Supporting Information for

Synthesis of Cylindrical Micelle from Hydrophilic Polymers Connected with a Single Supramolecular Structure-Directing Unit

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Materials and methods

Solvents and reagents were bought from commercial sources and used as it is if not mentioned otherwise. 4-cyano-4-((phenylcarbonothioyl)thio)pentatonic acid and the chain transfer agent were synthesized by literature reported procedure.[1-2] Before carrying out reaction, methacryloyl chloride was freshly distilled under reduced pressure. Oligoglycerol based protected first generation (G1-OH) dendrons were synthesized following the literature procedure.[3] ^{1}H NMR spectra were recorded on a Bruker DPX-300 MHz, DPX-400 MHz and DPX-500 MHz NMR spectrometer and all spectra were calibrated using TMS as the internal standard. Mass spectrometric data were acquired by an electron spray ionization (ESI) technique on a Q-TOF-microquadruple mass spectrometer (Micro mass). UV/Vis spectra were recorded in a Perkin Elmer Lamda 25 spectrometer equipped with a Peltier system for temperature-variable experiments. Atomic force microscopy (AFM) images were taken in an Innova instrument from Bruker. TEM measurements were carried out in a Technai G2 (FEI) microscope with an accelerating voltage of 200kV. Molecular weight of the polymer was determined by Waters gel permeation chromatography (GPC) equipped with Waters 515 HPLC pump and Waters 2414 refractive index (RI) detector using THF solvent. Molecular weight and PDI were calculated with respect to Polystyrene standards. Fluorescence experiments were performed with a FluoroMax-3 spectrophotometer from HORIBA Jobin Yvon.

Synthesis of G1-methacrylate (M1):

Glycerol based first generation dendron G1-OH (1.0 g, 3.2 mmol) was taken in round bottom flask and 10 mL anhydrous DCM was added. Triethylamine (1.3 mL, 9.36 mmol) was added to solution and the solution was cooled to 0 ºC in an ice-bath. To this cold solution, a solution of methacryloyl chloride (0.46 mL, 4.6 mmol) in 2 mL anhydrous CH_2Cl_2 was added dropwise

under N_2 atmosphere. After the addition was over, the temperature was allowed to come to room temperature and the reaction mixture was stirred overnight. Then it was washed with distilled H_2O (3 x 30 mL) and the organic part was dried over anhydrous Na_2SO_4 and DCM was evaporated under reduced pressure to get the crude product as light yellowish liquid. The crude product was purified by column chromatography using ethylacetate and hexane as eluent (ratio 1:3) to get the pure product as light yellow liquid with 63% yield. ^{1}H NMR (500MHz, $CDCl_3$, TMS): δ (ppm) = 6.114 (S, 1H), 5.580 (s, 1H), 5.15 (m, 1H), 4.246 – 4.225 (m, 3H), 4.214 – 4.017 9 (m, 2H), 4.015 - 3.46 (m, 10H), 1.944 (s, 3H), 1.605 – 1.349 (s, 12H). HRMS (ESI): m/z for $(M + Na)^+$ = 411.1994 (obtained), $(M + Na)^+$ = 411.1995 (theoretical).

Synthesis of P3-P: To a solution of CTA (0.020 g, 0.018 mmol) and monomer M1 (0.351 g, 0.9 mmol) in 260 µL degassed DMF, 80 µL of a stock solution of recrystallized AIBN (0.88 mg, 0.0054 mmol) in DMF was added so that mole ratio of M1/AIBN/CTA = 50: 0.3: 1 and solid content was 100 mg/100 µL. The mixture was purged with dry argon gas for 15 min and then placed in a preheated oil bath set at 75 °C and stirred under argon atmosphere for 6 h. The reaction was quenched by immersing the vessel inside liquid nitrogen and then allowed to come back to room temperature. The crude polymer was precipitated in diethylether (4 x 10 mL) to remove the unreacted monomer. The precipitated polymer was collected by centrifugation. Upon drying a sticky polymer was obtained with 75% yield. Conversion = 91%, Molecular weight (theo) = 18.5 kDa, M_n (GPC) = 12.5 kD (polystyrene standard), $Đ$ = 1.07. Molecular weight (UV) = 14.8 kDa. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) = 8.761 (s, 4H), 4.906 (s, 2H), 6.75 s, (1H), 4.823 (m, 1H), 4.223-3.465 (broad peaks, pendant dendron Hs), 2.0-1.5 (bs, backbone protons), 1.472 – 1.222 (s, Me), 1.019 – 0.851 (broad peaks, protons from alkyl chains).

