

Supplementary Information

Synthesis and self-assembly of phthalocyanine-tethered block copolymers

Junko Aimi,^{a,} Motonori Komura,^b Tomokazu Iyoda,^b Akinori Saeki,^c Shu Seki,^c*

Masayuki Takeuchi,^a and Takashi Nakanishi^{a,b,}*

Dr. J. Aimi, Dr. M. Takeuchi,

Organic Materials Group, Polymer Materials Unit, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

E-mail: AIMI.Junko@nims.go.jp

Dr. T. Nakanishi

International Center for Materials Nanoarchitectonics (MANA), NIMS, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

E-mail: NAKANISHI.Takashi@nims.go.jp

Dr. M. Komura, Dr. T. Iyoda

Division of Integrated Molecular Engineering, Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8503, Japan.

Dr. A. Saeki, Dr. S. Seki

Department of Applied Chemistry, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan.

Experimental Section

Materials: All reactions were conducted under prepurified nitrogen or argon, using oven-dried glassware. Commercial chemicals, purchased from Aldrich Chemical Co., Inc., were used without further purification unless noted otherwise. Copper (I) bromide (99+%) was purified by dissolving it in glacial acetic acid, followed by stirring the solution under nitrogen for 12 h, washed with ethanol and diethyl ether and dried under vacuum for 24 h. MMA, and styrene were purified by passing through basic alumina and collected over molecular sieves under argon.

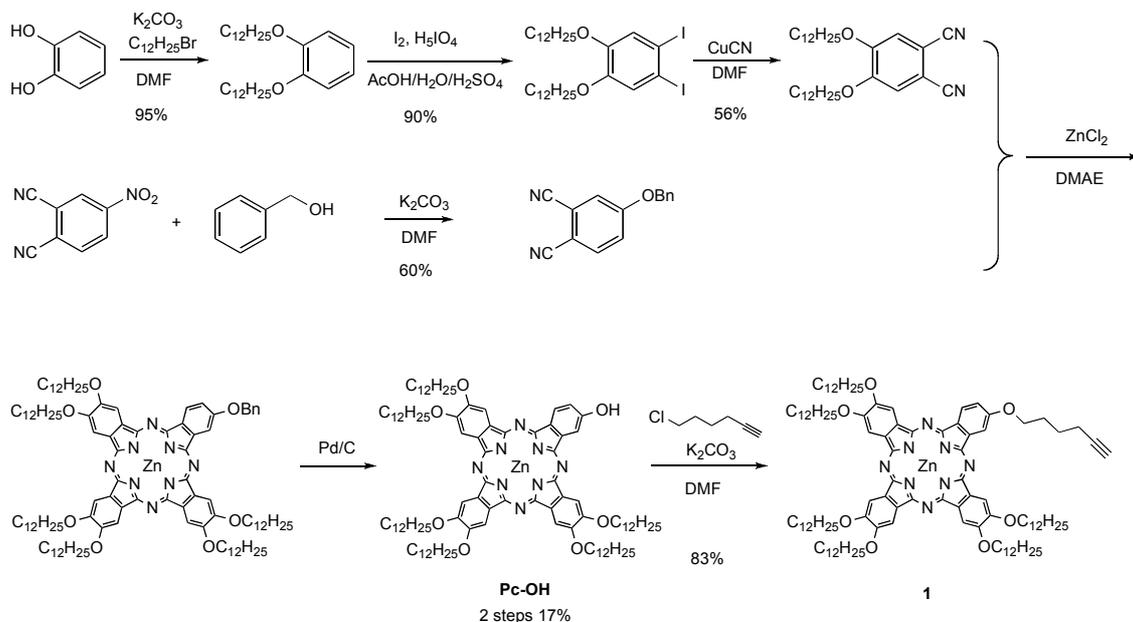
Measurements: ^1H and ^{13}C NMR spectroscopies were recorded on a JEOL type GSX-270 and GSX-500 spectrometers, where chemical shifts were determined with respect to non- or partially deuterated solvent residues as internal standards. Electronic absorption spectra were recorded on a JASCO Type V-670 spectrometer. Analytical GPC was performed at room temperature using a GPC column (TSK SuperMultipore HZ-M) on a Toshih HLC 8320 GPC system, equipped with RI and UV-Vis detectors. Differential scanning calorimetry (DSC) was performed on a TA instruments Q2000 with LNCS cooling accessory at a heating rate of 10–20 °C min⁻¹. The atomic force microscopy (AFM) measurements on the surface morphology of samples were conducted on a Nanocute (SII NanoTechnology Inc., now HITACHI High-Tech Science Corp.). Imaging was conducted in tapping mode using a silicon cantilever with a resonance frequency of 110–150 kHz and a spring constant of 15N/m (SI-DF20; Seiko Instruments, now HITACHI High-Tech Science Corp.). TEM images were

obtained with a Hitachi 7000 transmission electron microscope. Small and wide angle X-ray scattering (SWAXS) measurements were performed using Anton Paar SAXSess mc² instruments. Grazing-incidence small angle X-ray scattering (GI-SAXS) measurements were performed on a Rigaku MicroMaxTM-007HF instrument with a monochrome X-ray wavelength of 1.54 Å. The incidence angles was 0.20 - 0.21°.

The flash-photolysis time resolved microwave conductivity (FP-TRMC) measurement was carried out using a X-band (9 GHz) microwave circuit at low power (approximately 3 mW) and a nanosecond laser irradiation at 355 nm with photon density of 9.1×10^{15} photons cm⁻² pulse⁻¹. FP-TRMC samples were prepared by drop casting the samples on quartz plates.

Syntheses

Scheme S1 Synthesis of a phthalocyanine derivative **1**.



