

Supporting Information

**Self-Assembly and Multi-Stimuli Responsive
Behavior of PAA-*b*-PAzoMA-*b*-PNIPAM Triblock
Copolymers**

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Syntheses of the PAA-*b*-PMAzo-*b*-PNIPAM polymer

Materials. Acrylic acid (AA) (Shanghai Chemical Reagent Co., China, 97%) was dried over anhydrous magnesium sulfate, then distilled under reduced pressure and stored at -10 °C. *N*-isopropyl acrylamide (NIPAM, Aldrich, 97%) was recrystallized from benzene/*n*-hexane prior to use. 2, 2'-azobisisobutyronitrile (AIBN, 97%) was recrystallized twice in methanol and stored at 4 °C. Cumyl dithiobenzoate (CDB) was synthesized using a literature method.¹ 6-(4-methoxy-4'-oxy-azobenzene) hexyl methacrylate (AzoMA) was synthesized according to the method reported by Stewart.² Other chemicals were used without further purification.

RAFT Polymerization of AA using CDB as the RAFT Agent. The PAA-CTA macro chain transfer agent was synthesized by solution polymerization in tetrahydrofuran (THF). Typically, AA (6.8 mL, 99.1 mmol), AIBN (27.2 mg, 0.166 mmol), CDB (0.45 g, 1.65 mmol) and 7.0 mL THF were mixed in a glass tube. The purplish red homogeneous solution was bubbled with nitrogen for about 1 h. Then the tube was sealed and placed in an oil bath at 80 °C for 12 h. Afterwards, the reaction tube was quenched in ice water and opened. The mixture was diluted with THF and precipitated in a large amount of diethyl ether. The purification procedure was repeated three times from THF to diethyl ether, filtrated and dried in vacuum at room temperature overnight. Yield: 51%. M_n (NMR) = 0.27×10^4 g.mol⁻¹. The ¹H NMR spectrum of PAA-CTA is presented in Fig. S1.

RAFT Polymerization of MMAZO using PAA-CTA as the Macro-RAFT Agent. The PAA-*b*-PAzoMA-CTA macro chain transfer agent was synthesized solution polymerization in *N,N*-dimethylformamide (DMF). Typically, AzoMA (1.76 g, 4.44 mmol), AIBN (2.0 mg, 0.012 mmol), PAA-CTA (0.2 g, 0.074 mmol) and 14 mL DMF were charged into a glass tube. The yellow turbid liquid was bubbled with N₂ for about 1.5 h. After that the tube was sealed and

immersed into an oil bath at 75 °C for 24 h. Afterwards, the reaction tube was quenched in ice water and opened. The mixture was diluted with THF and dripped in excess diethyl ether. The yellow powder was purified by reprecipitating three times from THF to cold diethyl ether, filtrated and then dried in vacuum overnight at 40 °C. Yield: 70%. M_n (NMR) = 2.39×10^4 g.mol⁻¹. The ¹H NMR spectrum of PAA-*b*-PAzoMA-CTA is presented in Fig. S2.

RAFT Polymerization of NIPAM using PAA-*b*-PAzoMA-CTA as the Macro-RAFT Agent. The RAFT polymerization of NIPAM was taken as follows: NIPAM (0.36 g, 3.18 mmol), AIBN (1.0 mg, 0.006 mmol), PAA-*b*-PAzoMA-CTA (0.5 g, 0.026 mmol) and 6 mL DMF/dioxane (1:1) mixed solvent were added to a reaction tube. The orange solution was bubbled with nitrogen for 1.5 h. Then the tube was sealed and putted in an oil bath at 70 °C for 6 h. Afterwards, the reaction tube was quenched in ice water and opened. The mixture was diluted with THF and dripped in excess diethyl ether. The purification procedure was repeated three times from THF to cold diethyl ether, filtrated and dried in vacuum at room temperature for 24 h. Yield: 64%. M_n (NMR) = 2.88×10^4 g.mol⁻¹.

