Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

A supramolecular approach for fabrication of photo-responsive block-controllable supramolecular polymers

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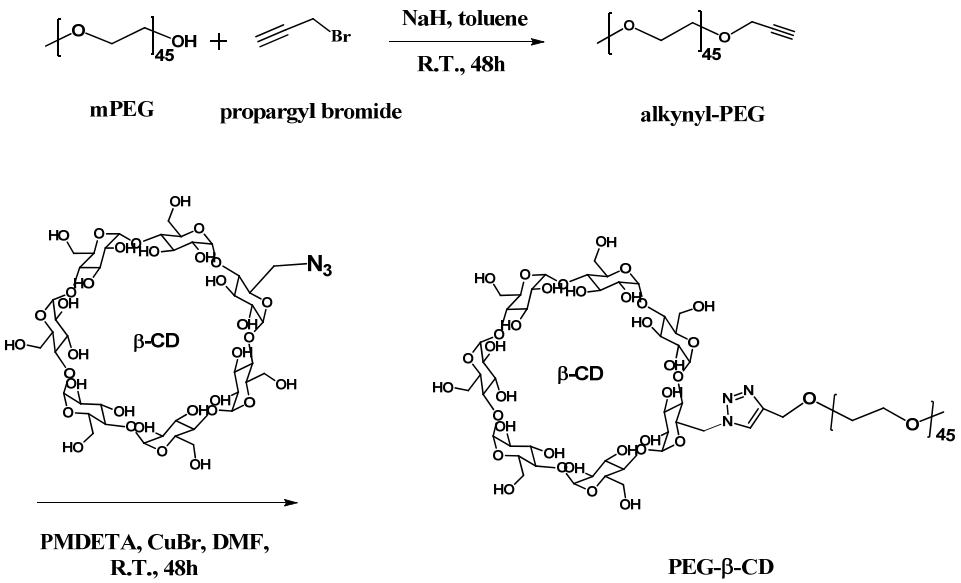

Scheme S1. Synthesis of poly(ethylene glycol)-β-cyclodextrin (PEG-β-CD).

Synthesis of mono-6-deoxy-6-(p-tolylsulfonyl)-β-cyclodextrin (β-CD-OTs)

β-Cyclodextrin (β-CD) (30 g, 26.95 mmol) was suspended in 200 mL of water. The flask was cooled to 0 °C in ice-water bath. Then NaOH (3.29 g, 82 mmol) in 10 mL of water was added dropwise, and *p*-toluenesulfonyl chloride (5.04 g, 26.45 mmol) in 15 mL of acetonitrile was added dropwise, causing a little of white precipitate. After 2 h of stirring at 0 °C, the precipitate was removed by suction filtration, and the pH of the filtrate was adjusted to 8 by dropping HCl aqueous solution, and the precipitate was obtained. Finally, to remove unreacted p-toluenesulfonyl chloride and β-CD, the resulting crude product was recovered by suction filtration and recrystallized in water three times. The final product was dried at 50 °C for 48 h under vacuum. (5.2 g, yield: 17 %).

Synthesis of mono-6-deoxy-6-azido-β-cyclodextrin (β-CD-N_3)

β-CD-OTs (1.03 g, 0.8 mmol) was suspended in 6 mL DMF. After heating to 70 °C, NaN_3 (0.26 g, 4 mmol), KI (0.032 g, 0.194 mmol) was added. The reaction mixture was stirred at 70 °C for 24 h. The reaction solution was cooled to room temperature and precipitated in 200 mL acetone twice. The white solid was dried under vacuum at 60 °C for 2 days. (0.94 g, yield: 91 %).