Pc-OH: A mixture of 4-benzyloxyphthalonitrile (338 mg, 0.68 mmol), 1,2-dicyano-4,5-di(dodecyloxy)benzene (50 mg, 0.23 mmol), and ZnCl_2 (62.7 mg, 0.46 mmol) in 2-(dimethylamino)ethanol (5 mL) was stirred and slowly heated. The mixture was refluxed under a nitrogen atmosphere for 24 h. After the mixture was cooled, methanol (50 mL) was added, and the resulting precipitate was filtered off. The residue was then treated with Pd/C (60 mg) in THF (70 mL) at room temperature under H_2 atmosphere for 6 h for the deprotection of the benzyl group. The reaction mixture was filtrated with celite and evaporated to dryness. The residue was subjected to size exclusion chromatography (SEC) with THF as an eluent, where the second fraction was collected and reprecipitated from $\text{CH}_2\text{Cl}_2/\text{MeOH}$, to give **Pc-OH** as a green solid in

17 % yeild. ^1H NMR (500 MHz) in THF- d_8 : δ 9.10 (s, 1H; ArH), 9.01 (d, $J = 8.5$ Hz, 1H; ArH), 8.60 (m, 6H; ArH), 7.44 (d, $J = 8.0$ Hz, 1H; ArH), 4.42 (br, 12H; OCH₂), 2.00 (m, 12H, OCH₂CH₂), 1.66 (brt, 12H; CH₂), 1.80 (m, 12H, CH₂), 1.2–1.8 (m, 96H; CH₂), 0.80 ppm (t, 18H; CH₃); MALDI-TOF MS (dithranol): m/z (%): 1700 (00) [M + +H].

1: Pc-OH (15 mg, 8.83 μmol) and 6-chloro-1-hexyne (2.14 μL , 17.6 μmol) were dissolved in a mixture of DMF and THF (8 mL, 1:1 v/v), and K₂CO₃ (6.0 mg, 44 μmol) was added portion wise. The reaction mixture was stirred at 65 °C for 12h under Ar. The solvent was removed under reduced pressure, and the residue was extracted with CH₂Cl₂. The compound **1** was obtained after reprecipitation from CH₂Cl₂/MeOH, yielding 83 %. ^1H NMR (500 MHz) in THF- d_8 : δ 9.24 (d, $J = 6.0$ Hz, 1H; ArH), 8.87 (m, 7H; ArH), 7.70 (d, $J = 6.0$ Hz, 1H; ArH), 5.20 (br, 1H; OCH₂), 4.56 (brt, 12H; OCH₂CH₂), 2.20 (t, 2H, CH₂), 2.15 (m, 12H, CH₂), 1.95 (t, 2H, CH₂), 1.80 (m, 12H, CH₂), 1.60 (m, 12H, CH₂), 1.2–1.8 (m, 84H; CH₂), 0.90 ppm (t, 18H; CH₃); MALDI-TOF MS (dithranol): m/z (%): 1777 (10) [M + +H].

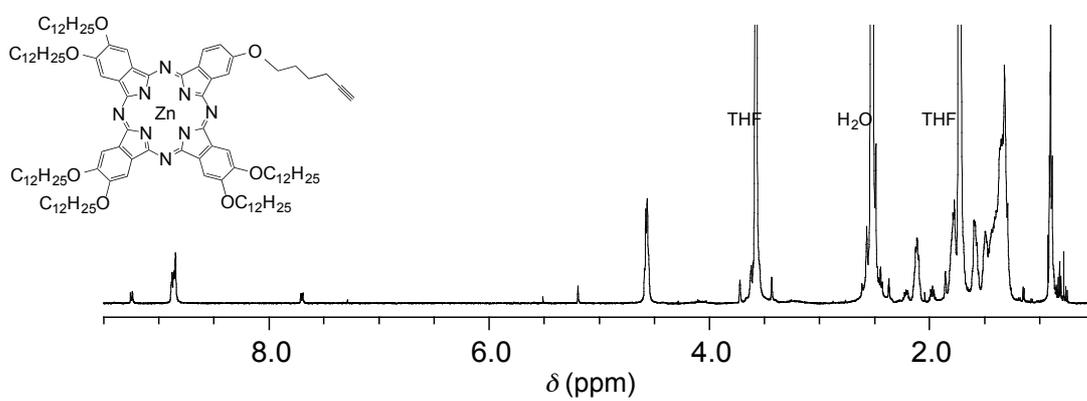
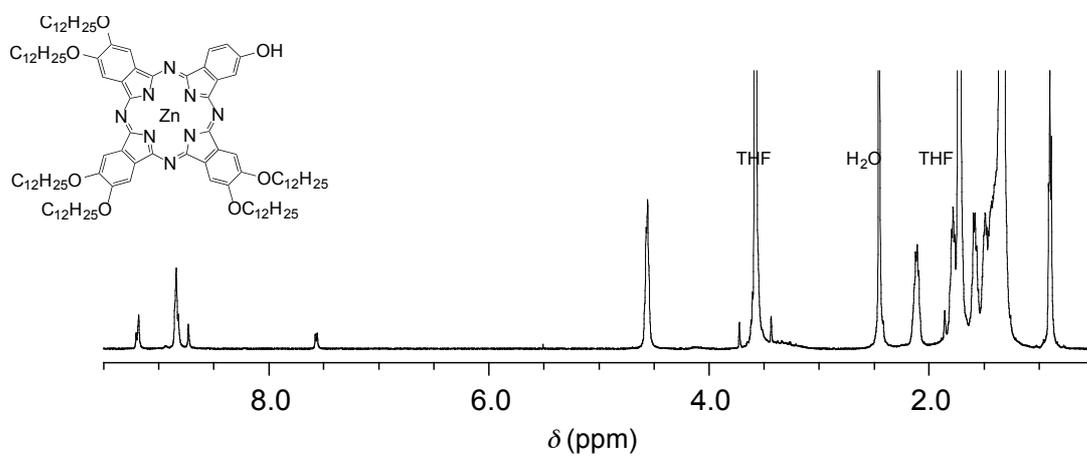
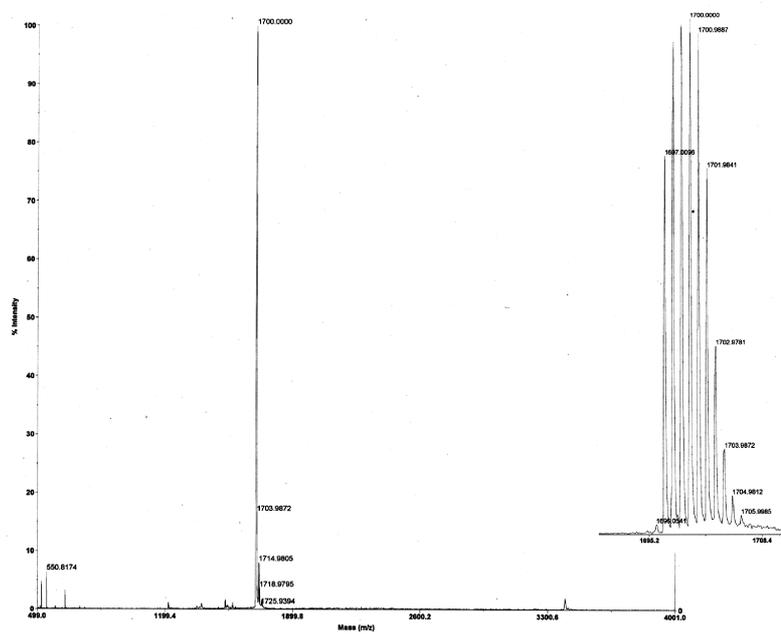
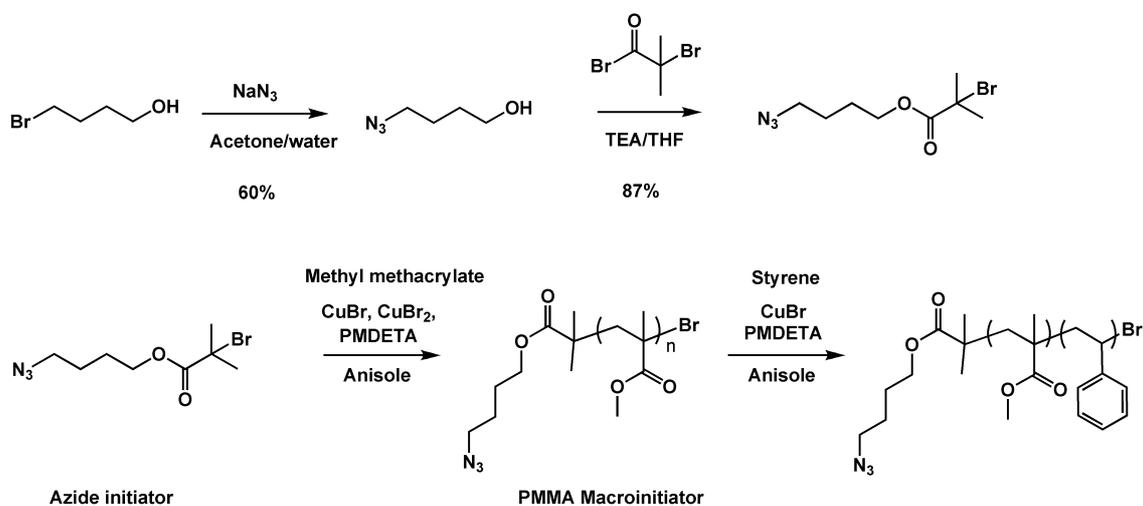