Synthesis of P3: P3-P (0.1 g) was taken in a round bottom flask quipped with a magnetic stir and dropping funnel. Then 3 mL of MeOH was added to it and cooled to 0 ^{o}C. 20 µL concentrated HCl (37 wt%, 12 N) was added to the dropping funnel containing 3 mL of MeOH. Then, the dilute HCl solution in MeOH was added dropwise to the ice-cold solution of P3-P and the mixture was stirred at rt for 4 h. Then, the MeOH was evaporated and the residue was dissolved in small amount of MeOH and precipitated in DCM twice. Yellow color sticky liquid was obtained upon centrifugation which was dried under vacuum to obtain the waxy P3 in quantitative yield. ^{1}H-NMR (500 MHz, DMSO-D_6, TMS): δ (ppm) = 8.685 (m, 4H), 6.910 s, (2H), 4.749 (m, 1H), 4.7-4.25 (broad, OH peaks), 4.223-3.30 (broad peaks, pendant dendron Hs), 2.0-1.5 (bs, backbone methacrylate protons), 1.472 – 1.222 (s), 1.019 – 0.851 (broad peaks, protons from alkyl chains).

Additional Figures

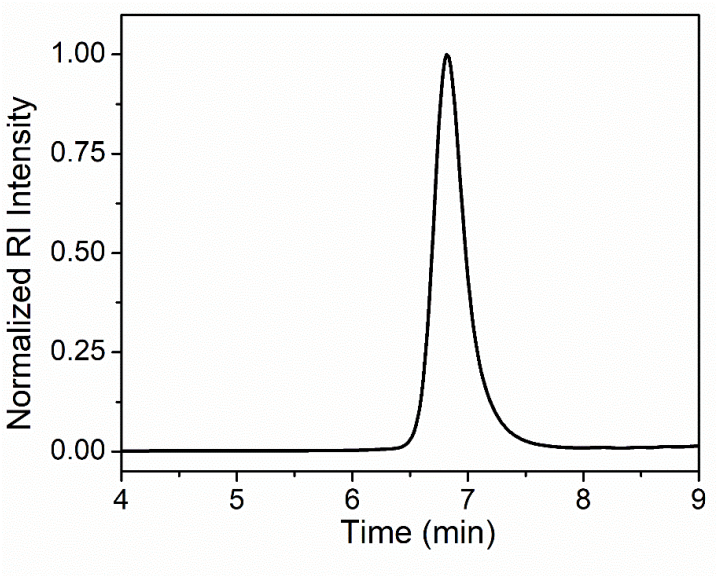

Figure S1. Size exclusion chromatography trace of P3-P in THF

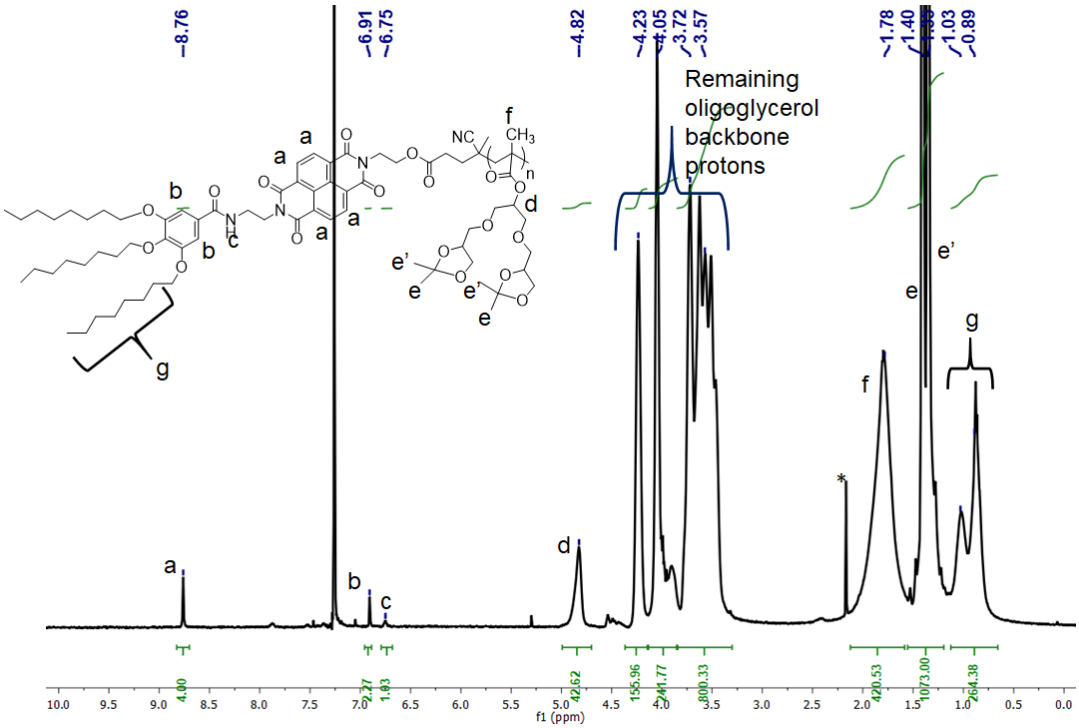

Figure S2. ^{1}H NMR of P3-P in $CDCl_3$. * indicates solvent. Relative integration of the peaks at δ = 8.76 ppm (H_a from the end group) and 4.82 ppm (H_d from the repeating unit) was used to estimate the degree of polymerization.

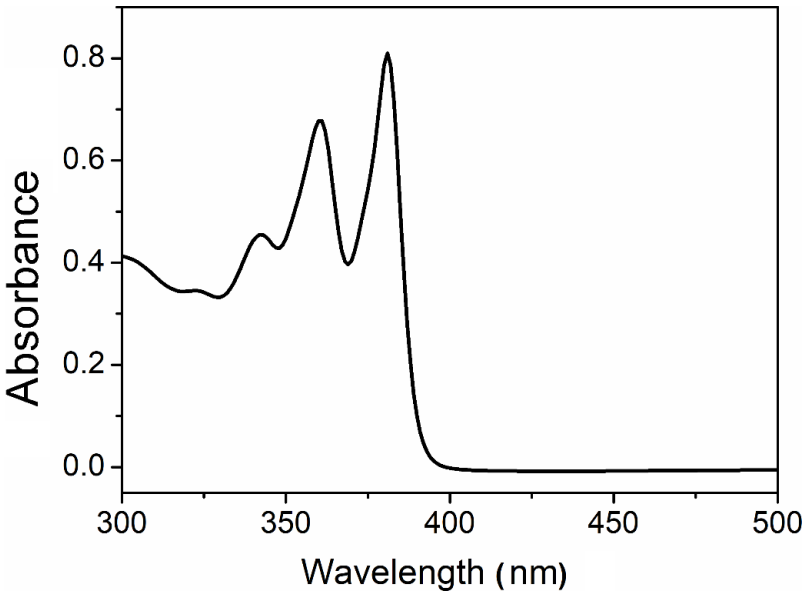

Figure S3: UV/Vis spectra of P3-P in $CHCl_3$ (c = 1.0 mg/mL, l = 1 cm). Absorption intensity at λ_{max} was compared with that of NDI containing CTA (Scheme 2) which has a well-defined molecular weight. Assuming the molar extinction coefficient to be same for these two samples, molecular weight of P3-P was estimated from these data.