Synthesis of monoalkynyl end-terminated PEG (Alkynyl-PEG)

A typical procedure was shown as follows: [1] PEG (10.0 g, 5.0 mmol) was dissolved in dry toluene (80 mL) and refluxed overnight at 90 °C. After azeotropic distillation of 30-40 mL of toluene at reduced pressure to remove traces of water, the reaction mixture was cooled to 0 °C in ice bath. NaH (0.96 g, 40 mmol) was added at 0 °C under nitrogen. After stirring for 1 h at room temperature, propargyl bromide (1.52 mL, 20 mmol) in 30 mL of dried toluene was added dropwise. The mixture was then stirred at room temperature for 48 h. After removing of insoluble salts, the filtrate was evaporated. The obtained solid was dissolved in 100 mL of CH_2Cl_2. After extraction with an aqueous solution of saturated sodium chloride (NaCl), the organic phase was dried over anhydrous magnesium sulfate ($MgSO_4$). After filtration, the solution was precipitated into cold petroleum ether three times. After drying in a vacuum oven overnight at 30 °C, alkynyl-PEG was obtained as a white solid (7.6 g, yield: 75.4%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 2.48 (t, -OCH$_2$C=C*H*-), 3.37 (s, -OC*H*$_3$), 3.65 (m, -OC*H*$_2$- of PEG main chain), 4.20 (d, -OC*H*$_2$C=CH).

Synthesis of poly(ethylene glycol)-β-cyclodextrin (PEG-β-CD)

β-CD-N_3 (1.16 g, 1.0 mmol), alkynyl-PEG (1.0 g, 0.5 mmol), and PMDETA (174 mg , 1.0 mmol) were dissolved in DMF. After purging with nitrogen for 30 min to eliminate the oxygen, CuBr (216 mg, 1.5 mmol) was introduced under nitrogen. Subsequently, the flask was sealed under nitrogen. After the reaction mixture was stirred for 48 h at room temperature, the reaction mixture was exposed to air, and then evaporated, and dissolved in chloroform ($CHCl_3$). The solid was redissolved in $CHCl_3$ and passed through a basic alumina column to remove copper catalysts. After removing the solvent, the residue was dissolved in 10 mL water, and then extracted with $CHCl_3$ to remove unreacted β-CD-N_3. The organic phase was dried over anhydrous $MgSO_4$. The final product was obtained by precipitation in excess of cold petroleum ether and dried in a vacuum oven overnight at room temperature (0.7 g, yield: 32.4%).

Critical micelle concentration (CMC) of supramolecular triblock copolymers

The critical micelle concentration (CMC) was determined by the fluorescence absorbance of supramolecular micelles with pyrene as a hydrophobic fluorescent probe at increasing concentrations to indicate the formation of supramolecular micelles. Pyrene will preferentially partition into hydrophobic microdomains showing strong fluorescence intensity while weak fluorescence intensity in water. In addition, the increase in the intensity ratio of peaks at 382 and 372 nm (I_3/I_1) of pyrene in the excitation spectra indicates the formation of micelles as shown in

Fig. S8 (a). Supramolecular triblock copolymer aggregates aqueous solution was diluted to different concentrations to perform the fluorescent measurements with the excitation wavelength 335 nm. The critical micelle concentration (CMC) was determined to be approximately 0.0026 mg mL^{-1} as shown in Fig. S8 (b).

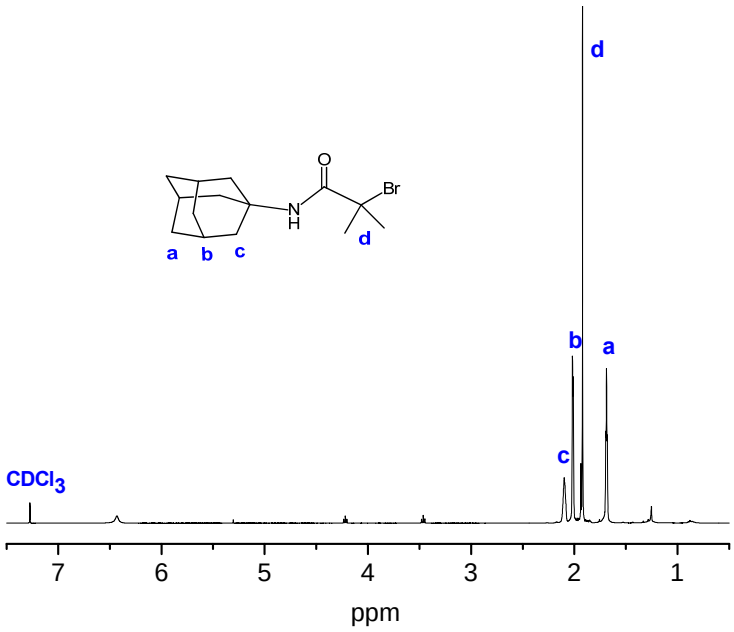

Fig. S1. ^{1}H NMR spectrum of adamantyl-containing ATRP initiator (Ad-Br).

