

Macroscopic Vertical Alignment of Nanodomains in Thin Films of Semiconductor Amphiphilic Block Copolymers

Supporting information

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Experimental

Synthesis of monomers

1. Synthesis of N,N'-bis(4-methoxyphenyl)-N-phenyl-N'-4-azidophenyl-(1,1'-biphenyl)-4,4'-diamine dimethoxy triphenyl diamine (DMTPD-N₃ 6):

Starting material for the synthesis was the DMTPD-aldehyde which was synthesized according to literature procedures published elsewhere.²

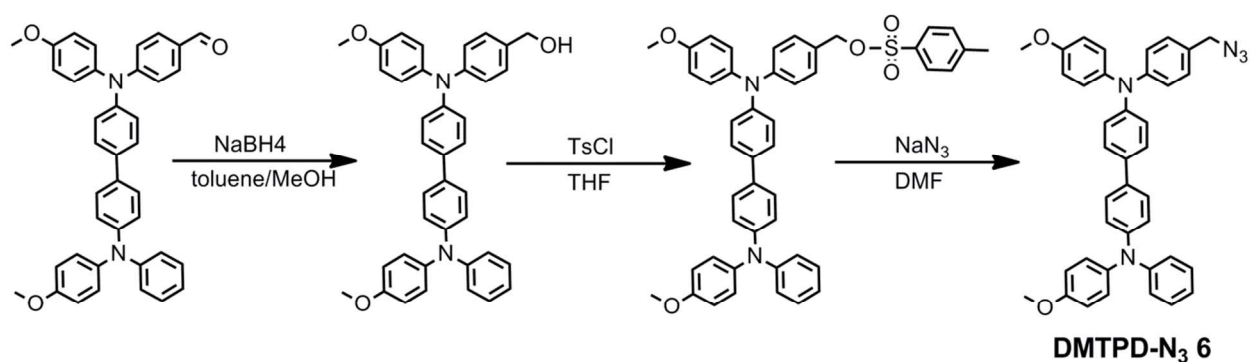


Figure S1. Synthesis of an azide carrying DMTPD-N₃ 6 starting from the DMTPD-mono aldehyde.

Dimethoxy triphenyl diamine alcohol (DMTPD-OH)

DMTPD-aldehyde (0.72 g, 1.3 mmol) was dissolved in 15 mL of a 1:1 mixture of dry toluene and dry ethanol under inert gas atmosphere. NaBH₄ (95 mg, 2.50 mmol) was added and the reaction was stirred for 2h at RT. The progress of the reaction was controlled by thin film chromatography. The solvents were evaporated, the residue was washed with H₂O two times, filtered and dried. The light yellow powder weighed 720 mg (99.5%). ¹H NMR (300 MHz, DMSO-d₆): δ (ppm) 7.52-6.83 (m, 24 H, ArH), 5.11 (t, 1 H, *J* = 5.2 Hz, CH₂OH), 4.43 (d, 2H, *J* = 4.0 Hz, CH₂OH), 3.74 (s, 6H, OCH₃).

Dimethoxy triphenyl diamine tosylate (DMTPD-Tos)

DMTPD-OH (579 mg, 1.00 mmol) was dissolved in 15 mL of THF under inert gas atmosphere. Triethylamine (0.7 mL) was added to the solution which was stirred for 10 min. Subsequently, tosylchloride (1.91 g, 10.0 mmol) was added and the reaction was stirred for 24 h at RT. The solvents were evaporated, dissolved in CHCl_3 and washed with a solution of NH_4Cl in H_2O . The organic phase was dried with sodium sulphate, filtered and evaporated. The raw product was further purified by column chromatography over silica cyclohexane:ethyl acetate 2:1 to remove side products. The pure fraction was flushed from the column with DCM:MeOH 1:1 afterwards. The fractions containing the product were evaporated. The light yellow powder weighed 558 mg (76.1%). ^1H NMR (300 MHz, DMSO-d_6): δ (ppm) 7.61-6.83 (m, 28H, ArH_{TPD} , $\text{ArH}_{\text{Tosyl}}$), 4.36 (s, 2H, CH_2O), 3.76 (s, 6H, OCH_3), 2.10 (s, 3H, ArCH_3).

Dimethoxy triphenyl diamine azide (DMTPD- N_3 6)

DMTPD-Tosylat (550 mg, 0.75 mmol) was dissolved in dry DMF under inert gas atmosphere. NaN_3 (97 mg, 1.50 mmol) was added and the reaction was heated to 100°C for 3 h. After cooling to RT the reaction was quenched with 10 mL of H_2O . The product was extracted with CHCl_3 , the organic phase was dried with sodium sulfate, filtered and evaporated. For further purification, the compound was cleaned by column chromatography over silica with a gradient of hexanes:ethyl acetate 9:1 to 5:1. The product was obtained as a light yellow powder and weighed 330 mg (72.8%). ^1H NMR (300 MHz, DMSO-d_6): δ (ppm) 7.56-6.88 (m, 24H, ArH), 4.36 (s, 2H, CH_2N_3), 3.75 (s, 6H, OCH_3).