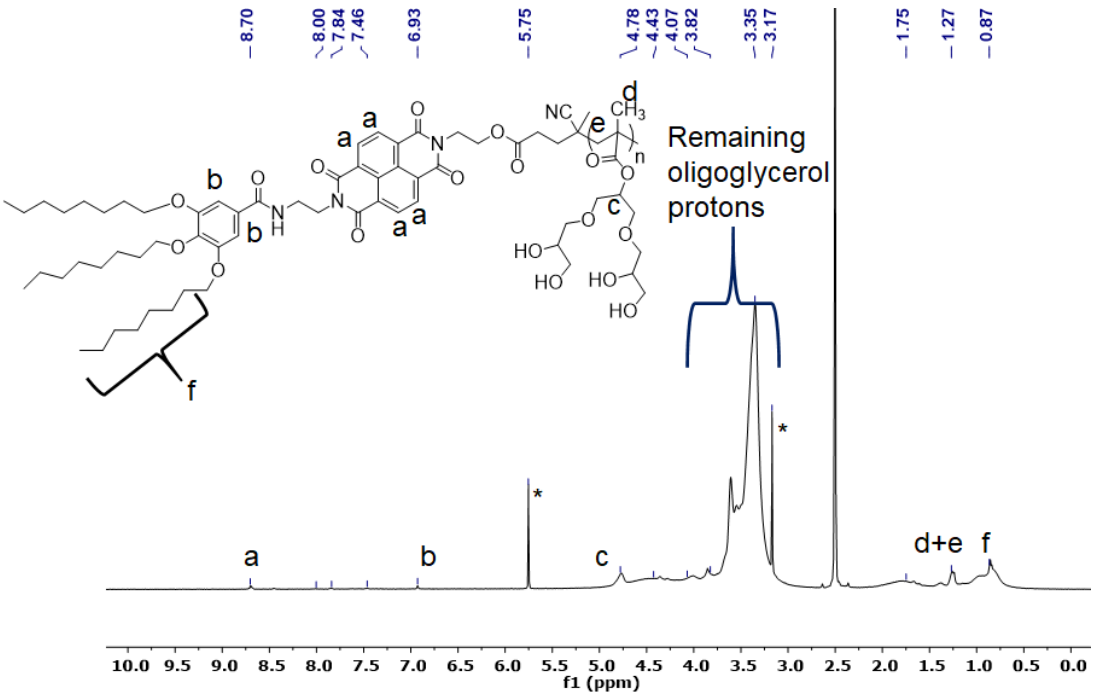

Figure S4: ^{1}H NMR of P3 in DMSO-D6. * indicates solvent.

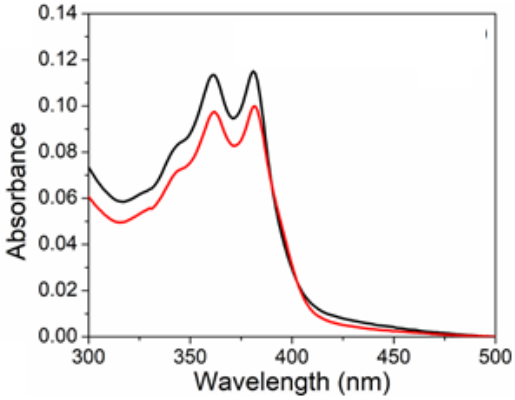

Figure S5. UV/Vis spectra of freshly prepared (black line) and aged (24 h) (red line) solution of P1 in 20% THF/H_2O. *c* = 1.0 mg/mL, *l*= 0.1 cm.

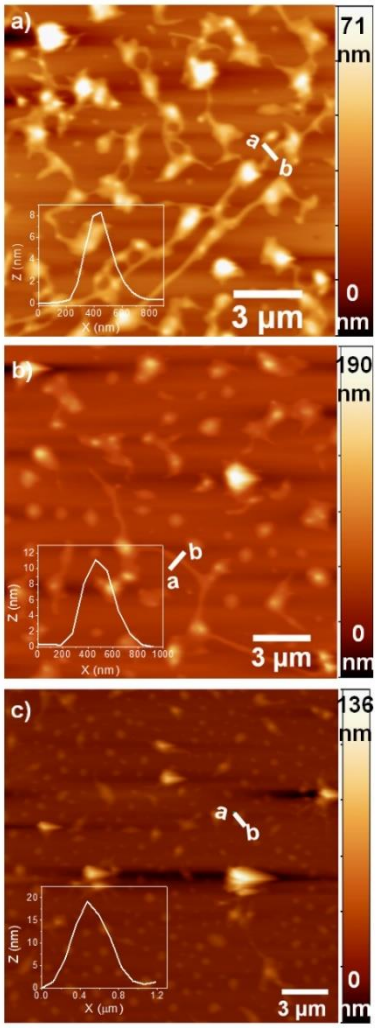

Figure S6. Concentration dependent morphology evolution of P1(AFM height image) after 24h in 20% THF-water; c = a) 0.75 mg/mL, b) 1.5 mg/mL, and c) 3.0 mg/mL. Height profile in the inset is for a-b.