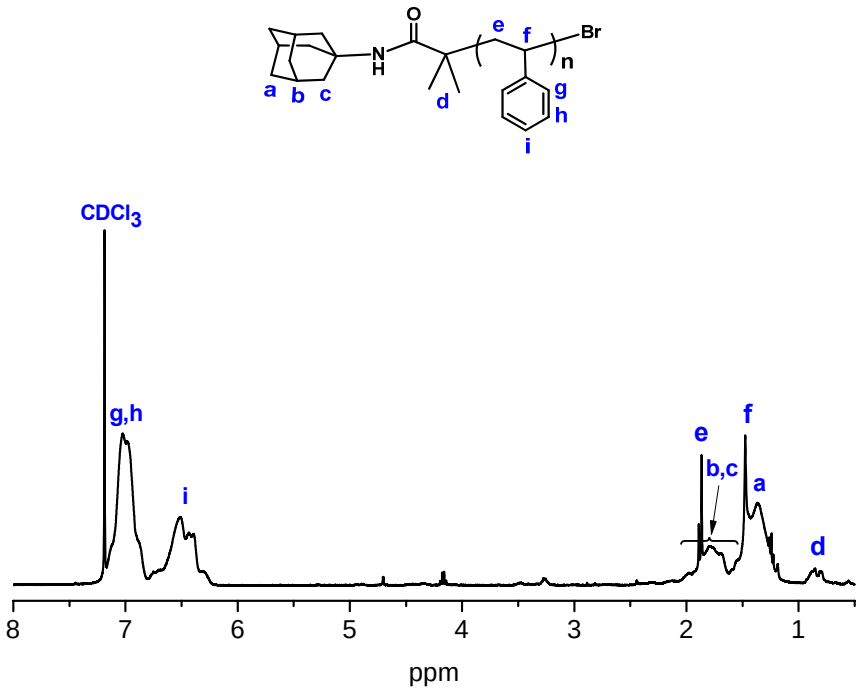

Fig. S2. [1]H NMR spectrum of adamantyl-terminated polystyrene (Ad-PS-Br).

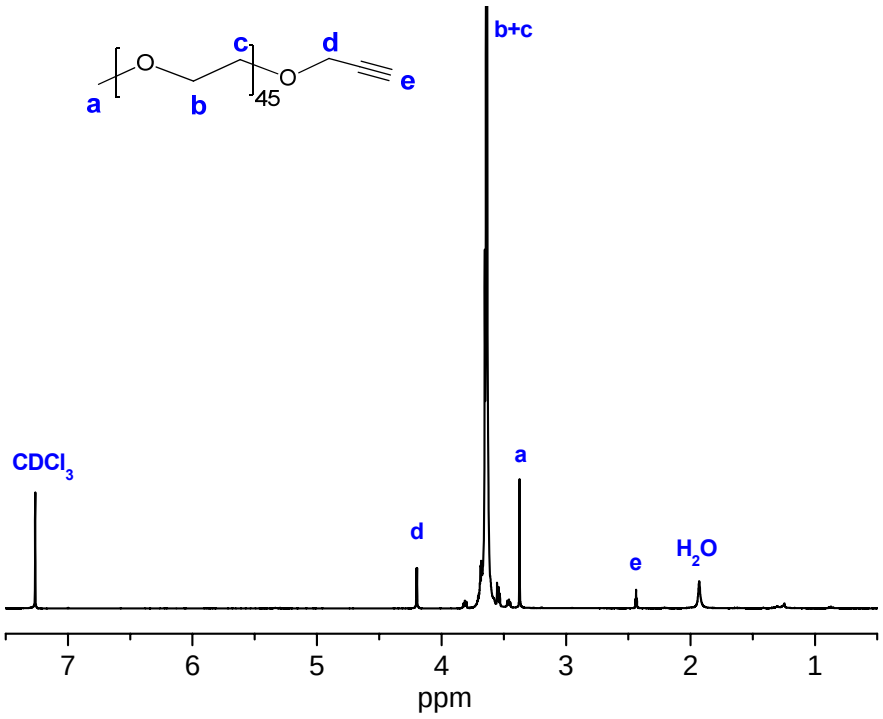

Fig. S3. [1]H NMR spectrum of alkynyl-PEG.

