

## ***Supporting Information***

### **Light-Induced Reversible Self-Assembly of Multi-Compartment Patchy Micelles**

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## 1. Materials

Monomer 4-vinyl pyridine (4VP) was purchased from Aldrich and purified by distillation prior to polymerization. 6-[4-(4-butylphenylazo) phenoxy] hexyl methacrylate (AzoMA) was synthesized according to the procedure reported by Stewart and Imrie.<sup>1</sup> 2,2'-azobis(isobutyronitrile) (AIBN) was used as initiator and recrystallized before use. The reversible addition-fragmentation chain transfer (RAFT) agent 4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanylpentanoic acid (CDSA) was purchased from Aldrich and used without further purification. Diblock polymer P4VP-*b*-PAzoMA was synthesized according to our previous work.<sup>2</sup> Deionized water was collected from Milli-Q system with the resistance of 18.2 MΩ. Other reagents (A.R. grade) were purchased from Adamas-beta and used as received.

## 2. Synthesis of poly(4-vinylpyridine)-block-poly[6-[4-(4-butyloxyphenylazo) phenoxy] hexyl methacrylate] (P4VP-*b*-PAzoMA)

The synthesis route to AzoMA monomer and block copolymer is provided in **Figure S1** according to Stewart and Imrie and our previous work.<sup>1, 2</sup> Macromolecular RAFT agent P4VP-CDSA was synthesized by a typical RAFT polymerization of 4VP with CDSA initiated by AIBN. A Schlenk tube was charged with degassed 4VP (5.00 g, 47.6 mmol), AIBN (14.5 mg, 0.0883 mmol), CDSA (106.6 mg, 0.264 mmol), DMF (5 mL) and a magnetic stirrer. The mixture was purged with dry nitrogen and subjected to three freeze-pump-thaw cycles to remove any dissolved oxygen. Then the tube was sealed under vacuum and immersed in an oil bath at 65 °C for 24 h. The reaction was stopped and the tube was quickly cooled down with liquid nitrogen. The mixture was diluted with DMF and precipitated into excess cold diethyl ester. The product was purified by reprecipitating three times from DMF to cold diethyl ester and dried in vacuum at room temperature overnight. P4VP-CDSA was obtained as a pink powder. Yield: 4.45 g (87.6 %). Degree of polymerization (denoted as: DP) (<sup>1</sup>H NMR) = 150. Thus, the obtained product was denoted as P4VP<sub>150</sub>-CDSA.

Target diblock copolymer P4VP-*b*-PAzoMA was synthesized via a second RAFT polymerization of AzoMA monomers with P4VP-CDSA. A Schlenk tube was charged with degassed P4VP<sub>150</sub>-CDSA (290 mg, 0.0183 mmol), AIBN (1.00 mg, 0.00613 mmol), AzoMA monomer (700 mg, 1.65 mmol), DMF (1 mL), THF (2 mL) and a magnetic stirrer. The mixture was purged with dry nitrogen and subjected to three freeze-pump-thaw cycles to remove any dissolved oxygen. Then the tube was sealed under vacuum and immersed in an oil bath at 75 °C for 24 h. The reaction was stopped and the tube was quickly cooled down with liquid nitrogen. The mixture was diluted with dichloromethane and precipitated into excess cold diethyl ester. The product was purified by reprecipitating three

times from dichloromethane to cold diethyl ester and dried in vacuum at room temperature overnight. P4VP-*b*-PAzoMA was obtained as a yellow powder. Yield: 641.3 mg (73.6 %). Degree of P4VP and PAzoMA polymerization was calculated by <sup>1</sup>H NMR spectra (Figure S2c).

The corresponding <sup>1</sup>H NMR spectra of monomers and copolymers P4VP-*b*-PAzoMA are shown in Figure S2.

### 3. Formation of P4VP-*b*-PAzoMA reverse micelle and crosslinking of P4VP cores

First, the stock solution of block copolymers P4VP<sub>150</sub>-*b*-PAzoMA<sub>75</sub> was dissolved in chloroform (CHCl<sub>3</sub>) at room temperature overnight. The reverse micelles (2 mg/mL) were obtained after adding an equal amount of toluene and evaporating CHCl<sub>3</sub> completely at 60 °C for 8 h. Then 1,4-diiodobutane (DIB) was added to toluene solution to crosslink the P4VP core with a molar ratio of I and pyridyl groups of 4VP = 1.0 at 45 °C for 3 d.

### 4. Hierarchical self-assembly of multicompartment patchy micelles

The crosslinked micelles with PAzoMA corona were dispersed in dimethylformamide (DMF) with the concentration of 0.1 mg/mL by adding 20 fold DMF to toluene solution as described above. Then deionized water was mixed with DMF firstly to reduce the exothermic effect when the solvents were mixed. The pre-prepared DMF/H<sub>2</sub>O mixed solution was added into the swollen micelles DMF solution which was swollen for different time at the rate of 1 mL/h under mild stirring. The PAzoMA corona of the reverse micelle tended to collapse and aggregate into subunits with different patches due to the unfavorable interaction between AzoMA and DMF. Subsequently, subunits progressively self-assembled into colloidal chain, dumbbell, triangular, tetrahedron, and raspberry-shaped micelle (i.e., hierarchical self-assemblies) by continually addition of water. For the study of the effect of swollen time on hierarchical self-assembly, subunits with various swollen time were added with 15 vol% H<sub>2</sub>O.

