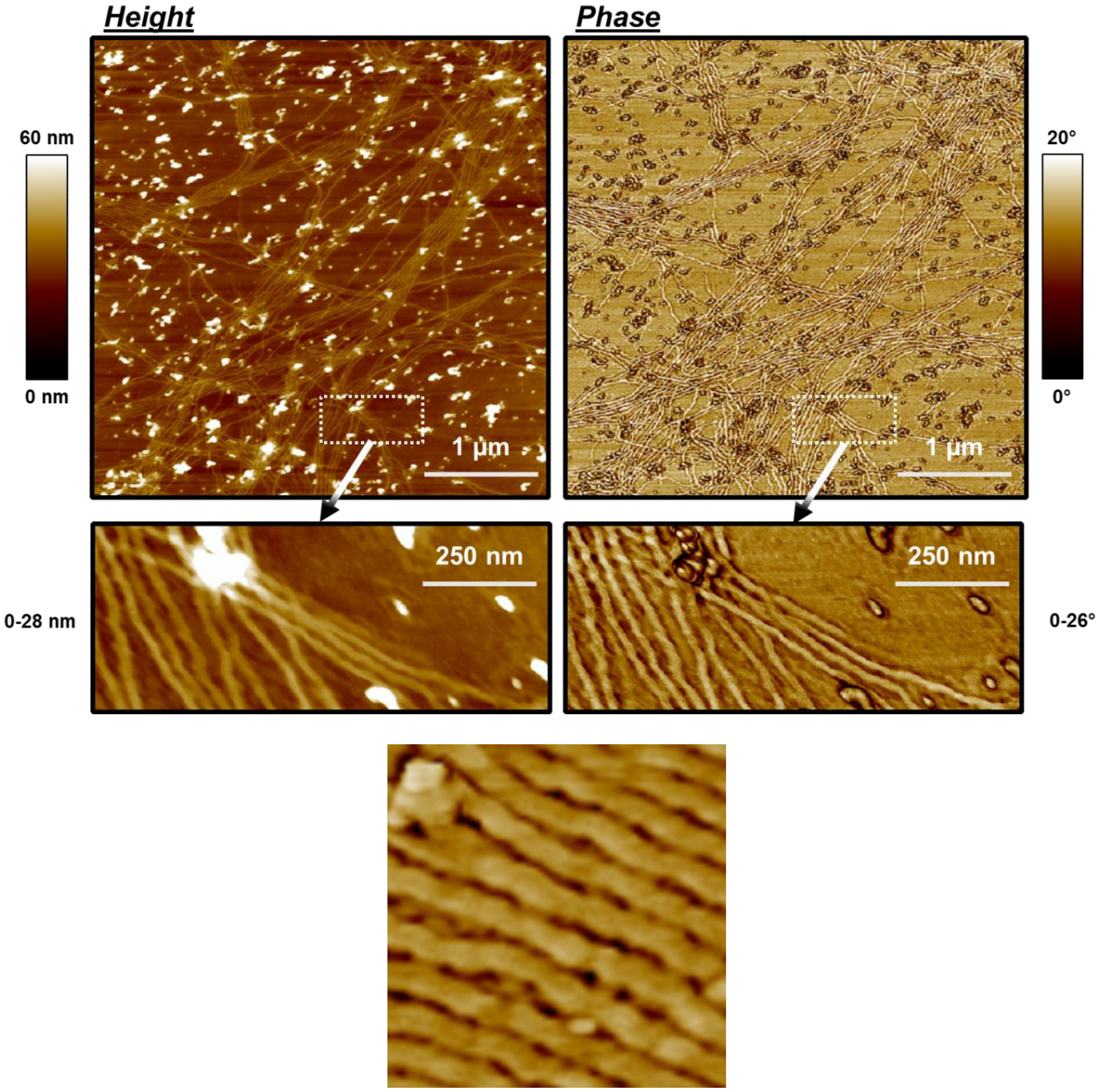

Figure S5. (up) Tapping-mode AFM height (left) and phase (right) images of a **P3OT-*b*-P3BT** thin deposit on a ITO-glass substrate. (down) Zoom (300 nm x 300 nm) of a phase image.