Figure S1 ¹H NMR spectra of **PcOH** and **1** in THF-*d*8.

a) PcOH



Scheme S2 Synthesis of N_3 -PMMA and N_3 -PMMA-*b*-PS (N_3 -BCP).



N_3 -PMMA: Azide-bearing ATRP initiator was first synthesized according to the reported procedure. Typical procedure of ATRP follows: Deoxygenated anisole (10 mL), MMA (10 mL, 9.39×10^{-2} mol) and N_3 -initiator (96 μL , 4.69×10^{-4} mol) were mixed together in a 50 mL Schlenk flask, and the mixture was degassed by three freeze-pump-thaw cycles. CuBr (23.5 mg, 1.64×10^{-4} mol), CuBr_2 (15.7 mg, 7.04×10^{-5} mol) and PMDETA (48.9 μL , 2.35×10^{-4} mol) were then added, and the flask was placed in an oil bath thermostated at 65 °C. Samples were taken at timed intervals and analyzed by ^1H NMR and gel permeation chromatography (GPC) to follow the progress of the reaction. The reaction was stopped after 1 h by cooling the reaction down to room temperature and opening the flask to air. N_3 -PMMA was purified by precipitation from the acetone solution to methanol and freeze-dried from its absolute benzene solution for 24 h. M_n (GPC) = 10.7 kg/mol, M_w/M_n = 1.19 (Table 1, entry 3).

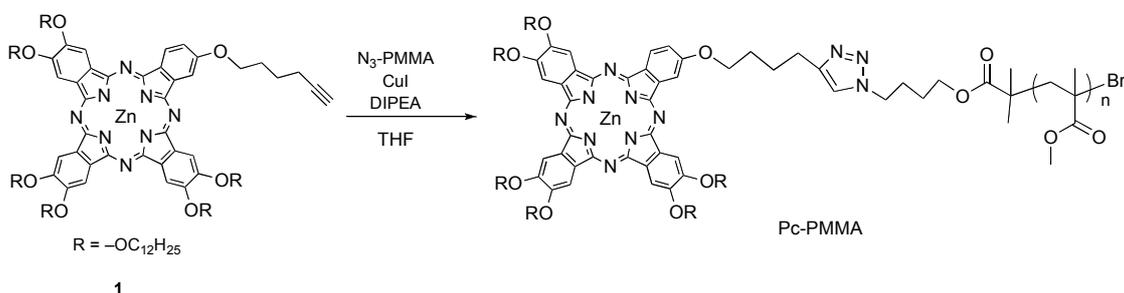
N₃-PMMA-*b*-PS (N₃-BCP): N₃-PMMA macroinitiator ($M_n = 10.7$ kg/mol, $M_w/M_n = 1.19$) (0.5 g, 4.67×10^{-5} mol) and anisole (1.0 mL) were added to a dry Schlenk flask followed by styrene (3.2 mL, 2.8×10^{-2} mol). Then, CuBr (6.7 mg, 4.67×10^{-5} mol) and PMDETA (9.75 μ L, 4.67×10^{-5} mol) were added to the flask. The resulting mixture was degassed by three freeze-pump-thaw cycles. An initial sample was taken and the sealed flask was placed in an oil bath thermostated at 70 °C. The polymerization was monitored by GPC and ¹H NMR. The reaction was stopped after 27 h by opening the flask and exposing the catalyst complex in the solution to air. The molecular weight and polydispersity were estimated by GPC, resulting a polymer N₃-PMMA-*b*-PS with $M_n = 36.4$ kg/mol and $M_w/M_n = 1.27$ (Table 1, N₃-BP3).