Figures

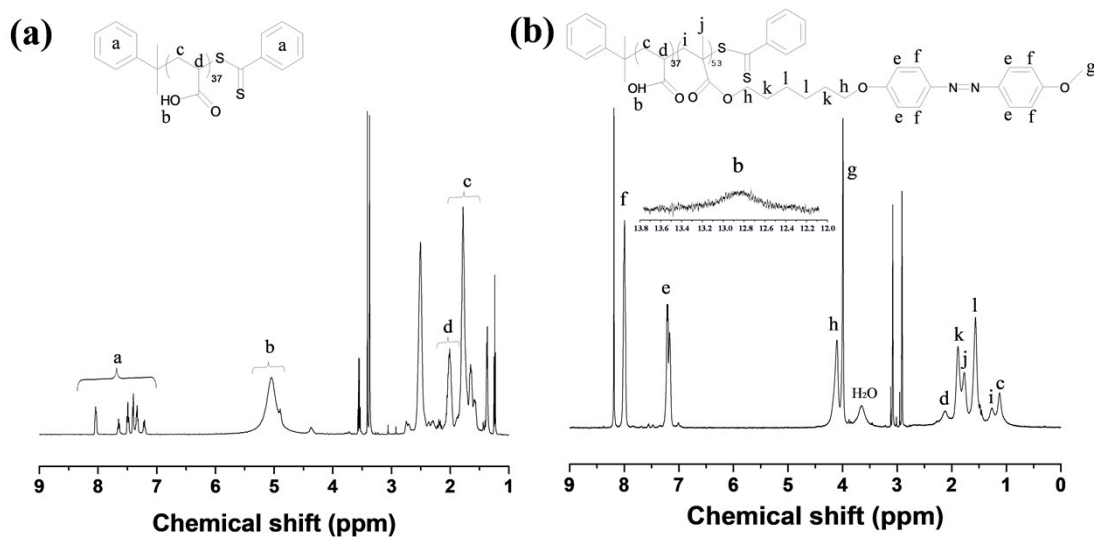


Fig. S1 ^1H NMR spectrum of (a) PAA precursor and (b) PAA-*b*-PAzoMA precursor.

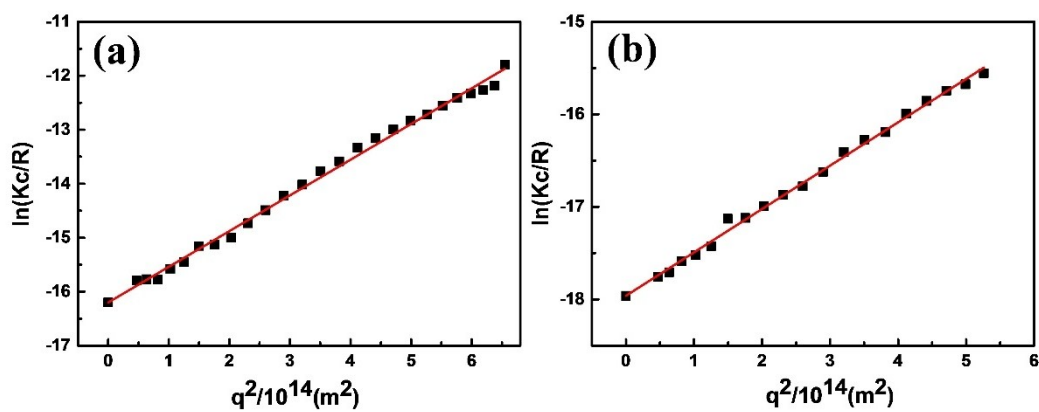


Fig. S2 Plot for the angular dependence of the excess Rayleigh ratio $R(q)$ of PAZN aggregates fabricated from (a) Diox and (b) THF.