## 5. Definitions and measurements of the parameters $X_n$ and PDI

### Number-average degree of the colloidal chain ( $X_n$ )

The parameter  $X_n$  characterizes the number-average length of the colloidal chain and is given by

$$X_n = \frac{\sum X N_x}{\sum N_x}$$

where  $X$  is the number of subunits in each colloidal chains and  $N_x$  is the number of colloidal chain with the degree of self-assembly  $X$ . In the experiments, the parameter  $N_x$  was captured by mathematical statistics from the TEM images by collecting more than 400 colloidal chains.

## Polydispersity index (PDI)

The parameter PDI was defined to characterize the size distribution of the colloidal chains and is given by

$$PDI = \frac{\sum_x X^2 N_x \sum_x N_x}{(\sum_x X N_x)^2}$$

## 6. Light-induced reversible hierarchical self-assembly (RHSA)

For the disassembly of multicompartment patchy micelles into subunits, the aggregates solution was irradiated using a LED lamp with 365 nm UV light (intensity: 90 mW cm<sup>-2</sup>) for various periods of time. For the re-assembly of disrupted subunits into initial multicompartment patchy micelles, the solution was irradiated upon 450 nm visible light for 30 min and kept at room temperature for 24 h. All experiments were carried out under ambient conditions.

## 7. Characterizations

**Transmission Electron Microscopy (TEM).** The morphologies of self-assemblies at various stages were measured by Transmission Electron Microscopy on JEM-1400 JEOL at an accelerating voltage of 100 kV. 5  $\mu$ L of the self-assemblies solution was dropped onto a grid coated with pure carbon film and then dried under room temperature. Some TEM samples were exposed to I<sub>2</sub> vapor for staining the P4VP block.

**Field Emission Scanning Electron Microscope (FESEM).** The surface morphology of the films was observed by a Field Emission Scanning Electron Microscope (Hitachi S4800) with an accelerating voltage of 15.0 kV.

**Dynamic Light Scattering (DLS) Measurements.** Hydrodynamic radius  $R_h$  was measured by dynamic light scattering with a laser light scattering (LLS) spectrometer (ALV/CGS-5022) equipped with an ALV-High QE APD detector and an ALV-5000 digital correlator using a He-Ne laser (the wavelength  $\lambda = 632.8$  nm) as the light source. In DLS measurements, the intensity correlation function was measured at 25 °C at a scattering angle of 90 ° and each sample was measured once for 300 seconds.

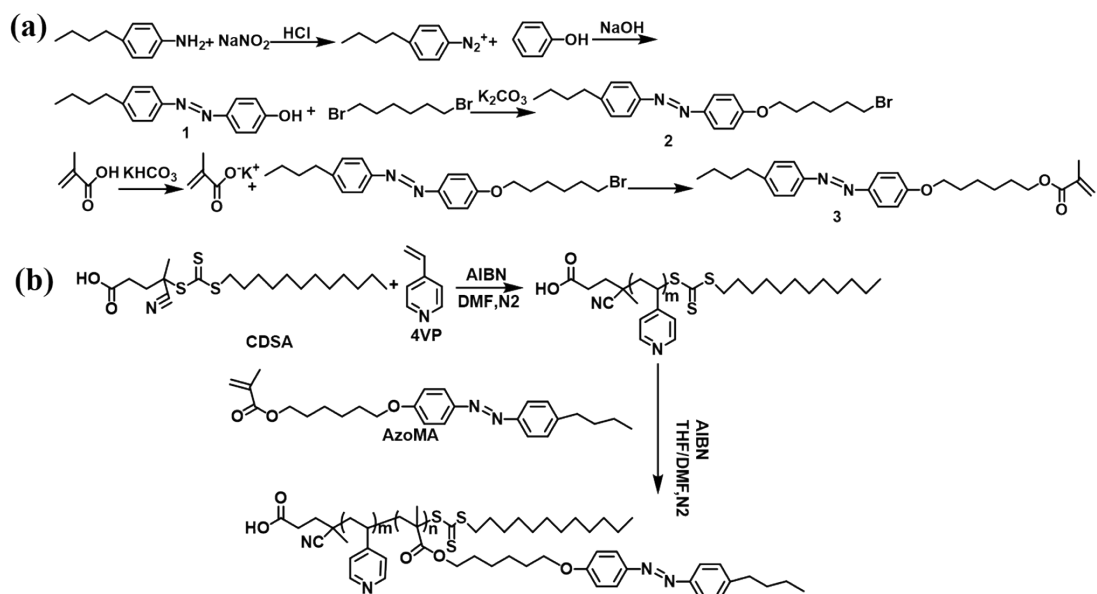
**Ultraviolet-Visible spectrophotometer (UV-vis).** The UV-Vis absorbance spectra were obtained using UV-2550 SHIMADZU and the optical density (turbidity) was measured at a wavelength of 690 nm using a quartz cell.

**Fourier Transform Infrared spectroscopy (FT-IR).** The Fourier transform infrared spectroscopy measurements were conducted by using Nicolet 5700 FT-IR spectrometer in transmission mode.