2. Synthesis of 2,2,2-trifluorethyl 4-vinylbenzenesulfonate (TfeSS 3):

Under Argon, Sodium styrenesulfonate (10 g, 43.6 mmol) was added in small portions to thionyl chloride (15.93 ml, 218 mmol) with 10 min at 0°C while stirring. To the resulting suspension DMF (22 ml) was added dropwise under cooling. The reaction system became homogeneous and it was stirred for 3 h at RT. The mixture was poured into ice water to quench unreacted thionyl chloride. The organic layers were extracted with diethyl ether and washed with 2% HCl solution and water repeatedly. The mixture was dried over sodium sulfate and the solvent was removed under reduced pressure. The product 4-vinylbenzene-1-sulfonyl chloride (8.5 g, yield: 96%) was immediately freeze-dried to suppress the hydrolysis of the sulfonyl chloride and was used without further purification.

2,2,2-Trifluorethanol (3.42 ml, 45.3 mmol) and triethylamine (6.43 ml, 46.1 mmol) was dissolved in CH₂Cl₂ (41.9 ml) and cooled to 0°C. Styrene sulfonyl chloride (8.5 g, 41.9 mmol) was dropwise added to the solution and kept for 2 h at 0°C. After stirring at RT overnight the reaction mixture was washed twice with water and the organic layer was dried over sodium sulphate. The solvent was removed under reduced pressure and the raw product was purified by column chromatography (DCM:pentane 1:2) to obtain 10 g (90%) of a viscous oil, which crystallized at 4°C.

Size exclusion chromatography (SEC)