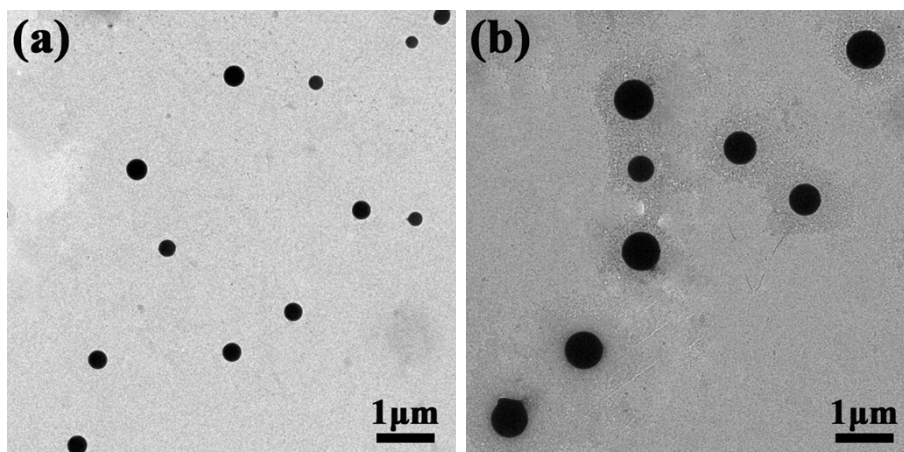


Fig. S3 TEM images of PAZN micelles from Diox at different initial concentration (a) 0.1 mg ml⁻¹, (b) 1 mg ml⁻¹.

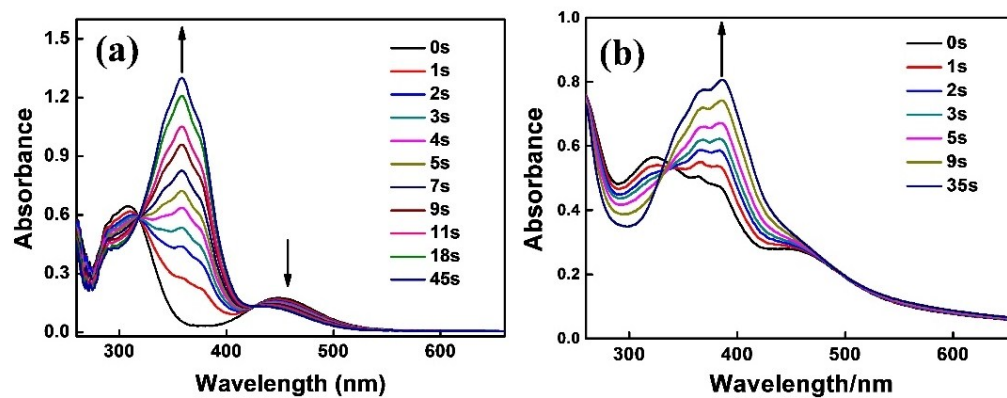


Fig. S4. UV-vis absorption spectra upon irradiation with 450 nm light. (a) PAZN in Diox, (b) PAZN micelles in water. 0s is the spectrum after irradiation of 365 nm until photostationary state.

