Photo- and Thermo-responsive Star-shaped Diblock Copolymer with Porphyrin Core Prepared via Consecutive ATRPs

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1. Characterization

¹H NMR spectra were carried out on a Bruker Avance 400MHz spectrometer at ambient temperature, using CDCl₃ or DMSO-d₆ as solvent, TMS for ¹H calibration. Element analysis was obtained on a Carlo Erba-MOD1106 instrument. Fourier transform infrared (FT-IR) spectra were recorded on a FT-IR 8400S (Shimadzu) spectrometer by incorporating samples in KBr disks. Molecular weights (M_n ,GPC) and polydispersity (M_w/M_n) were measured on a gel permeation chromatograph (GPC) using a Waters e2695 separations module, two waters styragel columns (HR4 and HT3, 300 mm × 7.8 mm, 5 µm particles; exclusion limits: 5000-30,000 and 500-30,000 g mol-1, respectively) and a Waters 2414 refractive index dector maintained at 35 °C, linear polystyrene was used as calibration standards, THF was used as a mobile phase at a flow rate of 1.0 mL/min. Ultraviolet-visible (UV-vis) spectra were measured on a UV-2600 (Shimadzu) spectrophotometer. Shimadzu RF-5301PC fluorescence spectrophotometer was used to measure fluorescence spectra (Ex/Em slit: 5/5 nm). The Cloud Points (CP) of PAzo-b-PAM aqueous solution was measured using a UV-2600 (Shimadzu) equipped with a digital temperature controller. The temperature was increased at a rate of 0.5°C/min, and transmittance of polymer solutions at 500 nm was monitored as a function of temperature.

2. Synthesis of 5, 10, 15, 20-tetra(4-hydroxyphenyl)-porphine(THPP)

4-hydroxybenzaldehyde (3.4 g, 28 mmol), pyrrole (2mL, 28 mmol) and DMSO (6 mL) were added to 120 mL of propionic acid and refluxed for 2 h. The solution was allowed to cool over night (0 °C). The reaction mixture was filtered and washed thoroughly with propionic acid until the filtrate became clear and the crude product was dried over night under vacuum (80 °C). The crude product was dissolved in 100 mL diethyletheranhydrous, and then filtered and washed thoroughly with diethyletheranhydrous until the filtrate was clear. The filtrate was collected and evaporated to obtain a purple residue (Scheme S1, Yield: 1.14 g, 24.15%).

FT-IR (KBr, cm⁻¹): 3430 cm⁻¹(ν_{-OH}), 3357 cm⁻¹(ν_{N-H}), 969 cm⁻¹(δ_{N-H}), 729 cm⁻¹, 810 cm⁻¹, 990 cm⁻¹(pyrrole) [Figure S1(A)]. ¹H NMR (δ , DMSO- d_6 , ppm): 9.96(s, 4H, Ar-OH), 8.88(s, 8H, pyrrole-H), 8.02(d, 8H, Ar-H), 7.23(d, 8H, Ar-H), -2.86(d, 2H, pyrrole-NH) Figure S2(A)]. Anal. Calcd for C₄₄H₃₀N₄O₄: C, 77.86; H,4.46; N, 8.25; O,9.43. Found: C, 77.93; H, 4.44; N, 8.21; O,9.42.



Scheme S1 Synthetic route of THPP.



Scheme S2 Synthetic route of ZnTHPP.

3. Synthesis of 5, 10, 15, 20-tetra(p-hydroxyphenyl)-zincporphyrin(Zn-THPP)

The relevant metal salt zincacetate (372 mg, 5 mol) and THPP (200 mg, 1 mol) were combined under nitrogen in DMF (20 mL). The mixture was refluxed for 1 h and cooled. The reaction mixture was pour into deionized water (100 mL). The zinzolin solid precipitated, then was filtered to generate the purple crystals and dried at 65 °C under vacuum (Scheme S2, Yield: 203.4 mg, 91.50%).

FT-IR (KBr, cm⁻¹): 3430 cm⁻¹(v_{-OH}), 729 cm⁻¹, 810 cm⁻¹, 990 cm⁻¹ are the skeletal vibration of pyrrole, 1000 cm⁻¹(δ_{Zn-N}) [Figure S1(B)]. ¹H NMR (δ , DMSO- d_6 , ppm): 9.82 (s, 4H, Ar-OH), 8.83 (s, 8H, pyrrole-H), 7.89 (d, 8H, Ar-H), 7.18 (d, 8H, Ar-H) [Figure S2(B)]. Anal. Calcd for C₄₄H₂₈N₄O₄Zn: C, 77.86; H,4.46; N, 8.25; O,9.43. Found: C, 77.93; H, 4.44; N, 8.21; O,9.42.



Figure S1 FT-IR spectra of (A) THPP and (B) ZnTHPP.



Figure S2¹H NMR spectra of THPP (A) and ZnTHPP (B).