Eluent: pure THF

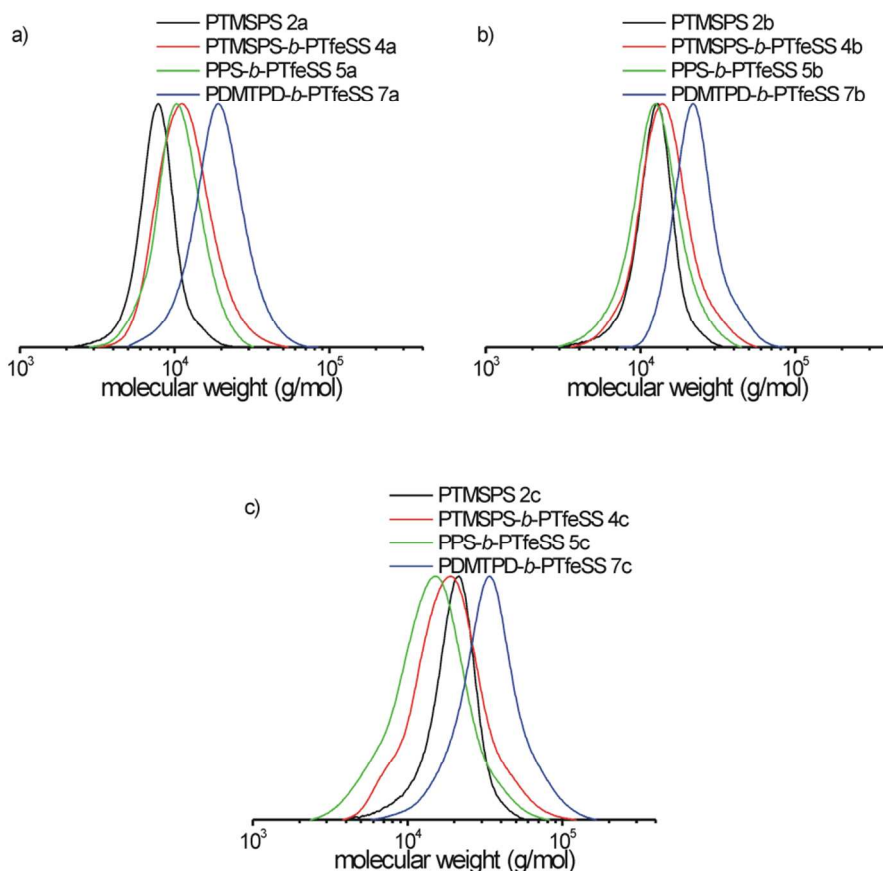


Figure S2. Normalized SEC traces of the intermediate steps to the different polymers PDMTPD-b- $\text{PEt}_3\text{NH}^+\text{SS}$ **8a** (a), PDMTPD-b- $\text{PEt}_3\text{NH}^+\text{SS}$ **8b** (b) and PDMTPD-b- $\text{PEt}_3\text{NH}^+\text{SS}$ **8c** (c). PTMSPS **2**: black, PTMSPS-b-PTfeSS **4**: red, PPS-b-PTfeSS **5**: green and PDMTPD-b-PTfeSS **7**: blue. The final polymers PDMTPD-b- $\text{PEt}_3\text{NH}^+\text{SS}$ could not be measured in SEC, due to a strong interaction of the polyelectrolyte with the column material. The eluent was THF and the SEC was calibrated according to polystyrene standards.

Eluent: THF with 0.25% tetrabutylammoniumbromide

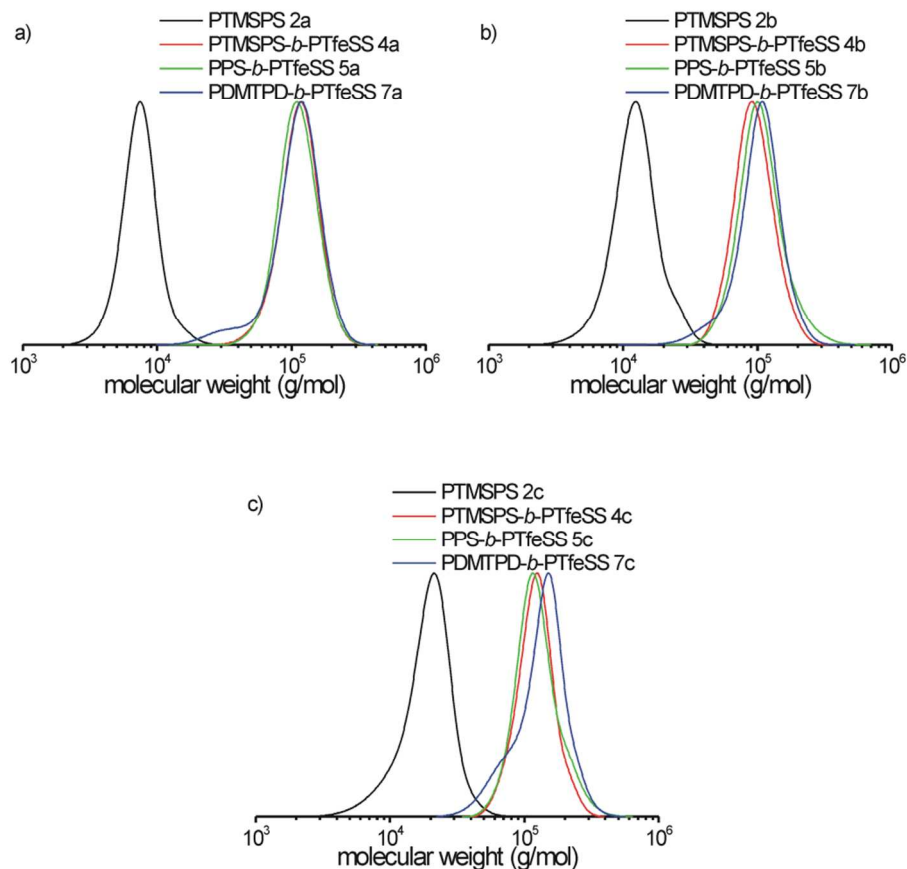


Figure S3. Normalized SEC traces of the intermediate steps to the different polymers PDMTPD-b- $\text{PEt}_3\text{NH}^+\text{SS}$ **8a** (a), PDMTPD-b- $\text{PEt}_3\text{NH}^+\text{SS}$ **8b** (b) and PDMTPD-b- $\text{PEt}_3\text{NH}^+\text{SS}$ **8c** (c). PTMSPS **2**: black, PTMSPS-b-PTfeSS **4**: red, PPS-b-PTfeSS **5**: green and PDMTPD-b-PTfeSS **7**: blue. The final polymers PDMTPD-b- $\text{PEt}_3\text{NH}^+\text{SS}$ could not be measured in SEC, due to a strong interaction of the polyelectrolyte with the column material. Here, the eluent was THF with 0.25% tetrabutylammoniumbromide and the SEC was calibrated according to polystyrene standards.