Table S1. Synthesis of N₃-PMMA and N₃-PMMA-*b*-PS.

Entry	Condition [initiator]:[monomer]:[Cu catalyst]:[PMDETA]	Temp. (°C)	Time (h)	conv. (%) ^a	M_n (g/mol) ^b	M_w/M_n ^b	f_{MMA} ^c
1	[I]:[MMA]:[CuBr]:[CuBr ₂]:[PMDETA]=1:400:0.35:0.15:0.5	65	2.0	35	16,000	1.14	
2	[I]:[MMA]:[CuBr]:[CuBr ₂]:[PMDETA]=1:400:0.35:0.15:0.5	65	5.8	50	22,000	1.10	
3	[I]:[MMA]:[CuBr]:[CuBr ₂]:[PMDETA]=1:200:0.35:0.15:0.5	65	1.0	40	10,700	1.19	
N ₃ -BCP1	[PMMA]:[St]:[CuBr]:[PMDETA]=1:1000:1:1 PMMA macroinitiator : $M_n = 22,000$, $M_w/M_n = 1.10$	70	33	83	79,600	1.16	0.20
N ₃ -BCP2	[PMMA]:[St]:[CuBr]:[PMDETA]=1:1000:1:1 PMMA macroinitiator : $M_n = 16,000$, $M_w/M_n = 1.14$	70	26	40	63,500	1.12	0.28
N ₃ -BCP3	[PMMA]:[St]:[CuBr]:[PMDETA]=1:1000:1:1 PMMA macroinitiator : $M_n = 10,700$, $M_w/M_n = 1.19$	70	27	31	36,000	1.27	0.34

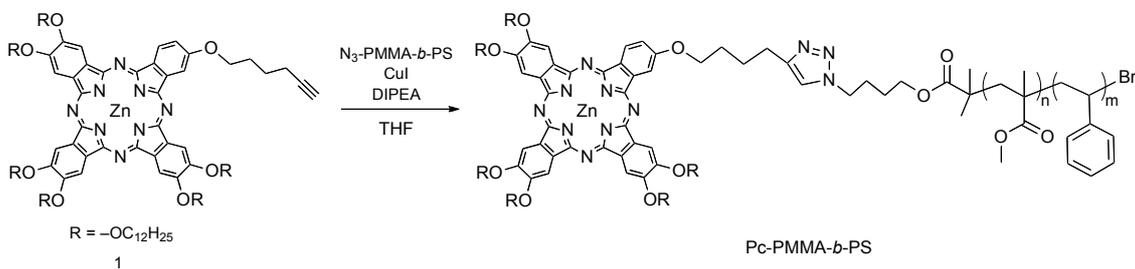
^a Based on ¹H NMR. ^b Number-averaged molecular weights and polydispersities determined by GPC analysis based on polystyrene standards. ^c Volume fraction of PMMA determined by ¹H NMR spectra.

Scheme S3 Synthesis of Pc-PMMA.



Pc-PMMA: To a THF solution (2 mL) of PMMA ($M_n = 16.0$ kg/mol; 156 mg) and **1** (20 mg, 11.2 μ mol) was successively added CuI (1 mg, 5.63 μ mol) and DIPEA (20 μ L, 1.12 mmol), and the reaction mixture was stirred at room temperature for 2 days under Ar. Then, the mixture was passed through alumina column to remove Cu catalyst, and evaporated to dryness. The residue was precipitated from THF/diethyl ether, giving Pc-PMMA as a green solid ($M_n = 22.2$ kg/mol, $M_w/M_n = 1.07$). The mole ratio of Pc in Pc-PMMA was estimated from the absorbance of the Q band using a molecular absorption coefficient of **1** ($\epsilon = 41000$ M⁻¹cm⁻¹, $\lambda = 608$ nm), was 83 %.

Scheme S4 Synthesis of Pc-PMMA-*b*-PS.



Pc-PMMA-*b*-PS (PcBCP): To a THF solution (2 mL) of PMMA-*b*-PS ($M_n = 79.6$ kg/mol; 170 mg) and **1** (10 mg, 5.62 μ mol) was successively added CuI (1 mg, 5.63 μ mol) and DIPEA (20 μ L, 1.12 mmol), and the reaction mixture was stirred at room

temperature for 3 days under Ar. Then, the mixture was passed through alumina column to remove Cu catalyst, and evaporated to dryness. The residue was precipitated in large amount of diethyl ether, giving Pc-PMMA-*b*-PS as a green solid ($M_n = 86.4$ kg/mol, $M_w/M_n = 1.18$). The mole ratio of Pc in Pc-PMMA was estimated from the absorbance of the Q band using a molecular absorption coefficient of **1** ($\epsilon = 41000$ M⁻¹cm⁻¹, $\lambda = 608$ nm), was 20 %.