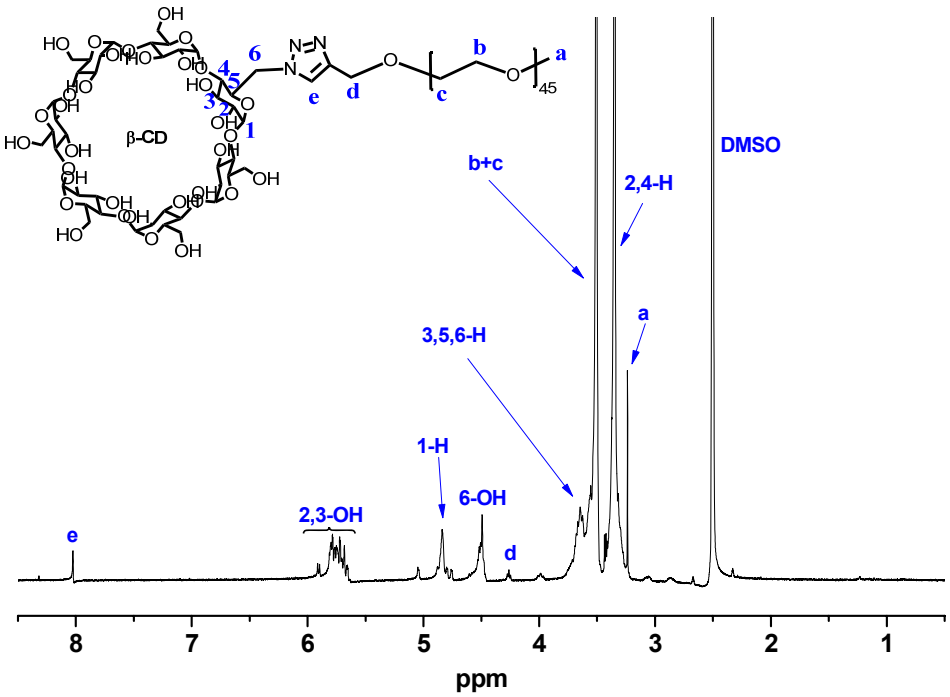

Fig. S4. ^{1}H NMR of β-CD-containing PEG (PEG-β-CD).

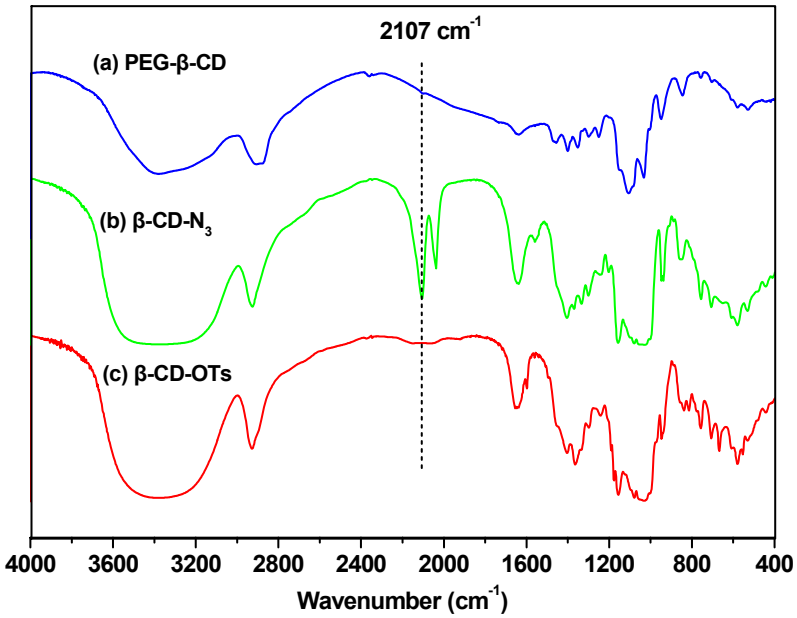

Fig. S5. FT-IR spectra of PEG-β-CD (a), β-CD-N_3 (b) and β-CD-OTs (c).