Differential scanning calorimetry (DSC)

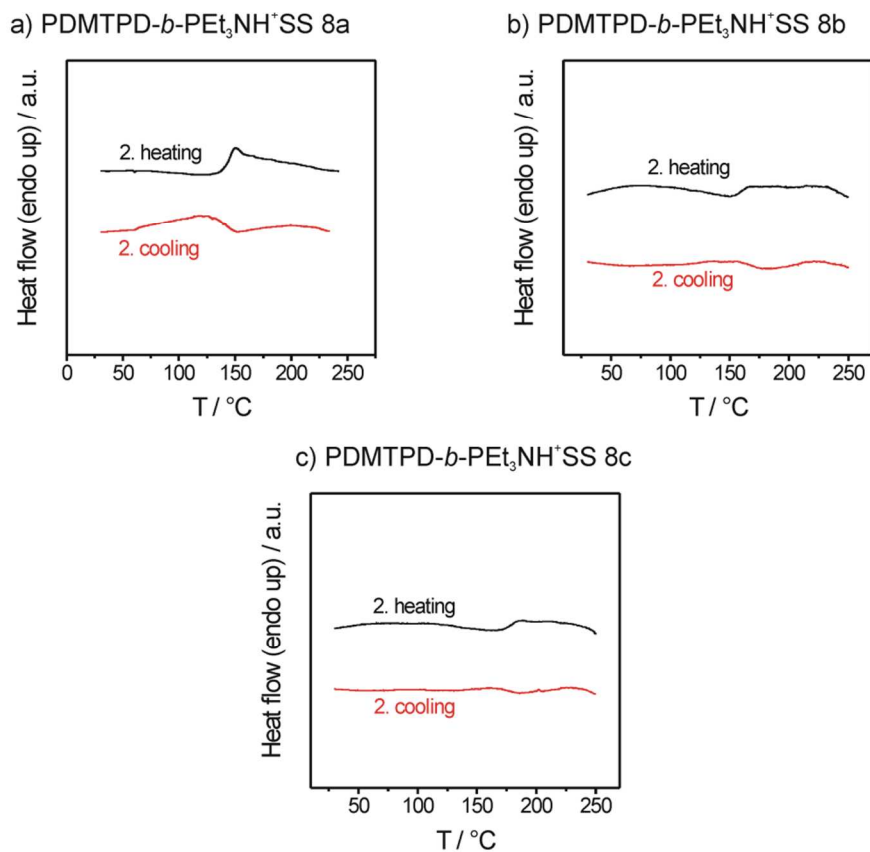


Figure S4. Differential scanning calorimetry (DSC) traces of the polymers PDMTPD-*b*-PEt₃NH⁺SS **8a** (a), PDMTPD-*b*-PEt₃NH⁺SS **8b** (b) and PDMTPD-*b*-PEt₃NH⁺SS **8c** (c) measured at 10 K/min. The individual polymers show only one T_g at 144 °C (a), 162 °C (b) and 178 °C (c) respectively.