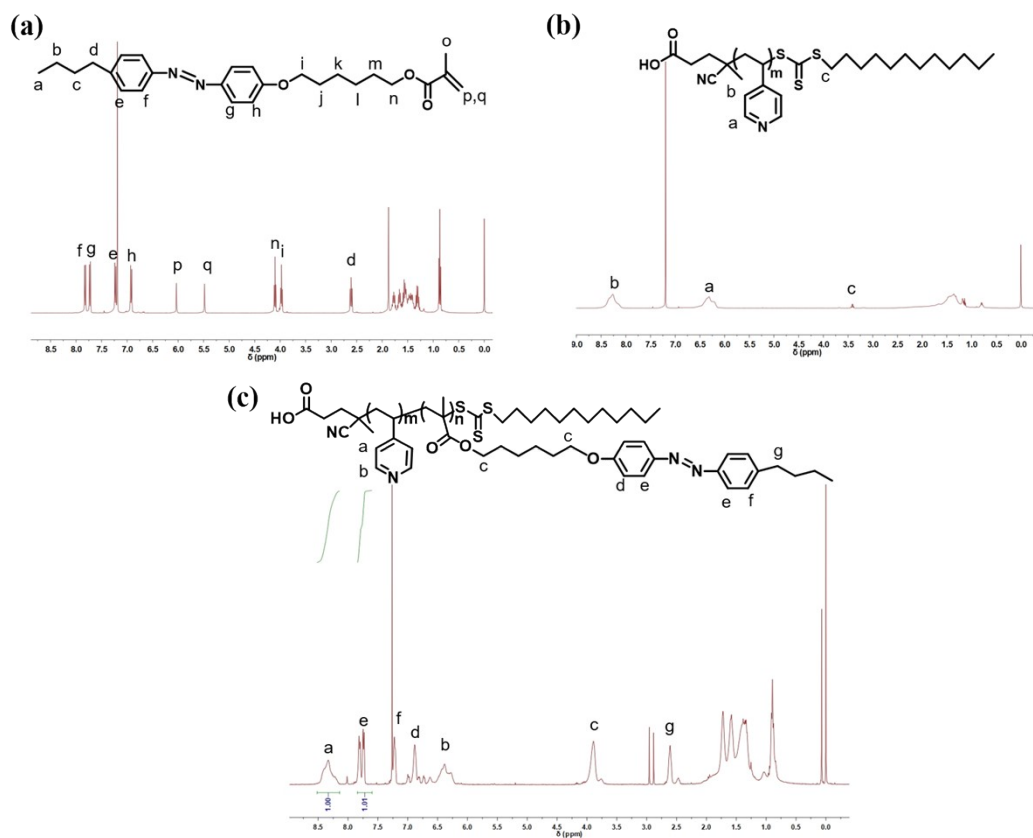
**Gel Permeation Chromatography (GPC).** Relative molecular weights and molecular weight distributions were measured by a GPC system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (HR3 (500-30,000), HR4 (5,000-600,000), and HR5 (50,000-

4,000,000), 7.8×300 mm, particle size 5 μm). GPC measurements were carried out at 35 °C using THF as eluents with a flow rate of 1.0 mL min<sup>-1</sup>. The system was calibrated with linear poly(methyl methacrylate) standards.

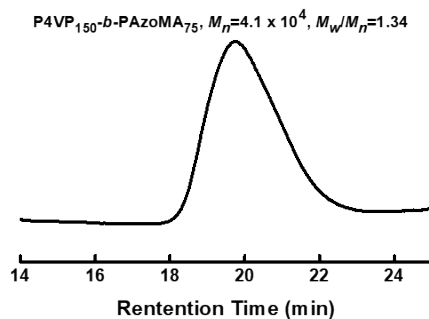
## 8. Figures and Figure Captions



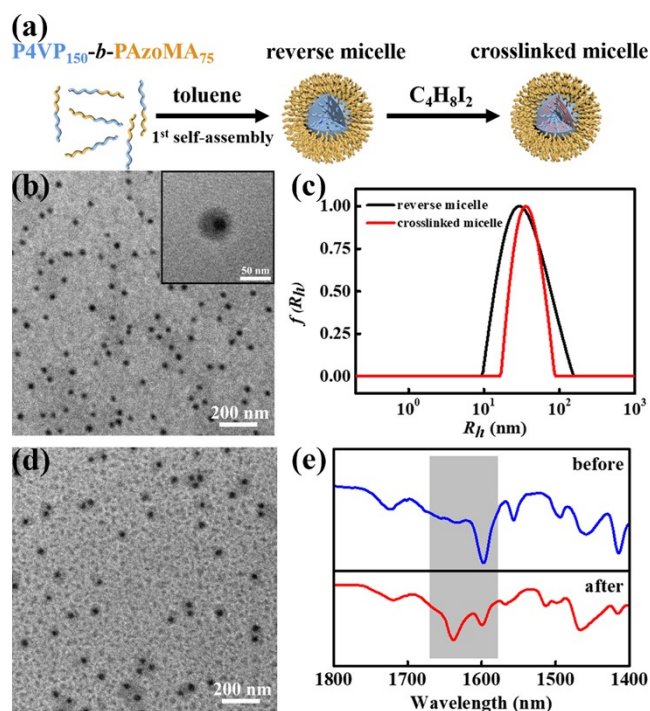
**Figure S1.** Synthetic route of (a)AzoMA monomer and (b)P4VP-*b*-PAzoMA block copolymer.



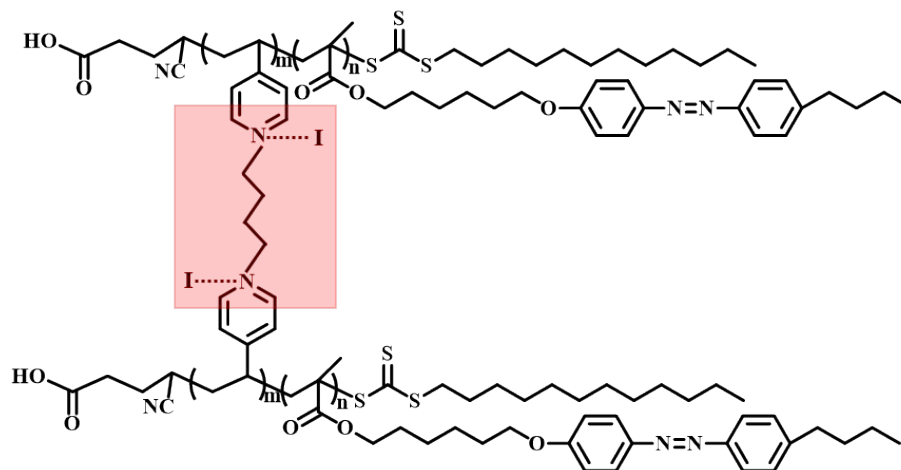
**Figure S2.**  $^1\text{H}$  NMR spectra of (a) AzoMA monomer, (b) macromolecular RAFT agent P4VP-CDSA and (c) P4VP<sub>150</sub>-*b*-PAzoMA<sub>75</sub> block copolymer in CDCl<sub>3</sub>.