STM measurements

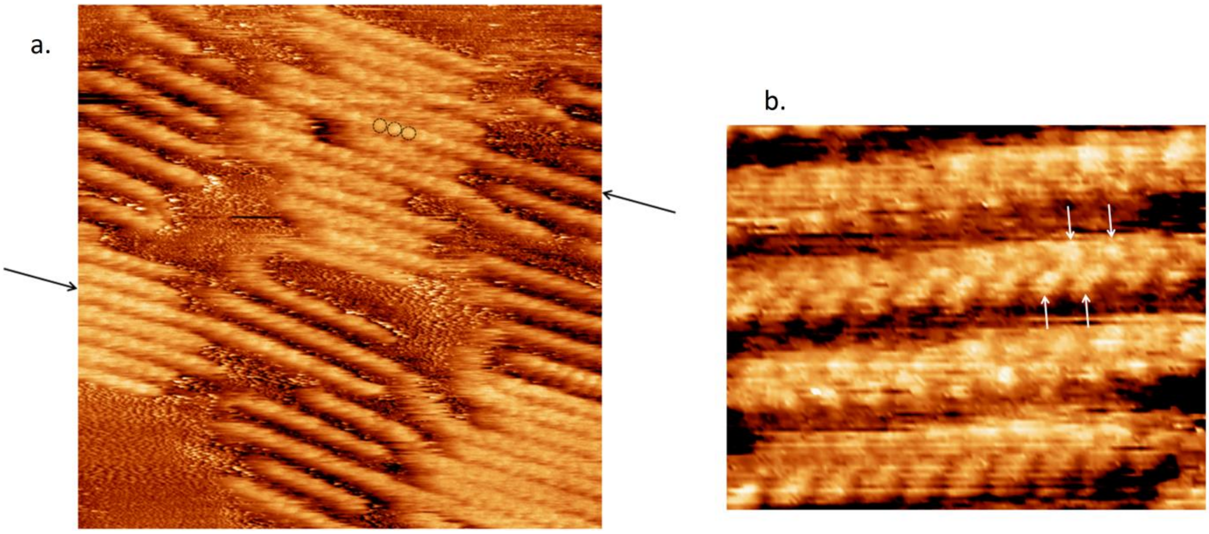

Figure S6. High resolution STM images of the block copolymer solution in TCB (c=7.31 x 10^{-3} mg/mL) on HOPG (a) 70 x 70 nm², black arrows indicate single molecules present in two blocks. (b) 8.7 x 7 nm², some bright spots, attributed to individual thiophene units are indicated by white arrows. Parameters of imaging: (a) I_t = 25 pA and V_t = -1100 mV. (b) I_t = 300 pA and V_t = -800 mV.

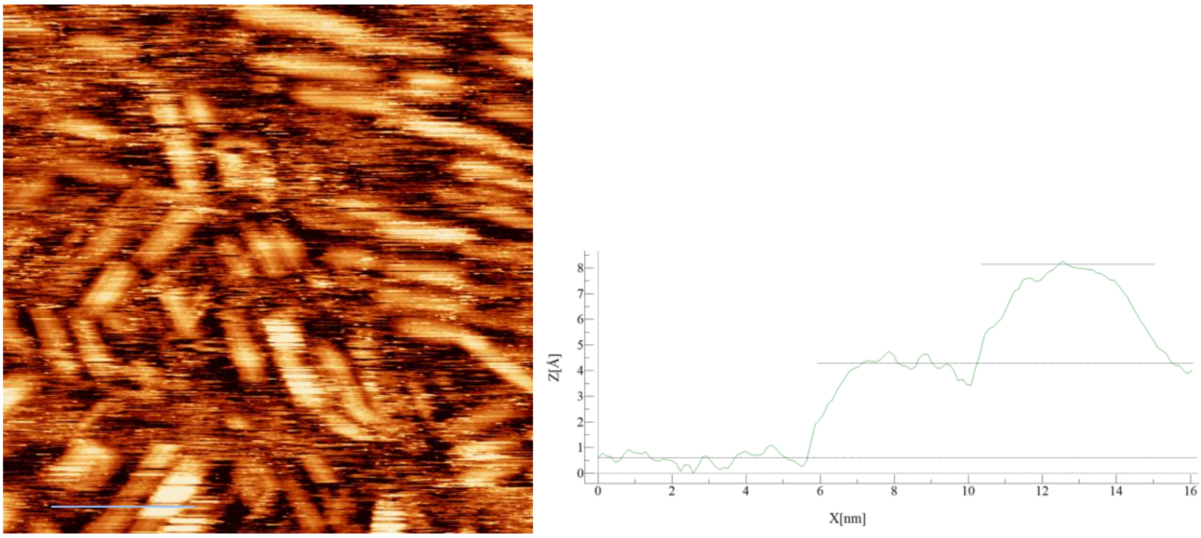

Figure S7. STM image (60 x 60 nm²) of the block copolymer solution in TCB (c= 1.46 mg/mL) on HOPG and the height profile corresponding to the blue line on the image. Parameters of imaging: I_t= 400 pA; V_t= -770 mV. The same orientations as the monolayer are maintained in subsequent layers. The thicker films are relatively homogeneous since the difference between the highest and the lowest corresponds to the height of two layers.

References

1. M. Verswyvel, F. Monnaie, and G. Koeckelberghs, *Macromolecules*, 2011, **44**, 9489–9498.

2. R. Tkachov, V. Senkovskyy, H. Komber, J.-U. Sommer, and A. Kiriy, *J. Am. Chem. Soc.*, 2010, **132**, 7803–7810.