Cryo-TEM

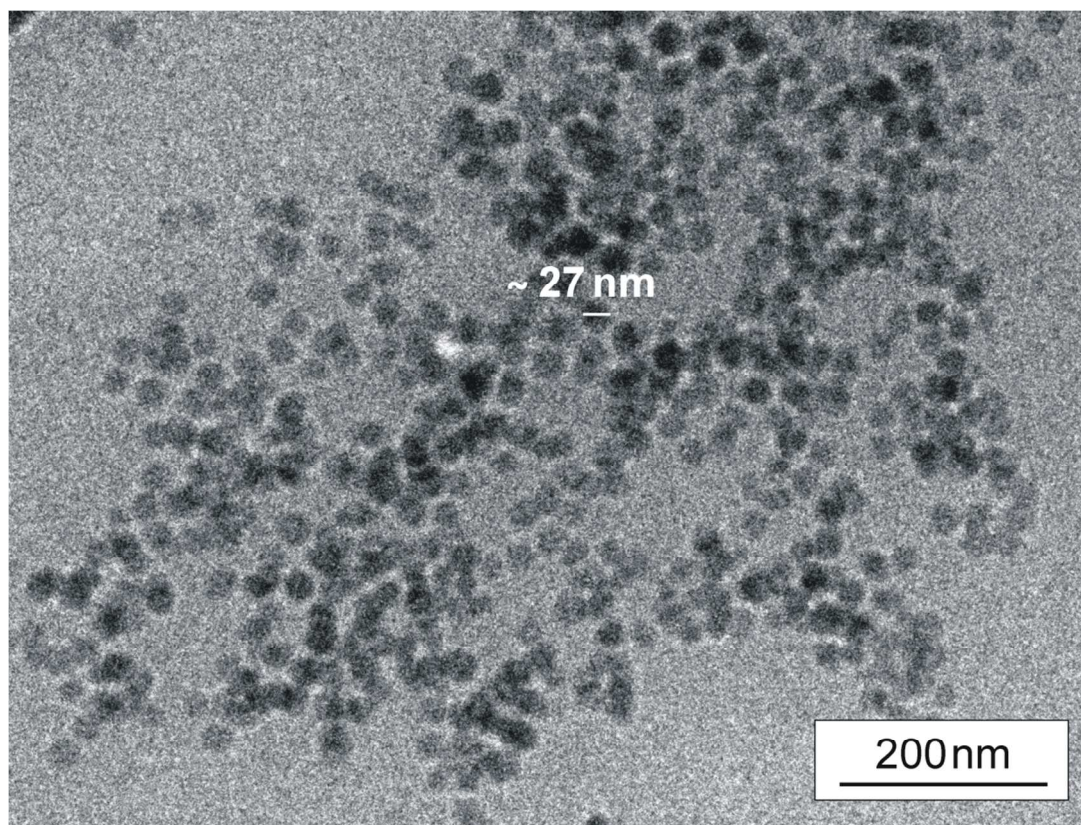


Figure S5. Typical Cryo-transmission electron micrograph of a 1 wt% solution of PDMTPD-b- $\text{PEt}_3\text{NH}^+\text{SS}$ **8c** in DMF.

Grazing incident small angle X-ray scattering (GISAXS)

Full scattering patterns of as cast samples:

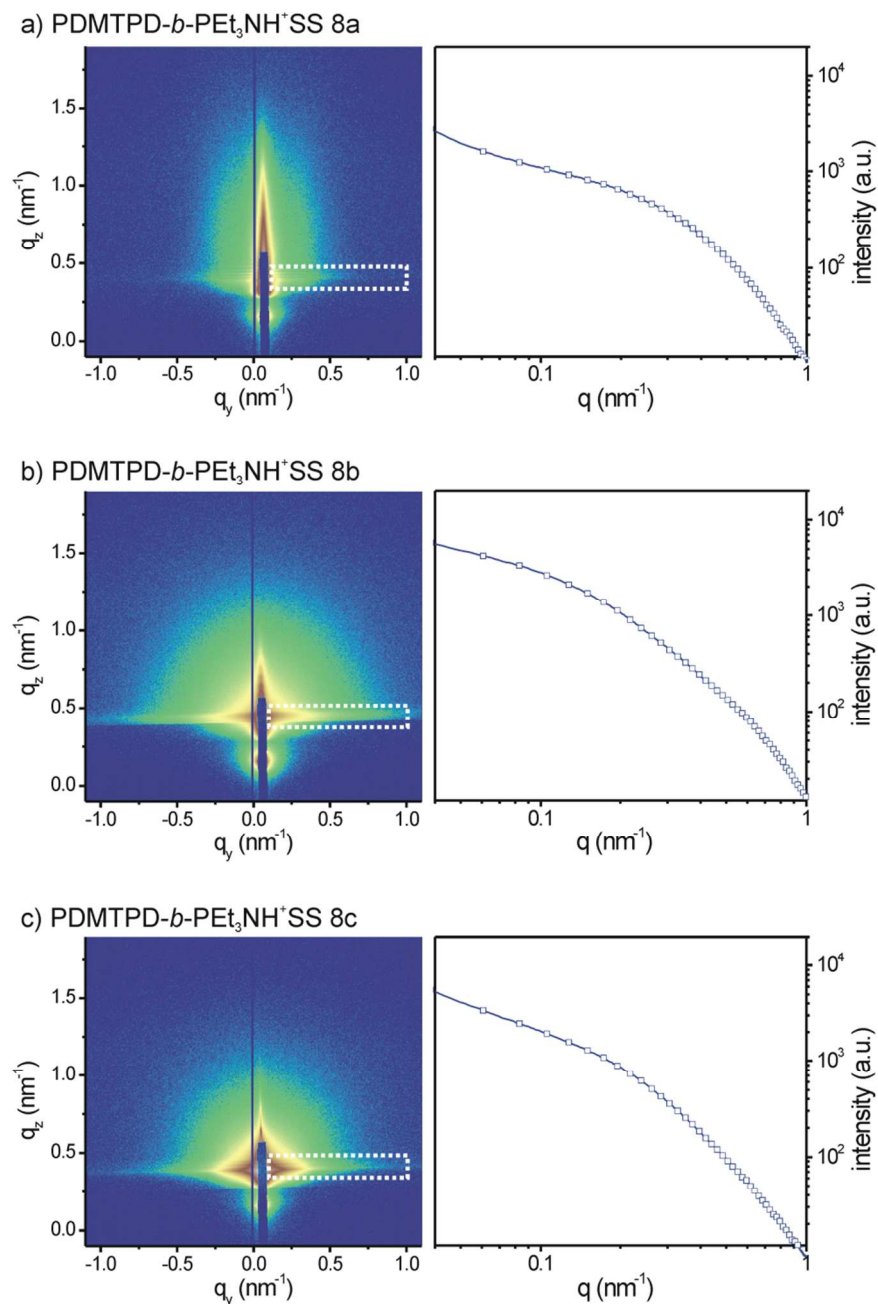


Figure S6. Grazing incident small angle X-ray scattering patterns of the thin films made by spin coating a 10 wt% solution of PDMTPD-*b*-PEt₃NH⁺SS **8a** (a), PDMTPD-*b*-PEt₃NH⁺SS **8b** (b) and PDMTPD-*b*-PEt₃NH⁺SS **8c** (c) in DMF.