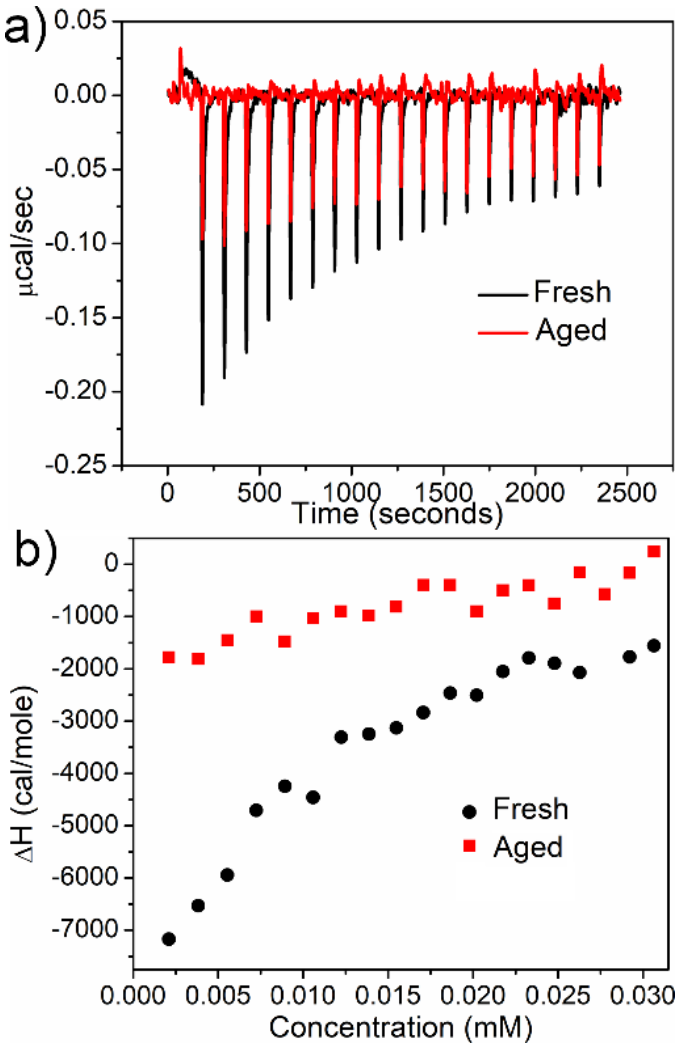

Figure S7: ITC dilution experiment of P1 aggregate (black- freshly prepared solution; red-72 h aged solution) in water: a) Heat release per injection of P1 (c =2.5 mg/mL) into water at 303K and b) Corresponding enthalpograms. ITC of freshly prepared solution of P1 reported before.[4] The data have been plotted for comparision purpose together with the aged sample.

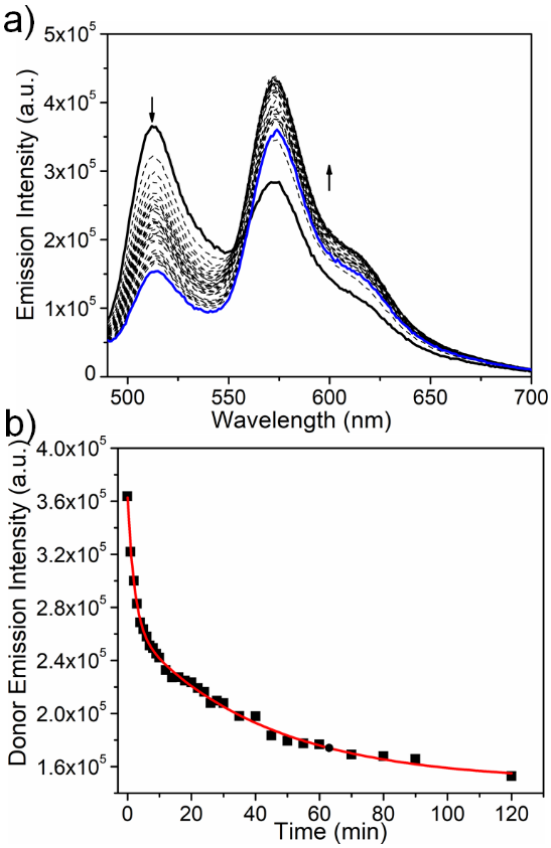

Figure S8: a) Emission spectra (λ_{ex} = 470 nm) of a physical mixture of DiI-encapsulated and DiO-encapsulated aged P1 in water (0.5 mM) at different time interval (black solid line and blue lines show spectra at the beginning and after 120 min, respectively). Arrows indicated direction of spectra change over time; b) Plot of donor emission intensity (λ_{em} = 508 nm) vs time. Red line is the fitted data using equation-1.

