Supporting Information for

A Light-Tunable Thermoresponsive Supramolecular Switch with Reversible and Complete "Off-On"/"On-Off" Conversion

Hao Yao,[†a] Zhen Yang,[†a] Xiaodong Fan,[*a] Xin Song[a], Jia He[a] and Wei Tian[*a,b]

[a]MOE Key Laboratory of Material Physics and Chemistry under Extraordinary Conditions and Shanxi Key Laboratory of Macromolecular Science and Technology, School of Science, Northwestern Polytechnical University, Xi'an, 710072, China.

[b]Xi'an Institute for Biomedical Materials & Engineering, Northwestern Polytechnical University, Xi'an, 710072, China.

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1. Materials and methods

Tripropargylamine (TPA) (98%) and 2-naphthoyl chloride (NPC) (98%) were purchased from J&K Chemistry. 4-Phenylazobenzoyl Chloride (PAC) (98%) were purchased from TCI. Polyethylene glycol-1500 (PEG-1500, molecular weight = 1500) (BioUltra) were obtained from Sigma-Aldrich. Polyethylene glycol monomethylether-1900 (mPEG-1900, molecular weight = 1900) were got from Alfa Aesar. 4-dimethylaminopyridine (DMAP) (99%) were purchased from J&K chemistry. The other reagents were analytical grade and produced by Tianjin Kermel Chemical Reagents Development Center (Tianjin City, China). All chemicals were used as received without further purification.

^{1}H NMR spectra were obtained with a Bruker Avance 300 spectrometer operating at 400 MHz (^{1}H) in DMSO-d6 or D_2O. FT-IR spectra were obtained using a Thermo Fisher Scientific Nicolet iS10. Samples analyzed were cast into thin films on KBr. Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS) was utilized to determine the monomer's molecular weight using a Bruker Ultraflex TOF mass spectrometer.

2D NOESY NMR spectra at 25 °C were obtained with a Bruker AVANCEIII 500 spectrometer using D_2O as the solvent.

The UCST transition of the supramolecular system was determined through turbidity measurements using a UV-Vis spectrometer (Shimadzu UV-2550 model) within the temperature range of 20 °C to 40 °C. Before conducting measurement, the aqueous polymer solution or mixture solution was placed in the spectrophotometer (path length, 1 cm) thermostated with a circulating water bath. The temperature ramp was 1 °C/min. The transmittance data of the solution at $\lambda = 500$ nm were recorded at temperature intervals of 0.5 °C. The temperature corresponding to the onset of transmittance reduction was defined as the cloud point.

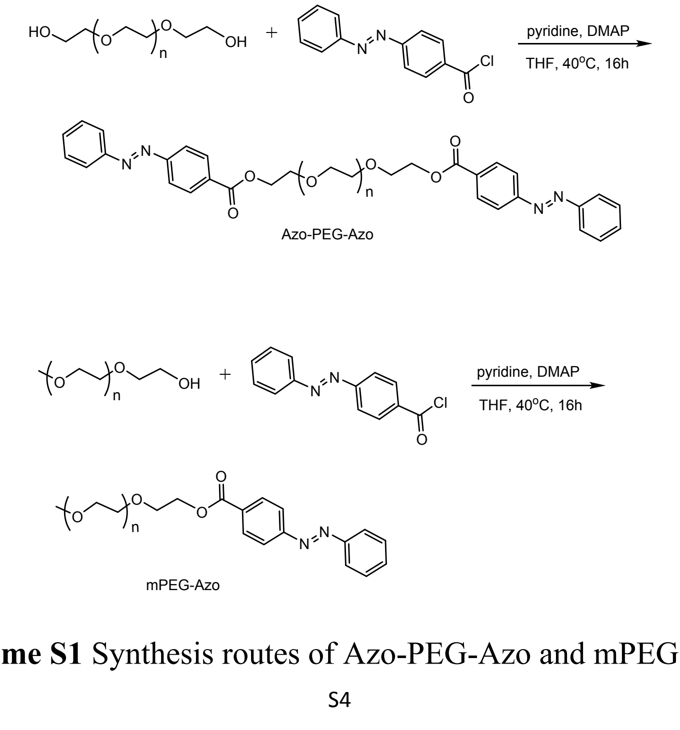
Images of the different morphologies of the supramolecular system corresponding to the temperature were obtained by TEM using a Hitachi H-600 electron microscope. For sample preparation, a 200-mesh copper grid was first placed in the mixed solution and then slowly moved into a constant-temperature incubator at a fixed temperature. After 10 min, the copper grid was quickly removed from the solution and then quenched in liquid nitrogen. After freeze-drying of the copper grid, images were taken with an acceleration voltage of 75 kV.

The assembly behavior of the supramolecular system was also revealed by dynamic light scattering (DLS) using Malvern Zetasizer Nano ZS instrument at different temperatures. The particle size distribution was determined by the general mode included in the DTS software.

Isothermal titration calorimetry (ITC) experiments was performed to measure the binding affinity directly. In a typical experiment, using single functionalized β-CD_3 and PEG-AZO_2 as model molecules, the aqueous solution of PEG-AZO_2 (1.0 mM) was trickled into the solution of β-CD_3 (0.033 mM), and an exothermic binding isotherm was obtained.