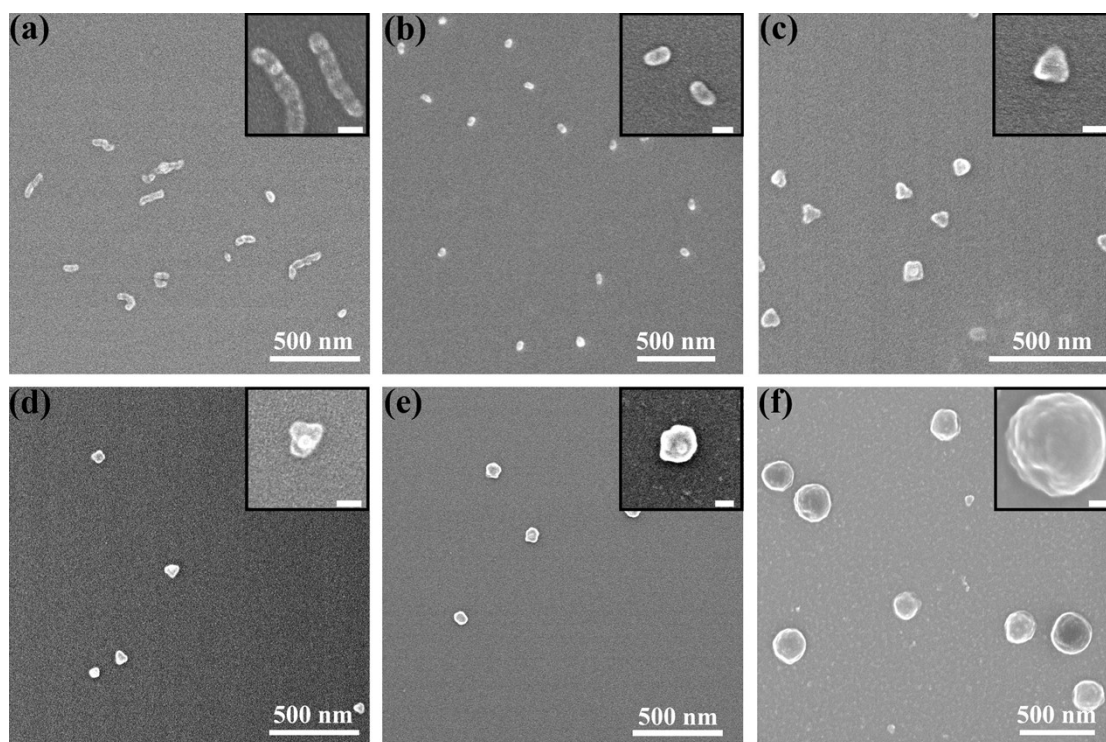
**Figure S3.** GPC trace of P4VP<sub>150</sub>-*b*-PAzoMA<sub>75</sub>.



**Figure S4.** (a) Schematic representation of the formation of core-corona micelle and the crosslinking of reverse micelle. (b) TEM image of reverse micelles in toluene. (c) Dynamic light scattering (DLS) results of hydrodynamic radius distribution of reverse micelles before and after crosslinking. (d) TEM image of crosslinked micelles. (e) FT-IR spectra of reverse micelles before and after crosslinking. The P4VP cores were stained by I<sub>2</sub> in TEM images.