Full scattering patterns of thermal annealed samples:

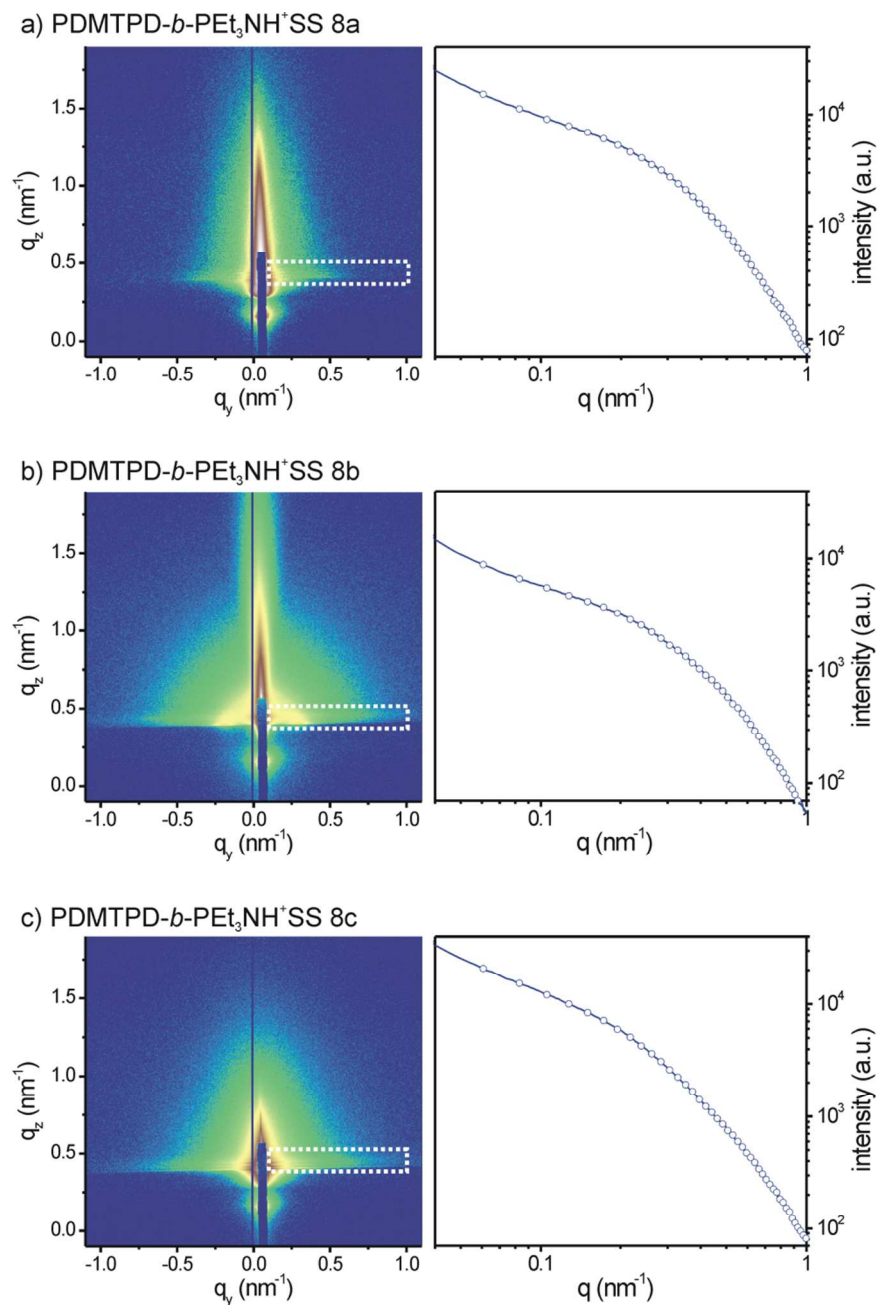


Figure S7. Grazing incident small angle X-ray scattering patterns of the thin films made by spin coating a 10 wt% solution of PDMTPD-*b*-PEt₃NH⁺SS **8a** (a), PDMTPD-*b*-PEt₃NH⁺SS **8b** (b) and PDMTPD-*b*-PEt₃NH⁺SS **8c** (c) in DMF. The films were annealed at 159°C (a), 177°C (b) and 193°C (c) for 6 h.