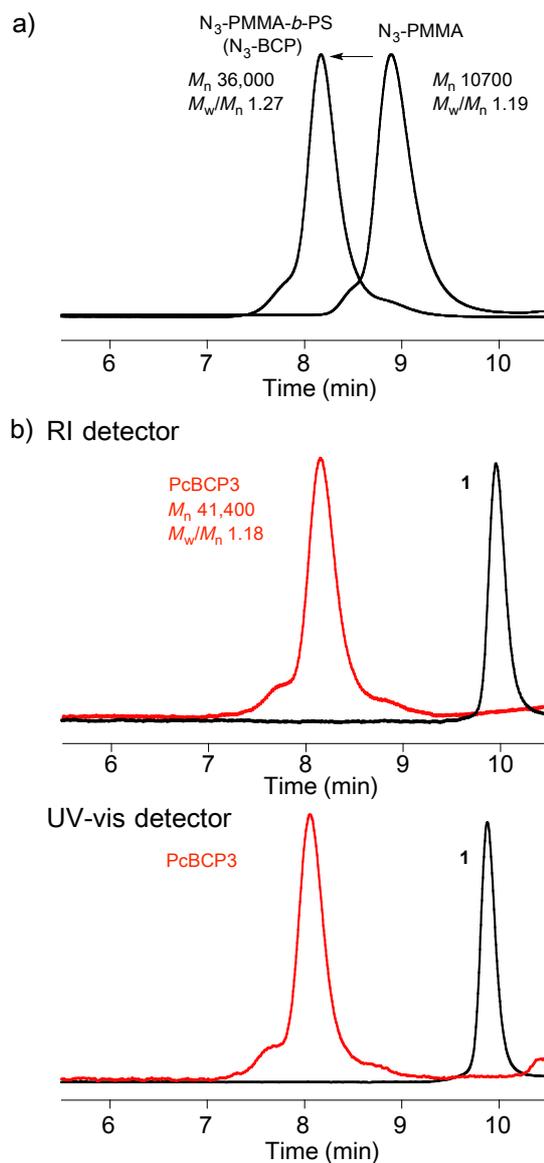


Figure S3 (a) GPC profiles during block extension of PMMA with styrene. (b) GPC profiles of Pc-PMMA-*b*-PS (**PcBCP3**) (red solid) after the purification in diethyl ether and **1** (black solid) with RI detector and UV-vis detector at 400 nm.

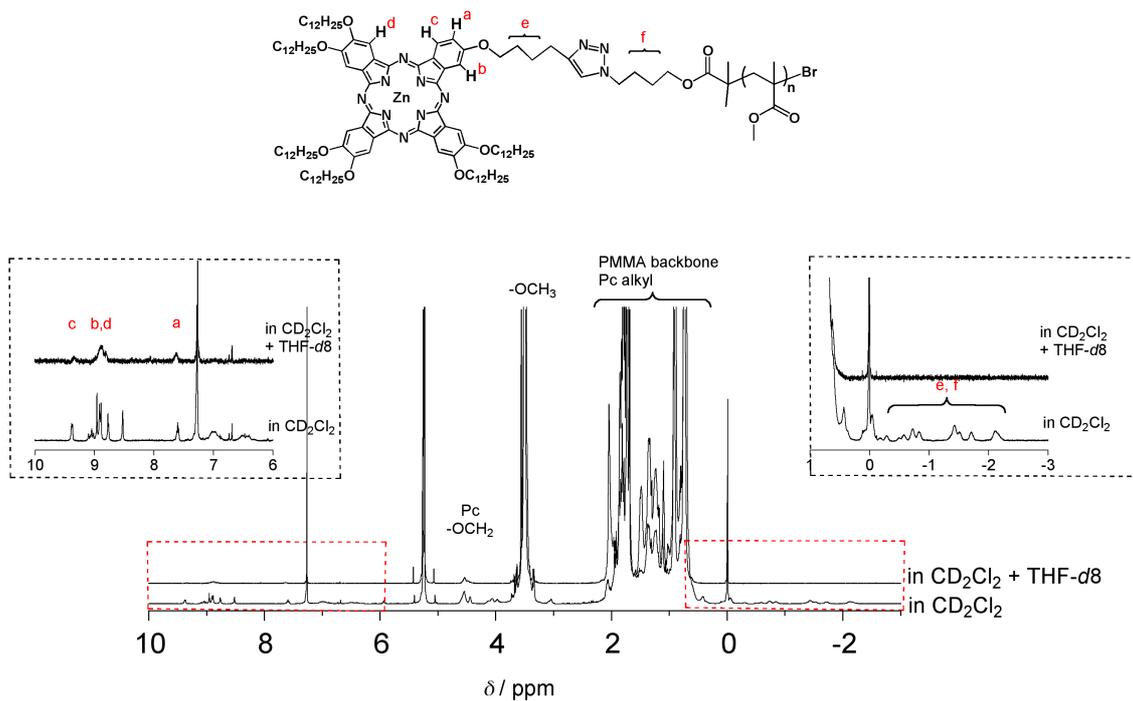


Figure S4 ^1H NMR spectra of Pc-PMMA in a mixture of CD₂Cl₂ and THF-*d*8.

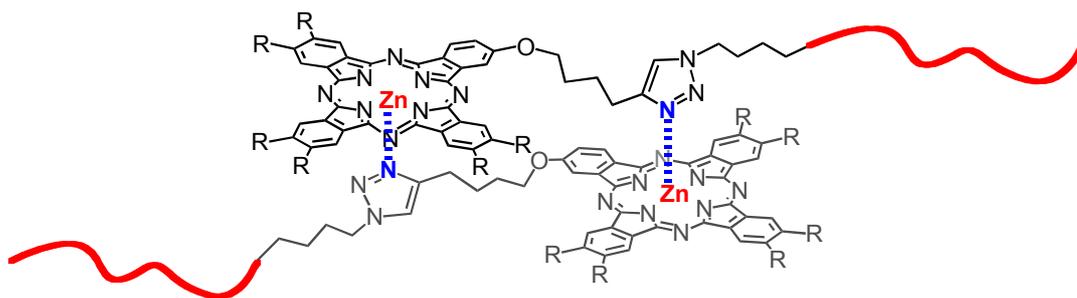


Figure S5 Dimeric structure of Pc-PMMA in non-coordinating solvents.