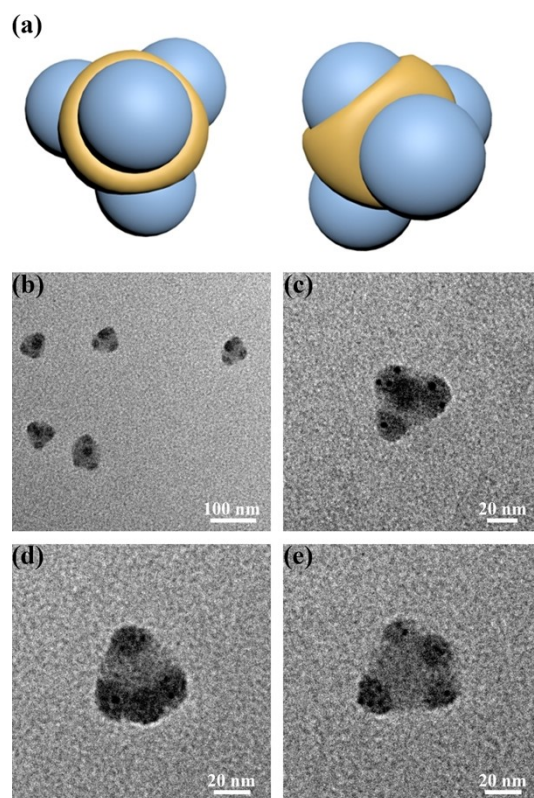


**Figure S5.** Chemical structures of P4VP-*b*-PAzoMA block copolymer crosslinked by 1,4-diiodobutane (DIB).

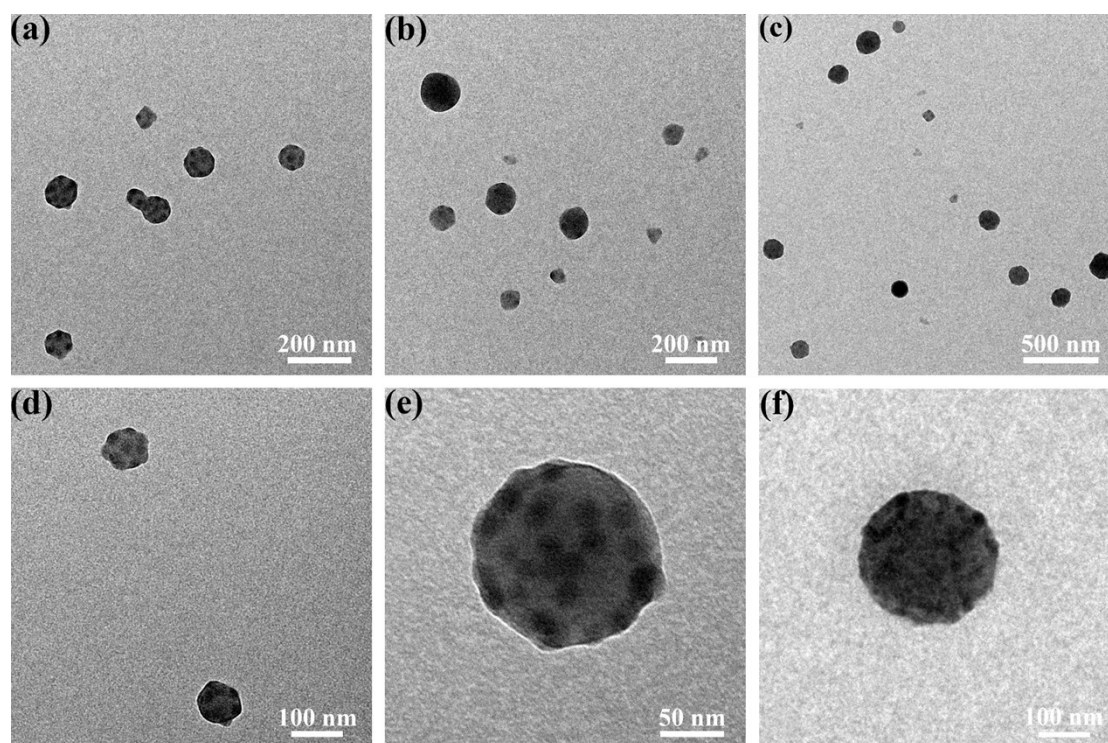


**Figure S6.** SEM images of (a) colloidal chains, (b) dumbbells, (c) triangles, (d) tetrahedrons, (e) and (f) raspberry-shaped compound micelles. Insets: Enlarged SEM images and scale bar: 50 nm.

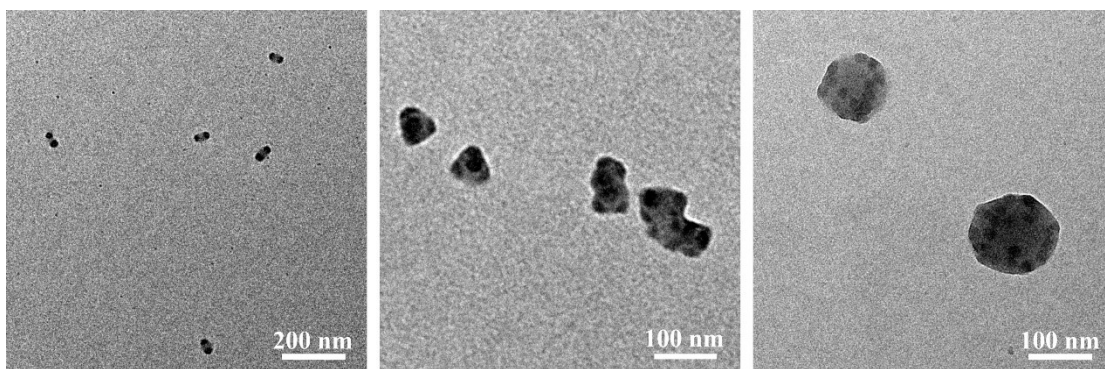




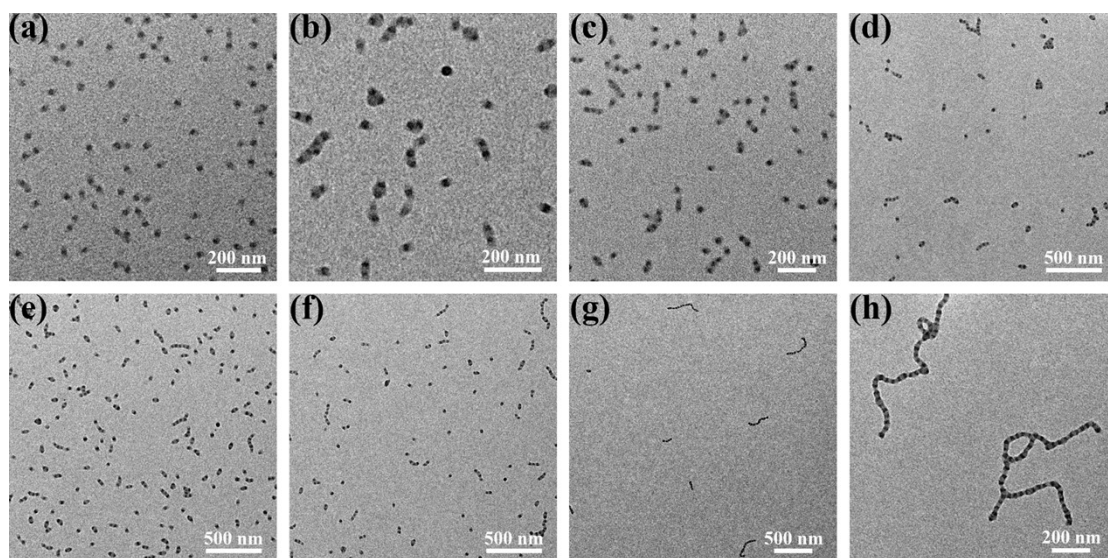
**Figure S7.** TEM images of the tetrahedrons with different collapse angles.