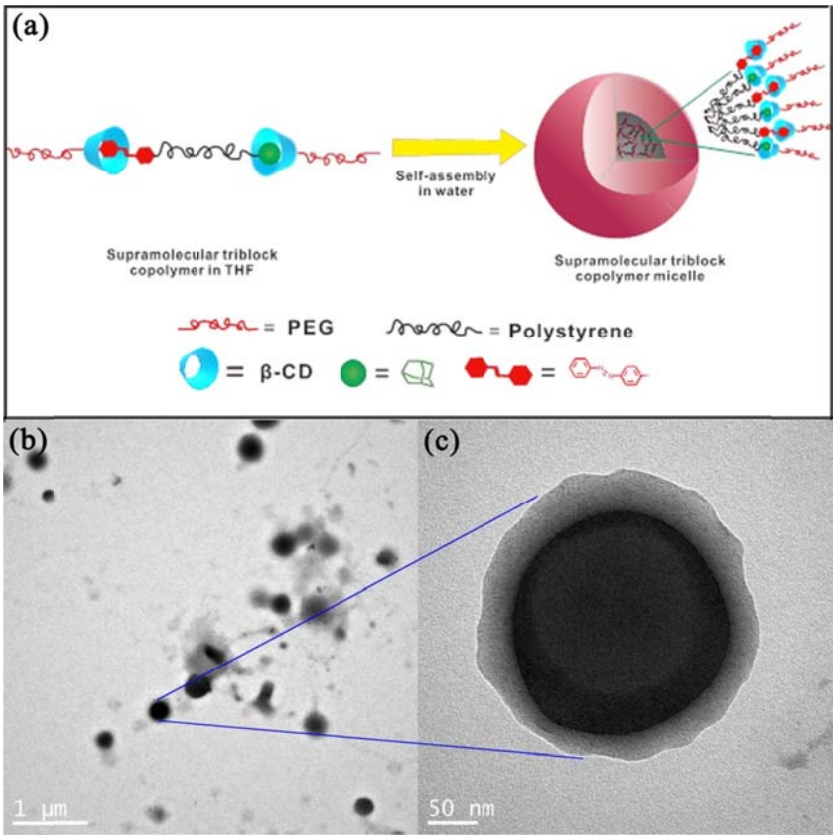

Fig. S6. The schematic of the self-assembly process (a), and TEM image of self-assembled supramolecular triblock copolymer micelles in water with THF as the common solvent (b), and the enlarged image (c).

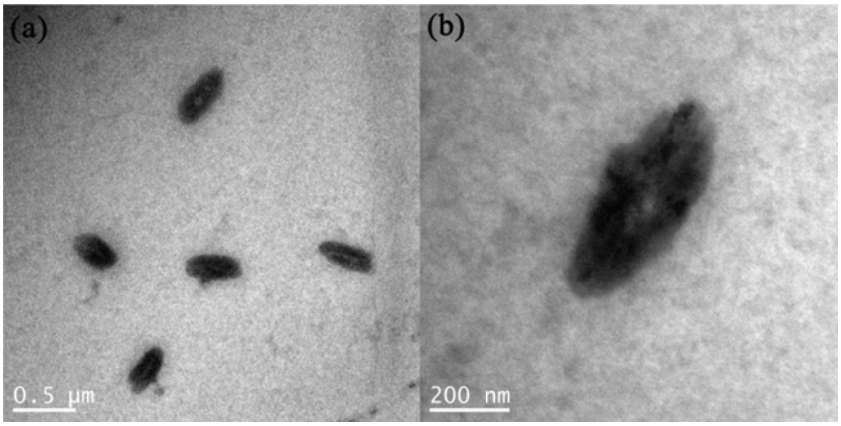

Fig. S7. TEM images of self-assembled micelles of PEG-β-CD/Ad-PS-Br supramolecular diblock copolymer in water with DMF as the common solvent: (a) the scale bar, 0.5 μm ; (b) the scale bar, 200 nm.