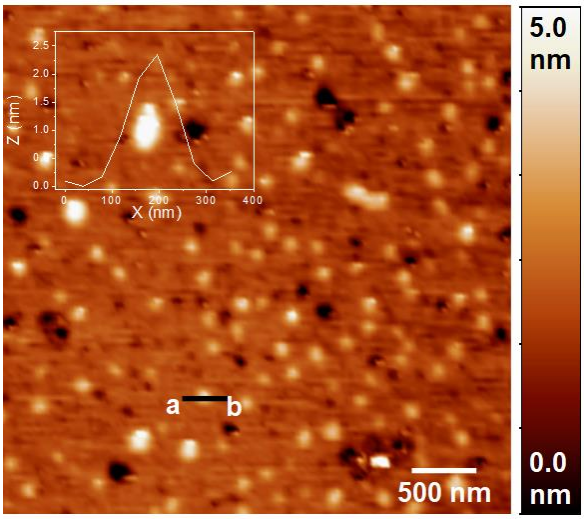

Figure S9: AFM image of freshly prepared P2 in water (c = 1 mg/mL, t = 0 h). Average Diameter 90±8 nm. Height profile in the inset is for a-b.

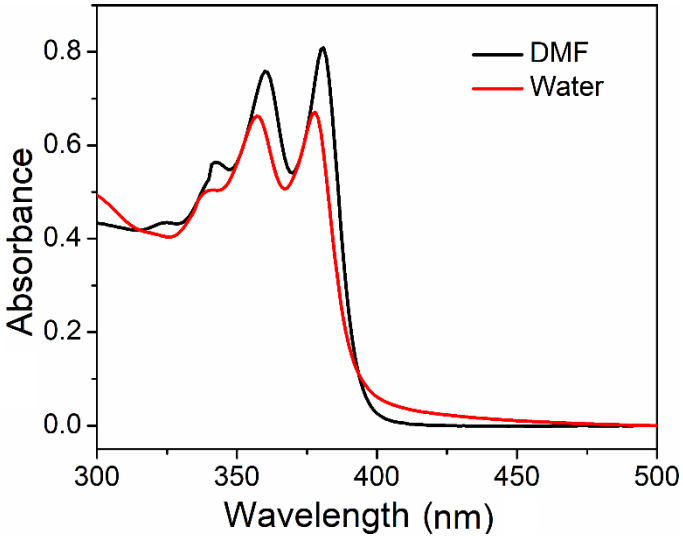

Figure S10. UV/Vis spectra of P3 in water and DMF (c = 1 mg/mL, l = 1 cm).

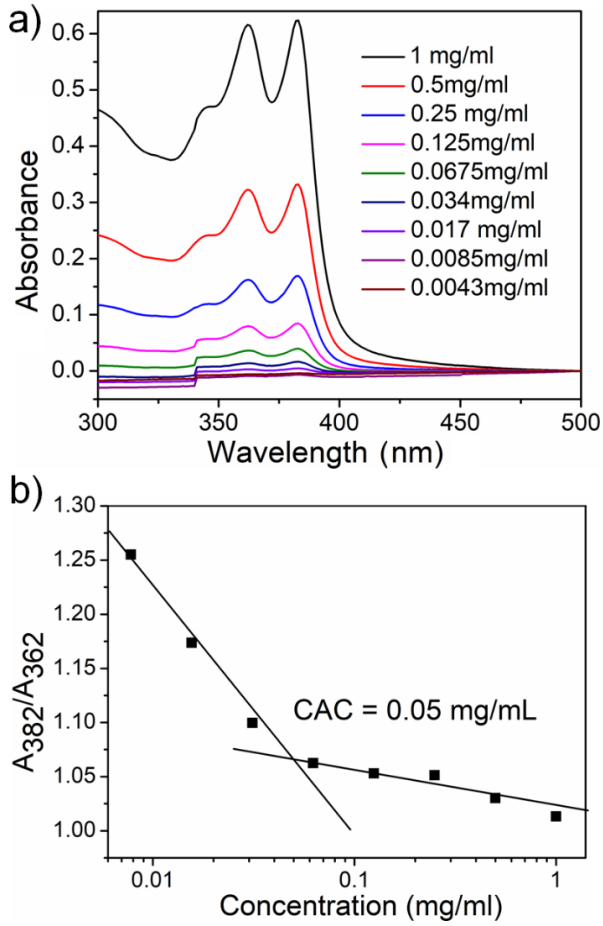

Figure S11. Determination of CAC of P3 using UV/Vis spectroscopy: a) UV/Vis spectra of P3 at different concentrations in water, b) Plot of ratio of absorbance at 382 nm and 362 nm with concentration.