**Figure S8.** TEM images of raspberry-shaped micelles by swollen different time and then adding 15 vol% H<sub>2</sub>O: (a)(d) 11 d, (b)(e) 12 d, (c)(f) 15 d.



**Figure S9.** TEM images of the multicompart patchy micelles stabilized at room temperature for 15 d.



**Figure S10.** TEM images of colloidal chains growing at different time after adding 15 vol% H<sub>2</sub>O: (a) 0 h, (b) 13 h, (c) 1 d, (d) 2 d, (e) 4 d, (f) 5 d, (g) 9 d, and (h) 14 d.

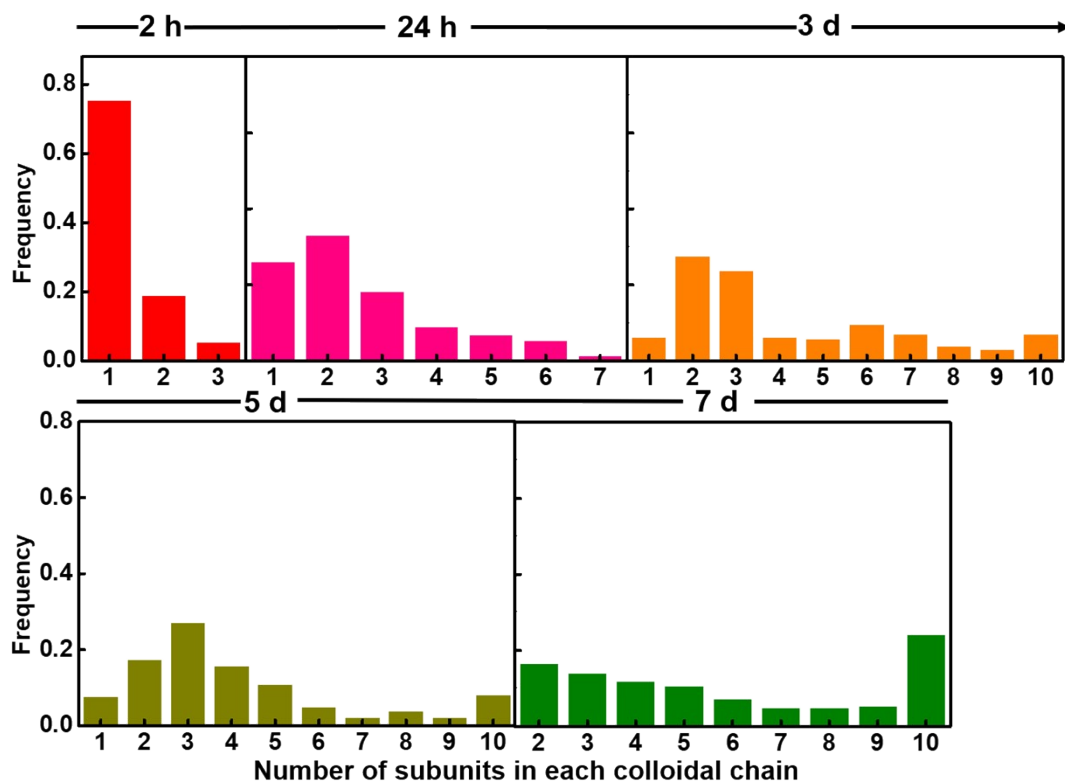


Figure S11. Evolution of the proportion of subunit numbers in each colloid chain as time processed.