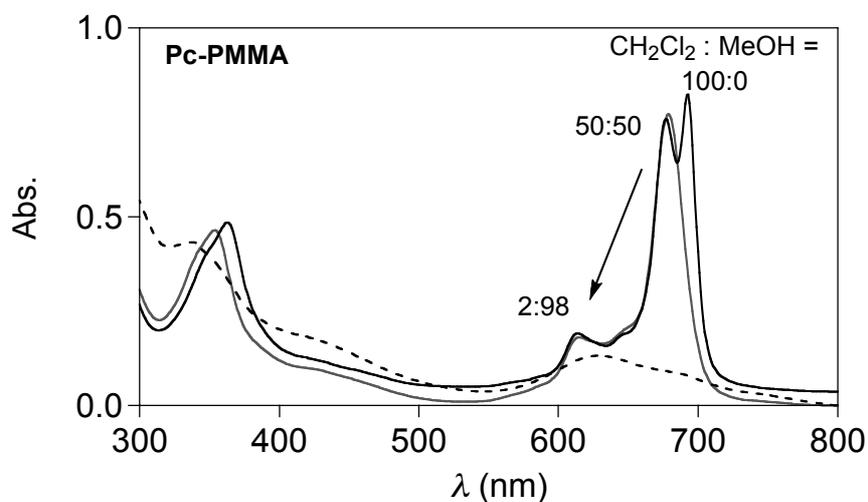


Figure S6 Absorption spectra of Pc-PMMA in mixture of $\text{CH}_2\text{Cl}_2/\text{MeOH}$.

-> Upon addition of a polar solvent (MeOH) to a solution of **Pc-PMMA** in CH_2Cl_2 , the split peak at 693 nm disappeared (gray solid line) and a similar spectrum to that of the Pc precursor **1** without the triazole ring was recorded. Addition of more MeOH (CH_2Cl_2 -MeOH = 2:98 v/v) gave rise to a new broad blue-shifted absorption band around 630 nm, while the monomeric Pc peak at 677 nm vanished (dashed line). This observation is characteristic of the cofacial (face-to-face) aggregation of Pcs through π - π interactions of the large aromatic rings, indicating that the terminal Pc moieties form a stacked structure in poor solvents.

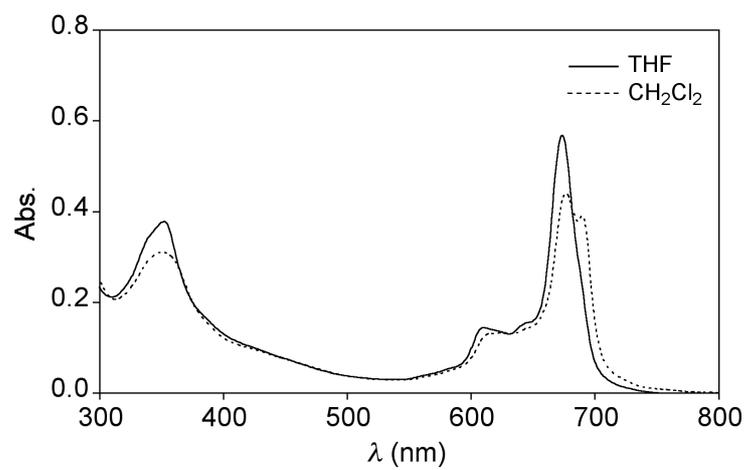


Figure S7 Absorption spectra of **PcBCP2** in THF or CH₂Cl₂.

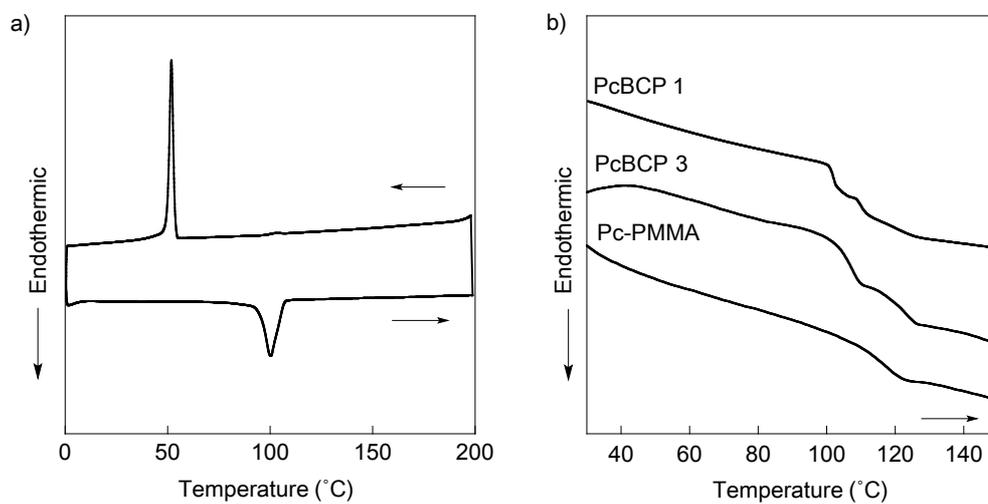


Figure S8 DSC profiles of Pc derivative **1** (a) with scanning rate at 10 °C min⁻¹ and Pc-containing polymers with scanning rate at 20 °C min⁻¹ (b).

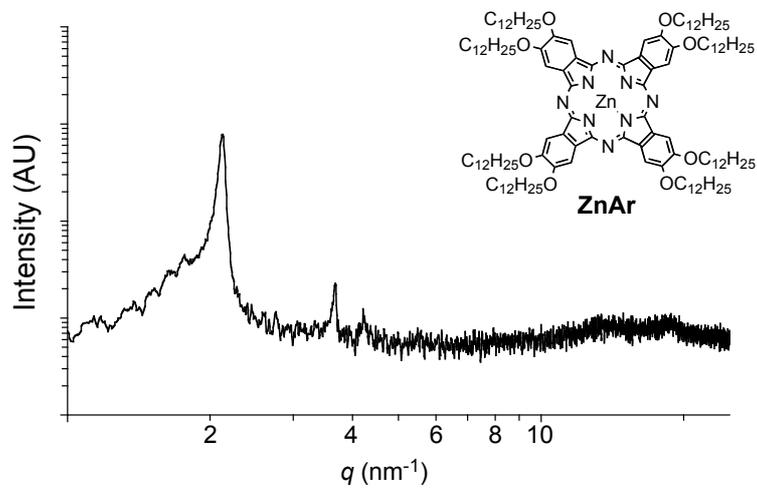


Figure S9 Small and wide angle X-ray scattering data of zinc complex of (octakis(dodecyloxy)phthalocyanine (**PcAr**) at 120 °C.