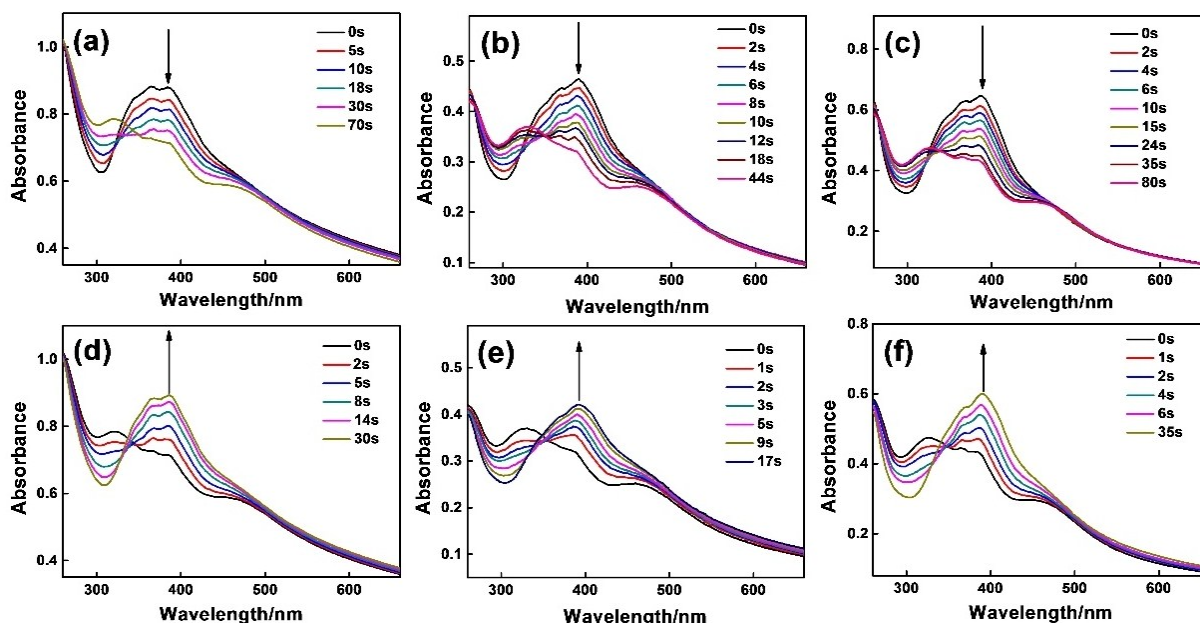


Fig. S5 UV-vis absorption spectra of PAZN micelles with different concentration, temperature and pH. (a, b, c) UV-vis absorption spectra upon irradiation with the 365 nm light. (d, e, f) UV-vis absorption spectra upon irradiation with the 450 nm light. (a, d) 1 mg mL^{-1} , $T = 20\text{ }^{\circ}\text{C}$, $\text{pH} = 6.9$; (b, e) 0.1 mg mL^{-1} , $T = 45\text{ }^{\circ}\text{C}$, $\text{pH} = 6.9$; (c, f) 0.1 mg mL^{-1} , $T = 20\text{ }^{\circ}\text{C}$, $\text{pH} = 2.2$.

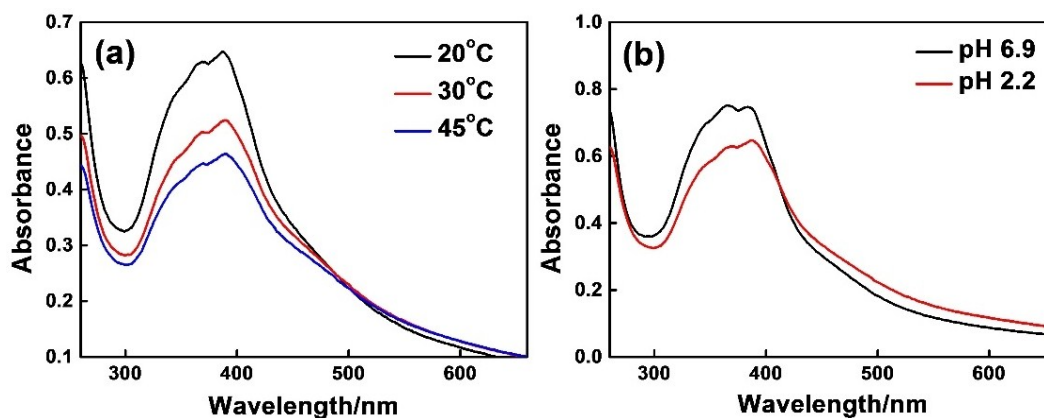


Fig. S6 UV-vis absorption spectra of PAZN micelles prepared at 0.1 mg mL^{-1} : (a) micelles with $\text{pH} = 2.2$ irradiated at different temperature; (b) micelles with different pH irradiated at $20\text{ }^{\circ}\text{C}$.

References

1. Chong, Y. K.; Krstina, J.; Le, T. P. T.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules*. **2003**, *36*, 2256-2272.
2. Stewart, D.; Imrie, C. T. *Polymer*. **1996**, *37*, 3419-3425.