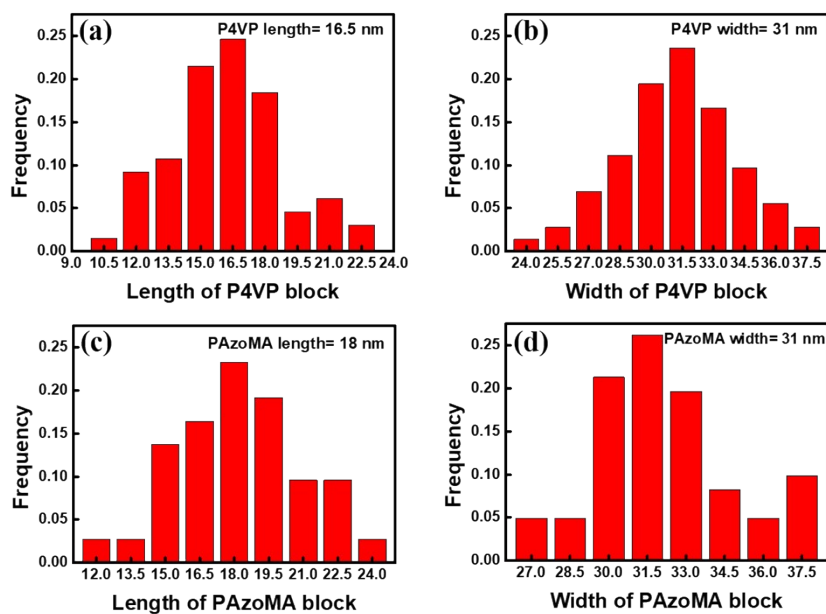
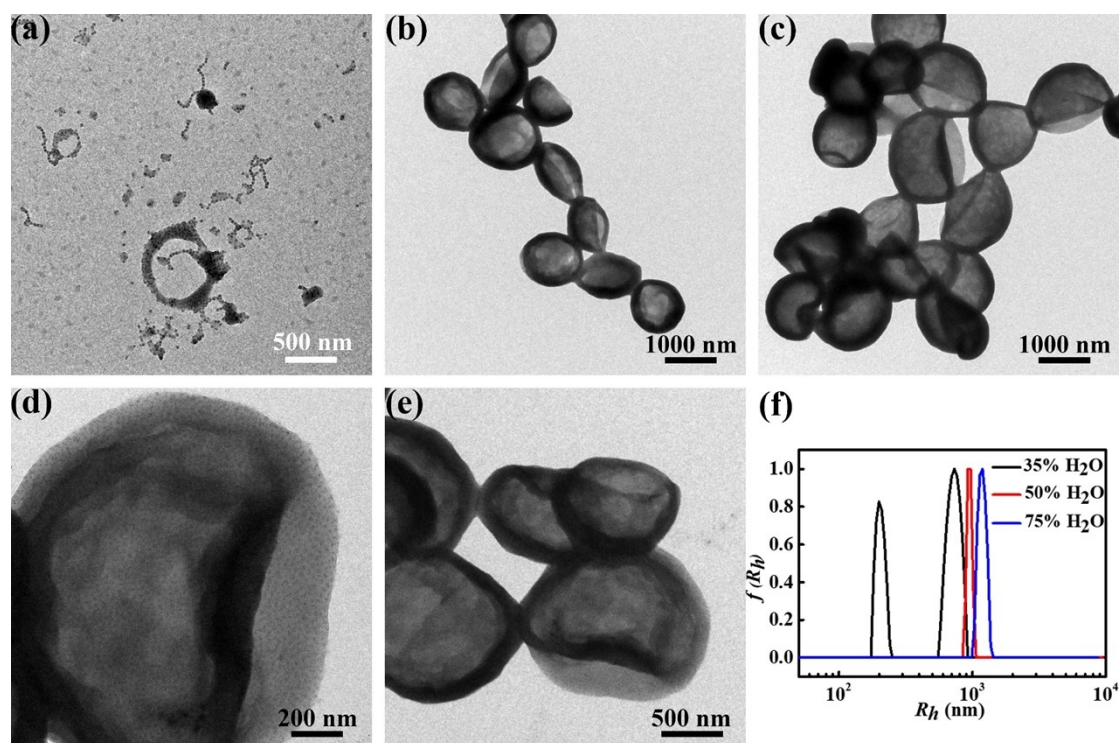
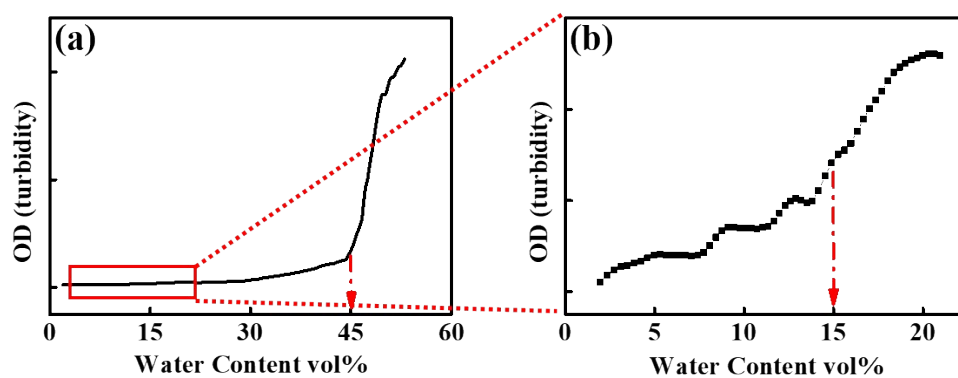


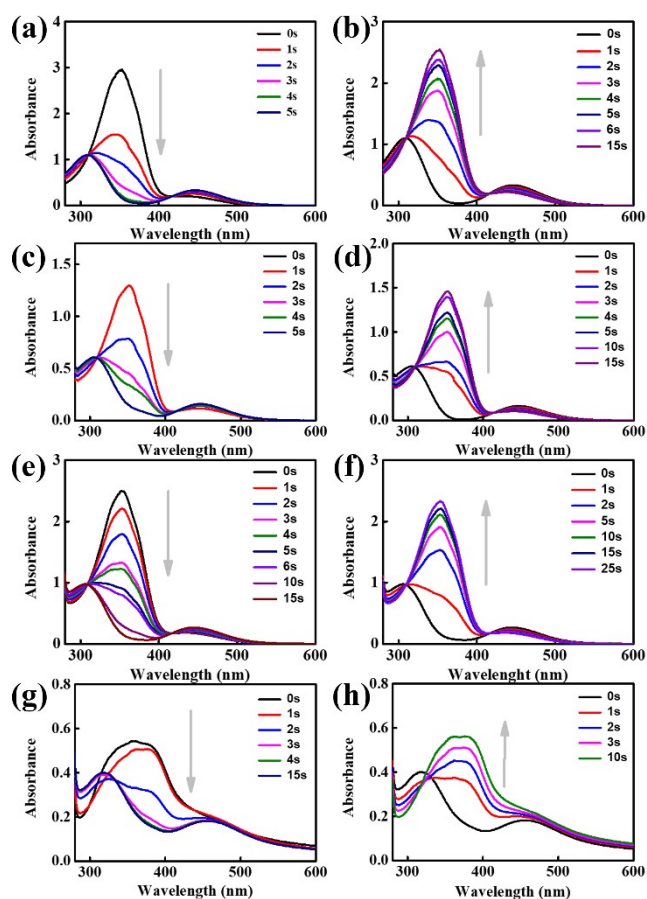
Figure S12. The length of specific colloidal chains segment structure: (a) P4VP block, (c) PAzoMA block. The width of specific colloidal chains segment structure: (b) P4VP block, (d) PAzoMA block.