Atomic force microscopy (AFM)

PDMTPD-b-PET₃NH⁺SS 3 before and after thermal annealing:

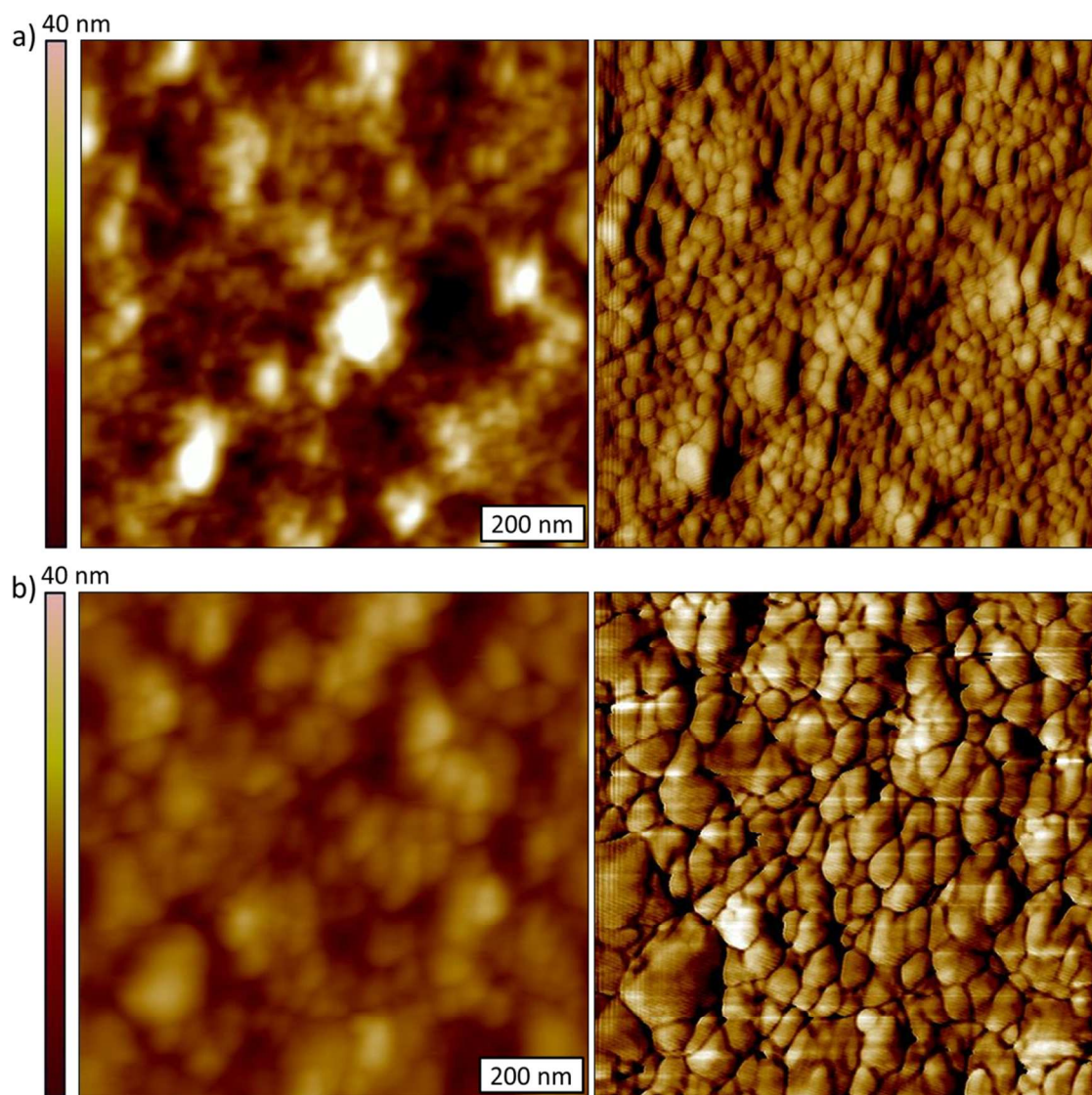


Figure S8. AFM images (height: left, phase: right) of sample PDMTPD-b-PET₃NH⁺SS **8c** before (a) and after (b) thermal annealing at 193°C for 6 h.