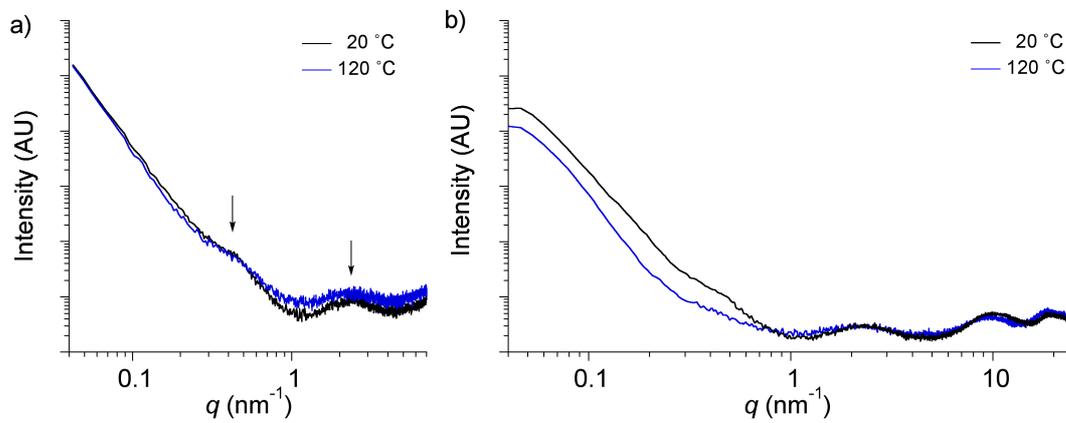


Figure S10 SAXS profiles (a) and SWAXS profiles (b) of **Pc-PMMA** at 20 °C and 120 °C.

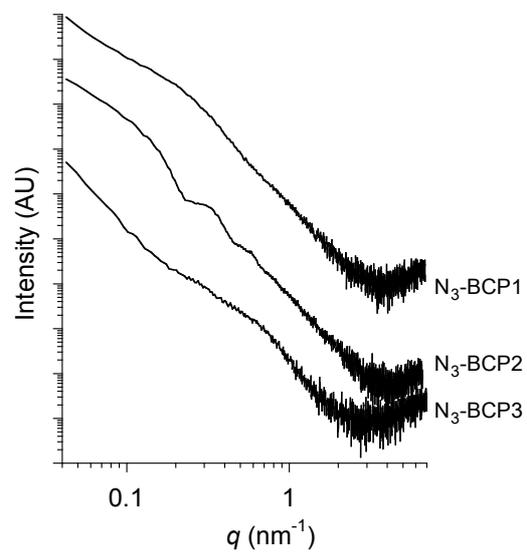


Figure S11 Small angle X-ray scattering profiles of N₃-tethered block copolymers (N₃-BCP1–N₃-BCP3).

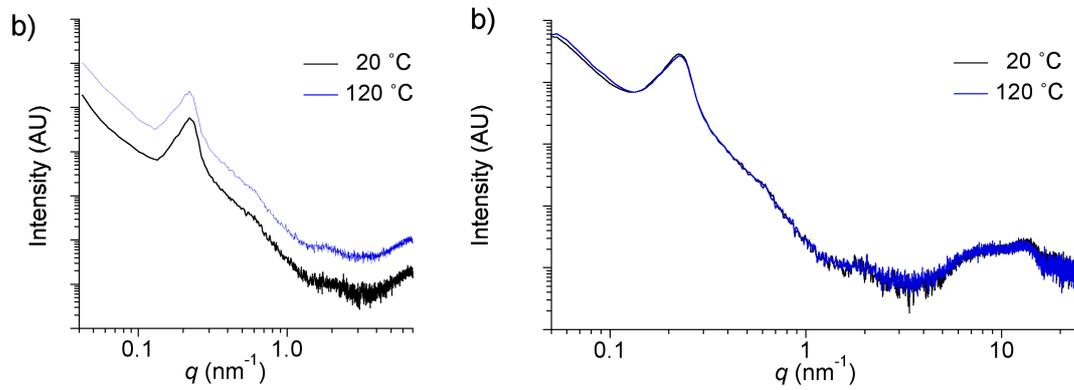


Figure S12 SAXS profiles (a) and SWAXS profiles (b) of **PcBCP2** at 20 °C and 120 °C.

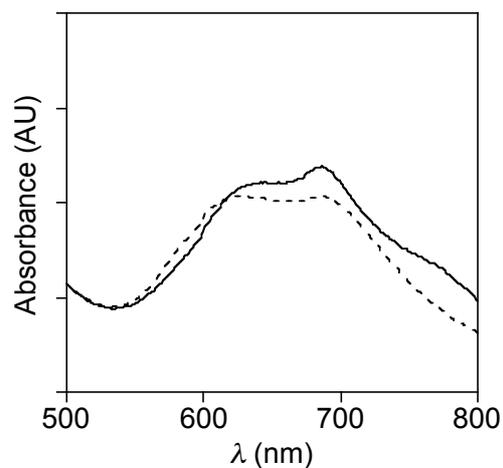


Figure S13 Absorption spectra of Pc derivative **1** as deposited film at 20 °C (solid line) and 110 °C (dashed line).

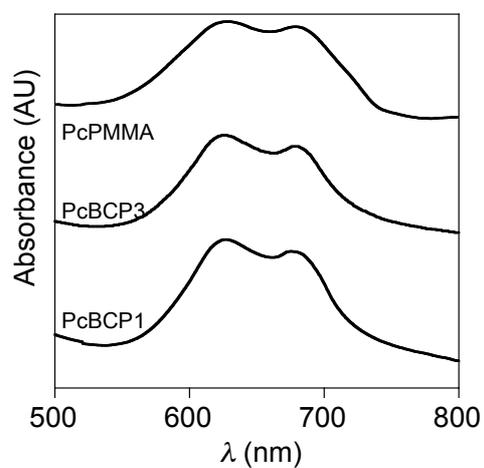


Figure S14 Absorption spectra of **Pc-PMMA**, **PcBCP1** and **PcBCP3** as deposited films at 20 °C.