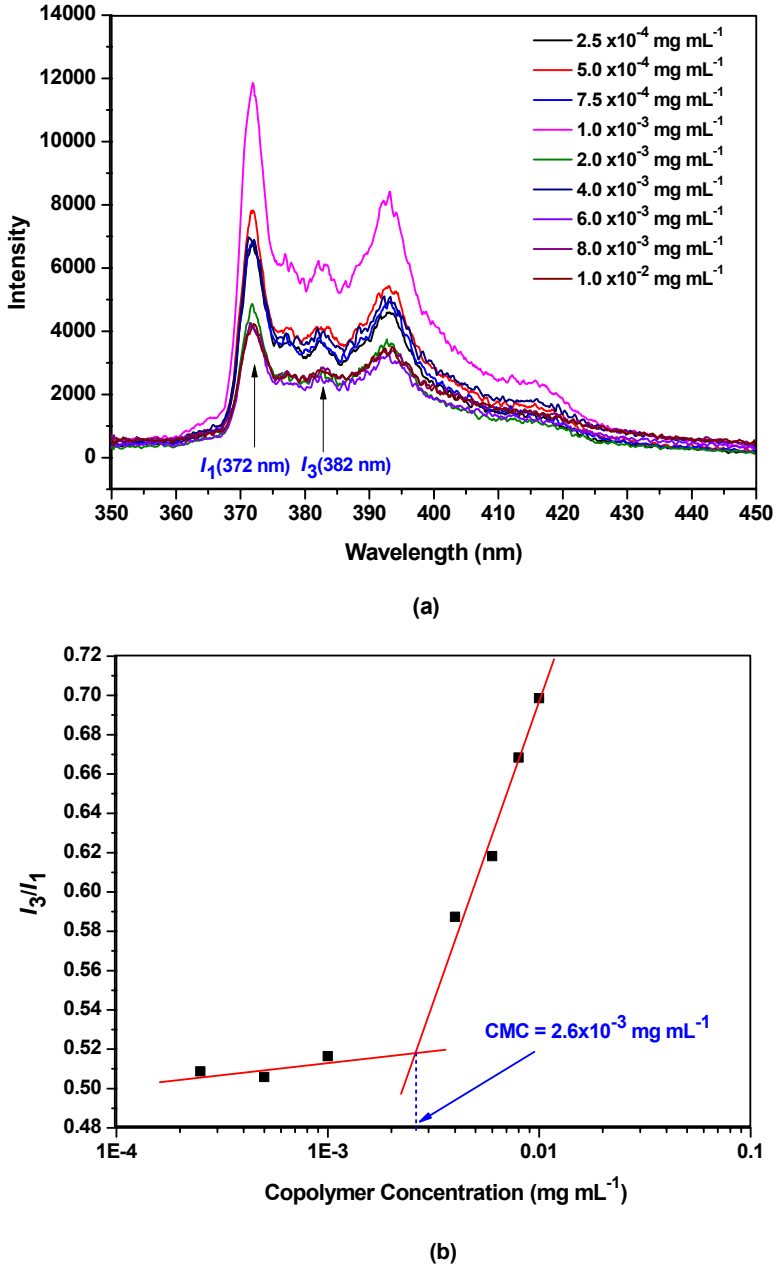

Fig. S8. (a) Fluorescence spectra of supramolecular triblock copolymers in water with pyrene. (b) Plots of I_3/I_1 vs copolymer concentration for supramolecular polymers in deionized water with different concentrations (from 0.00025 to 0.1 mg mL^{-1}).

References

1. X. Huan, D. Wang, R. Dong, C. Tu, B. Zhu, D. Yan and X. Zhu, *Macromolecules*, 2012, **45**, 5941-5947.