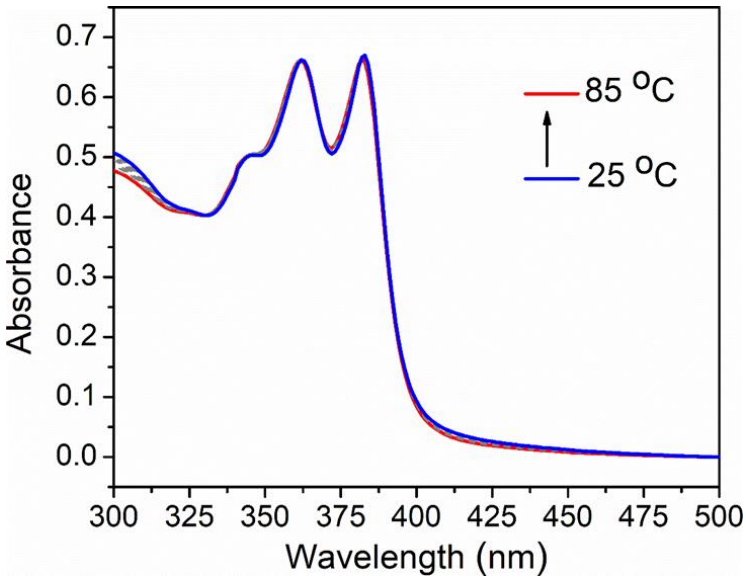

Figure S12. Variable temperature UV/Vis spectra of P3 in water (l = 1 cm, c = 1 mg/mL).

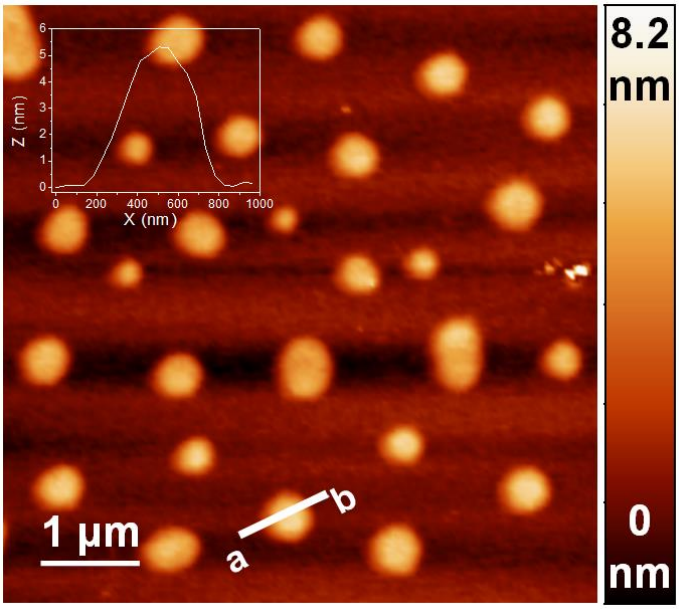

Figure S13. AFM image of P3 in water (freshly prepared solution, *c* = 1 mg/mL). Height profile in the inset is for a-b.

References:

(1) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed., Pergamon, Oxford, **1980**.

(2) Thang, S. H.; Chong, (Bill)Y.K.; Mayadunne, R. T. A.; Moad, G.; Rizzardo, E. A Novel Synthesis of Functional Dithioesters, Dithiocarbamates, Xanthates and Trithiocarbonates. *Tetrahedron Lett.* **1999**, *40*, 2435–2438.

(3) Wyszogrodzka, M.; Haag, R. A Convergent Approach to Biocompatible Polyglycerol "Click" Dendrons for the Synthesis of Modular Core–Shell Architectures and Their Transport Behavior. *Chem. - Eur. J.* **2008**, *14*, 9202–9214.

(4) Dey, P.; Rajdev, P.; Pramanik, P.; Ghosh, S. Specific Supramolecular Interaction Regulated Entropically Favorable Assembly of Amphiphilic Macromolecules. *Macromolecules* **2018**, *51*, 5182–5190.