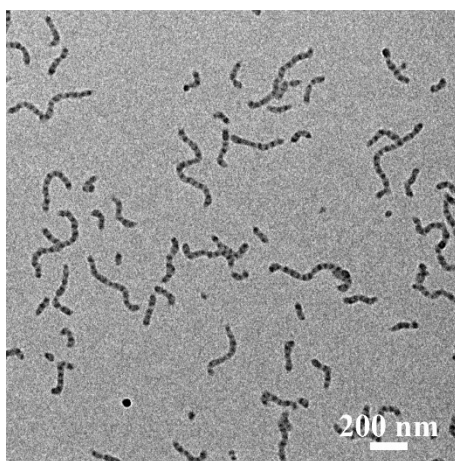
**Figure S13.** TEM images of aggregates with various water contents in second-step self-assembly (a) 35 vol%, (b) 50 vol%, (c) 75 vol%. (d) TEM image of the vesicle with 75 vol% H<sub>2</sub>O in the higher magnification, (e) TEM image of the compound vesicles stabilizing in mixed solution for 18 d. (f) Hydrodynamic radius distributions of hierarchical self-assemblies with different amounts of water added. I<sub>2</sub> stained the P4VP core in TEM images.



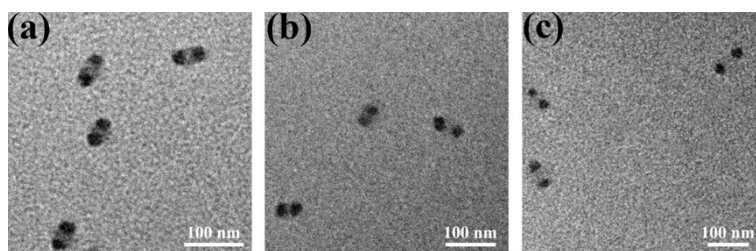
**Figure S14.** Turbidity (optical density) curves of the swollen micelles in DMF by adding various amount of water. (a) The complete turbidity curves of secondary self-assembly process. (b) Enlarged turbidity curve before 20 vol% water content.



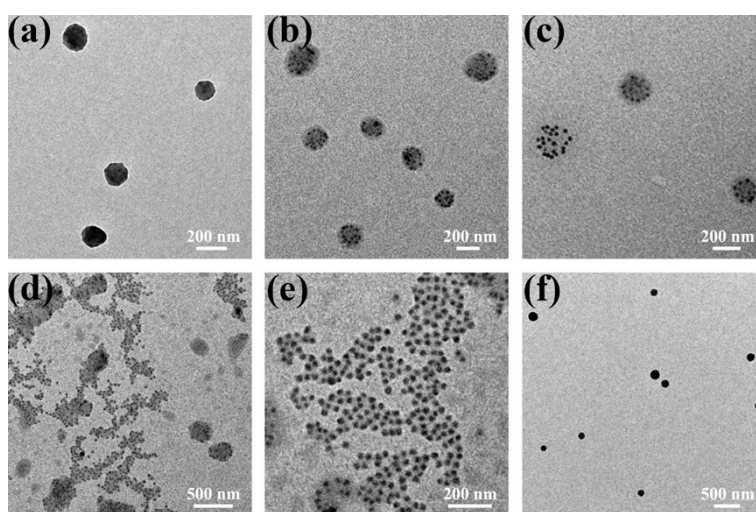
**Figure S15.** UV-Vis absorption spectra of solution after 365 nm light irradiation and following 450 nm light irradiation: (a)(b) polymer in  $\text{CHCl}_3$ , (c)(d) reverse micelles in toluene, (e)(f) swollen micelles in DMF. (g)(h) supra-colloidal chains in DMF/ $\text{H}_2\text{O}$  mixed solution.



**Figure S16.** TEM image of hierarchical self-assembly colloidal chains kept at 60 °C for 2 h. The P4VP cores were stained by  $\text{I}_2$  in TEM images.



**Figure S17.** TEM image of (a) initial dumbbell micelles and relatively loosely packing micelles under UV irradiation for different time: (b) 30 min and (c) 60 min.



**Figure S18.** TEM image of (a) raspberry-shaped compound micelles and disrupted subunits upon 365 nm UV light irradiation for different time: (b) 30 min, (c) 60 min, (d) 90 min and (e) 120 min. (f) TEM image of recuperative raspberry-shaped compound micelles by exposure to 450 nm visible light for 30 min and kept at room temperature for 24 h.

## 9. REFERENCES

1. D. Stewart and c. T. Imrie, Synthesis and Characterization of Spin-Labelled and Spin-Probed Side-Chain Liquid Crystal Polymers, *Polymer*, 1996, **37**, 3419-3425.
2. W. Wang, C. Du, X. Wang, X. He, J. Lin, L. Li and S. Lin, Directional Photomanipulation of Breath Figure Arrays, *Angew. Chem. Int. Ed.*, 2014, **53**, 12116-12119.