Solvent annealed samples with lower magnification:

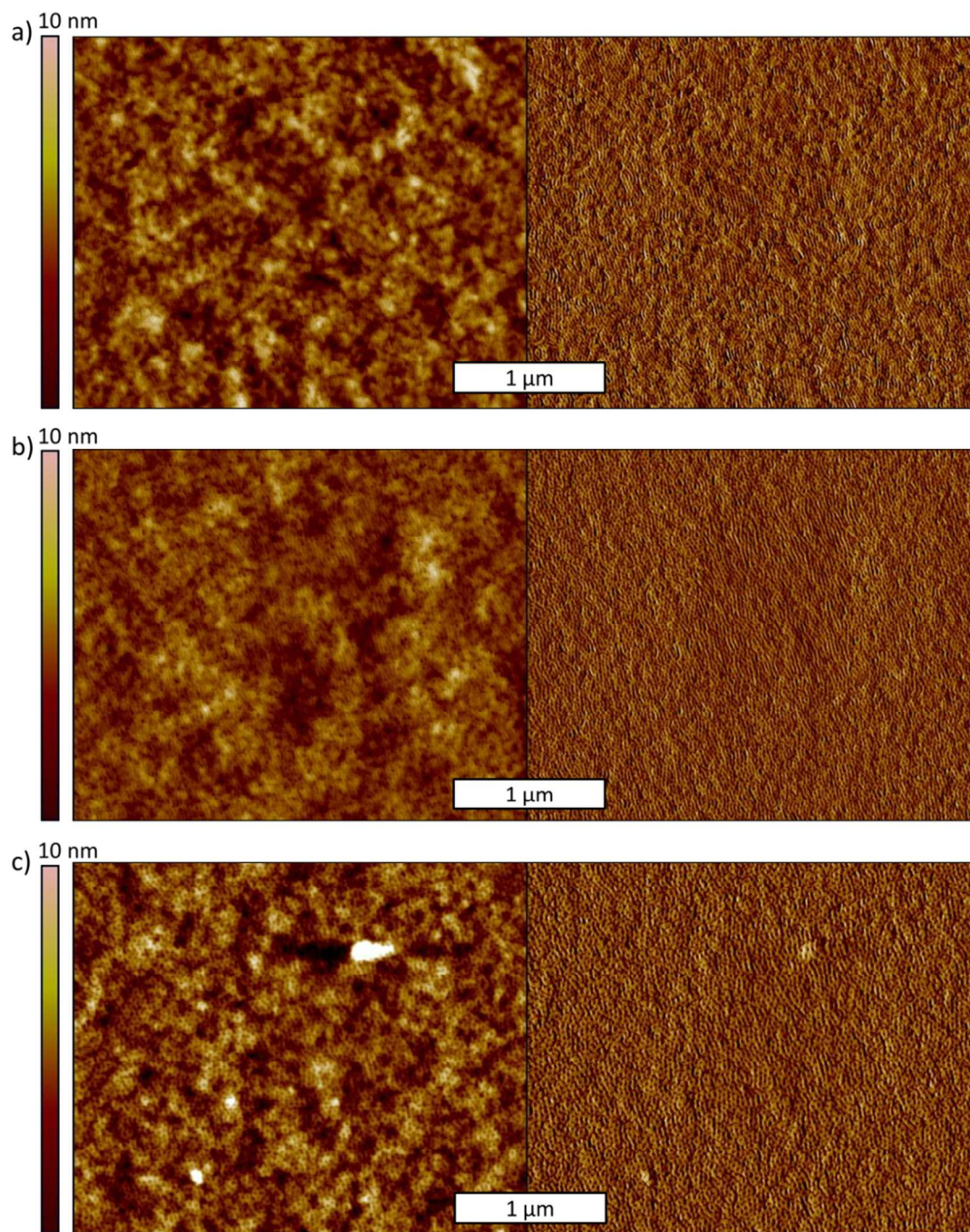


Figure S9. AFM height (left) and phase (right) images of thin films made by spin coating a 10 wt% solution of PDMTPD-b- $\text{PET}_3\text{NH}^+\text{SS}$ **8a** (a), PDMTPD-b- $\text{PET}_3\text{NH}^+\text{SS}$ **8b** (b) and PDMTPD-b- $\text{PET}_3\text{NH}^+\text{SS}$ **8c** (c) in DMF. The films were annealed in saturated DMF vapor for 4 days.

References

1. Lang, A. S.; Thelakkat, M. Modular Synthesis of Poly(Perylene Bisimides) Using Click Chemistry: A Comparative Study. *Polym. Chem.* **2011**, *2*, 2213-2221.
2. Sommer, M.; Lindner, S. M.; Thelakkat, M. Microphase-Separated Donor–Acceptor Diblock Copolymers: Influence of HOMO Energy Levels and Morphology on Polymer Solar Cells. *Adv. Funct. Mater.* **2007**, *17*, 1493-1500.