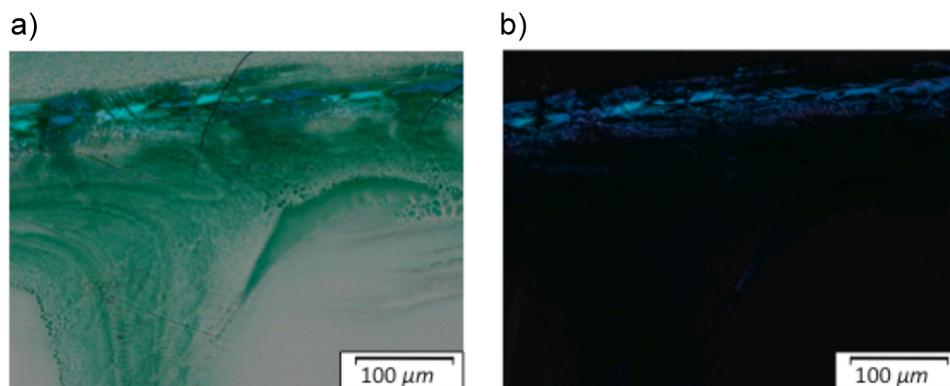


Figure S15 Optical (a) and polarizing optical microscopy (b) images with cross-polarizers of a film of **N₃-BCP2** containing 10 wt% of **1**.

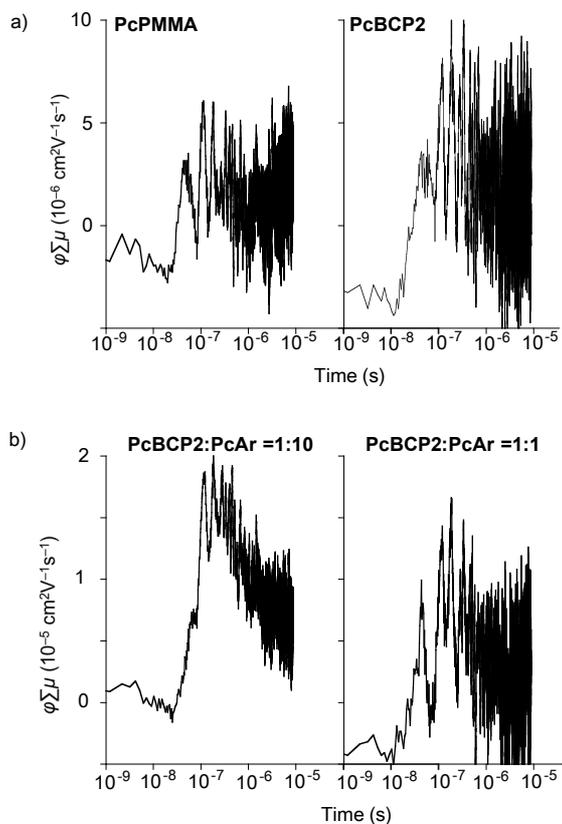
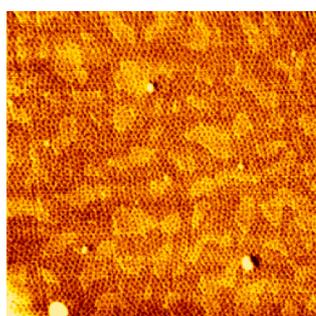
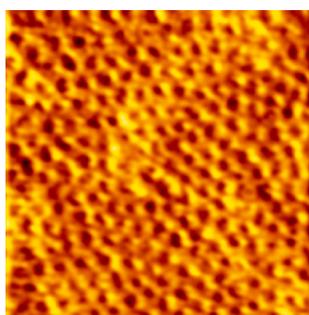


Figure S16 FP-TRMC data measured at 25°C upon laser-pulse irradiation at 355 nm (photon density, $9.1 \times 10^{15} \text{ photons cm}^{-2} \text{ puls}^{-1}$) for (a) films of **Pc-PMMA** and **PcBCP2**, and (b) blend films of **ArPc** and **PcBCP2** with molar ratios of 1/1 and 10/1, respectively.

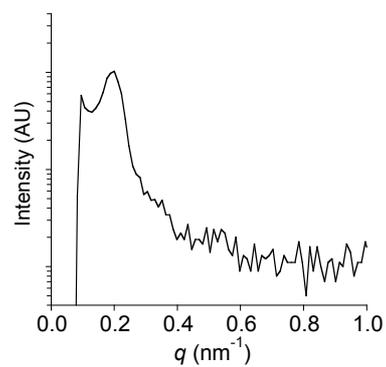
a) PcBCP2:ArPc = 1:1



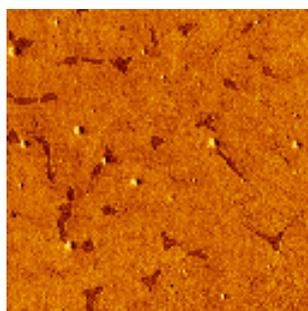
2 μm x 2 μm



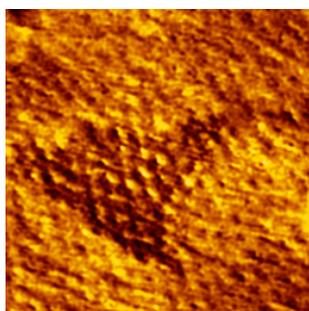
500 nm x 500 nm



b) PcBCP2:ArPc = 10:1



5 μm x 5 μm



500 nm x 500 nm

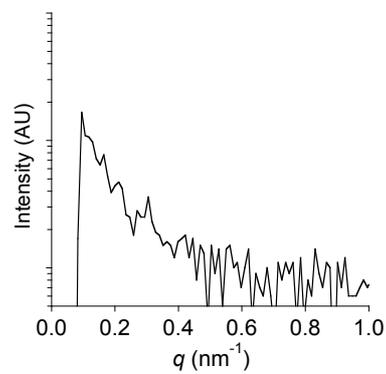


Figure S17 AFM phase images and GISAXS profiles of polymer blend films of **PcBCP2:ArPc = 1:1** (a) and **10:1** (b).