4. Synthesis of 5, 10, 15, 20-tetra(4-(2-bromopropoxy)phenyl)-zincporphyrin (ZnTHPP-Br)

ZnTHPP-Br was synthesized as follows (Scheme S3): ZnTHPP (300 mg, 4.05×10^{-4} mol), triethylamine (1.13 mL, 2×10^{-3} mol) and a mixed solution of ethyl ether and dichloromethane (100 mL, 1:1 v/v) were mixed under nitrogen in an ice bath. 2-Bromopropionyl bromide (0.83 mL, 2×10^{-3} mol) in dichloromethane (10 mL) was added dropwise over 15 min. The mixture was

allowed to warm to room temperature and then stirred for 24 h. The reaction mixture was then washed with deionized water three times, and the organic layer was reduced to a minimum under vacuum. The resulting solution was purified by silica flash chromatography [SiO₂, petroleum dichloromethane/methanol (200:1 v/v) as the eluent]. After the removal of solvent, the porphyrin was isolated as a purple powder.

FT-IR (KBr, cm⁻¹): 2850-2960 cm⁻¹ ($v_{-CH_2, -CH_3}$),1760 cm⁻¹ ($v_{C=0}$), 729 cm⁻¹, 810 cm⁻¹, 990 cm⁻¹ are the skeletal vibration of pyrrole [Figure S3]. ¹H NMR (δ , DMSO- d_{δ} , ppm): 8.82 (s, 8H, pyrrole-H), 8.25 (d, 8H, Ar-OH), 7.62 (d, 8H, Ar-H), 5.2 (q, 4H, -CH-), 1.87 (d, 12H, -CH₃) [Figure. S4]. Anal. Calcd for C₅₈H₄₆Br₄N₄O₈Zn : C, 53.10; H, 3.53; N, 4.27. Found: C, 53.05; H, 3.59; N, 4.28.



Scheme S3 Synthetic route of ZnTHPP-Br.



Figure S3 FT-IR spectra of ZnTHPP-Br.



Figure S4 ¹H NMR spectra of ZnTHPP-Br.

5. Synthesis of 6-[4-(4-methoxyphenylazo)phenoxy]hexylmethacrylate (AzoMA)

The 6-[4-(4-methoxyphenylazo)phenoxy]hexyl methacrylate (AzoMA) was synthesized following a previous method (Scheme S4).

FT-IR (KBr, cm⁻¹): 2850-2950 cm⁻¹($v_{-CH_2, -CH_3}$), 1715 cm⁻¹($v_{C=0}$), 1650 cm⁻¹($v_{C=C}$), 1600, 1585 cm⁻¹($v_{N=N}$), 725 cm⁻¹(δ_{-CH_2-}) [Figure S5]. ¹H NMR(CDCl₃, ppm): 7.87 (m, 4H), 6.99 (m,4H), 6.10 (s, 1H), 5.55 (s, 1H), 4.17 (t, 2H), 4.04 (t, 2H), 3.88 (s,3H), 1.95 (s, 3H), 1.87–1.80 (m, 2H), 1.77-1.70(m, 2H), 1.58-1.45(m, 4H) [Figure S6].



Scheme S4 Synthetic route of the monomer AzoMA.



Figure S5 FT-IR spectra of AzoMA.



Figure S6¹H NMR spectra of AzoMA.

6. FT-IR spectra of por-PAzo and PAzo-b-PAM

Figure S7 shows FT-IR absorption spectra of the *por*-PAzo and PAzo-b-PAM, respectively. From Figure S7a, the characteristic absorptions of *por*-PAzo could be clearly observed, as evidenced by the presence of a methyne stretching vibration (v_{C-H}) at 3088 cm⁻¹ and the azo group stretching vibration ($v_{N=N}$) at 1601, 1581cm⁻¹. For example, the strong absorbance at 3437 cm⁻¹ is assigned to the stretching vibration (v_{N-H}) of acylamino group and the characteristic absorption peaks originated from amide group are observed at 1657 cm⁻¹ ($v_{C=O}$) and 1549 cm⁻¹ (δ_{N-H}).



Figure S7 FT-IR spectra of *por*-PAzo ($M_n = 9100$) (a) and PAzo-b-PNIPAM ($M_n = 37000$) (b).

7. Dynamic light scattering (DLS) of PAzo-b-PNIPAM

The size of PAzo-b-PNIPAM is determined using dynamic light scattering (DLS), the results show that these copolymers form micellar nanoparticles when the temperature is lower than 23° C, these micelles have *por*-PAzo as the nuclear and hydrophilic PNIPAM chains as shell, thus hydrophilic PNIPAM chains play an important solubilization effect in aqueous solution for hydrophobic *por*-PAzo. But when the temperature is higher than 23° C, the PNIPAM chains show the hydrophobic property that leads the micelles to aggregate and then precipitate from the aqueous solution, so the diameter of PAzo-b-PNIPAM sharp increase as the temperature continuing to rise, in other words the solubilization effect is destroyed. At the macroscopic level, the solution has phase transition from clear to cloudy. Furthermore, the temperature of the diameter sharp increase conforms to the LCST coming from the determination of cloudy point.



Figure S8 Temperature-dependent the diameter of PAzo-b-PNIPAM ($M_n = 37000$) in aqueous solution.