2. Synthesis of Azo-PEG-Azo and Azo-mPEG

Azo-PEG-Azo and mPEG-Azo were synthesized via condensation reaction between PAC and PEG-1500 or mPEG-1900, respectively. PAC and PEG-1500 or mPEG-1900 were dissolved in anhydrous THF, and dry pyridine and DMAP was added to this mixture. The temperature of the solution was stirred at 40 ^{o}C for 24 h. After completion of the reaction, the product was filtered and concentrated and then purified by neutral alumina column chromatography using THF as the eluent. After removing the solvent by a rotary evaporator, the obtained residue was distilled under reduced pressure. The resulting yellow product was repeatedly dissolved in THF and precipitated in cold diethyl ether. ^{1}H NMR (DMSO, 400 MHz): δH (ppm) = 3.50 to 3.62 (m, 70H), 3.79 (t, 2H), 4.45 (t, 2H), 7.63 (m, 3H), 7.95 (d, 2H), 8.02 (d, 2H), and 8.19 (d, 2H). ^{1}H NMR (DMSO, 400 MHz): δH (ppm) = 3.24 (s, 3H), 3.50 to 3.62 (m, 178H), 3.79 (t, 2H), 4.45 (t, 2H), 7.64 (m, 3H), 7.96 (d, 2H), 8.02 (d, 2H), and 8.20 (d, 2H).



Scheme S1 Synthesis routes of Azo-PEG-Azo and mPEG-Azo

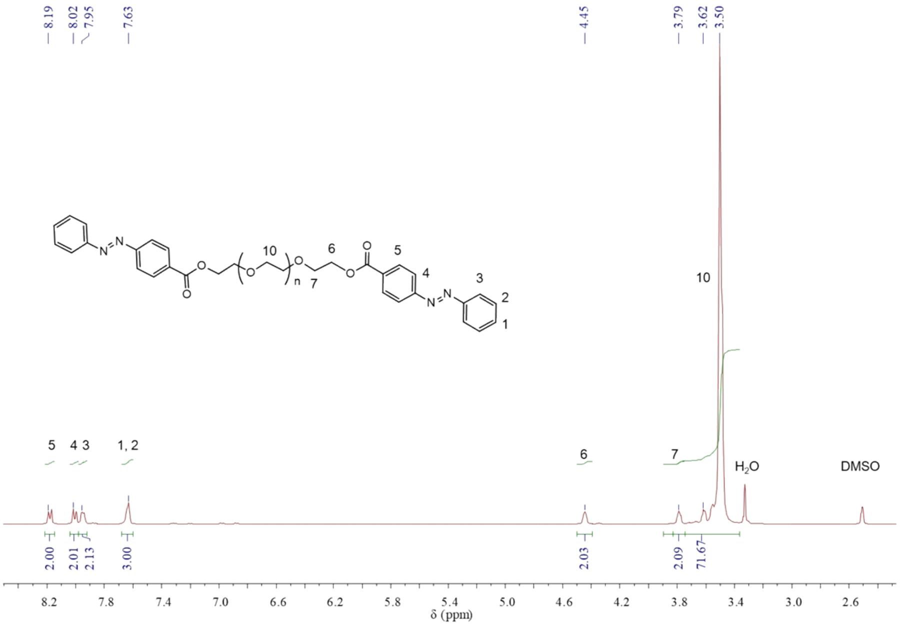


Figure S1. ^{1}H NMR spectrum of Azo-PEG-Azo

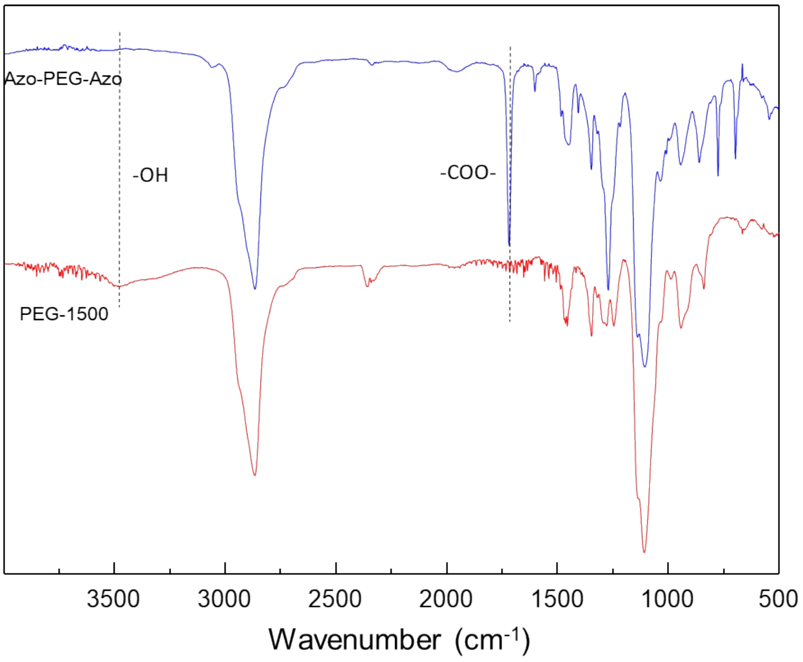


Figure S2. FTIR spectra of PEG-1500 and Azo-PEG-Azo

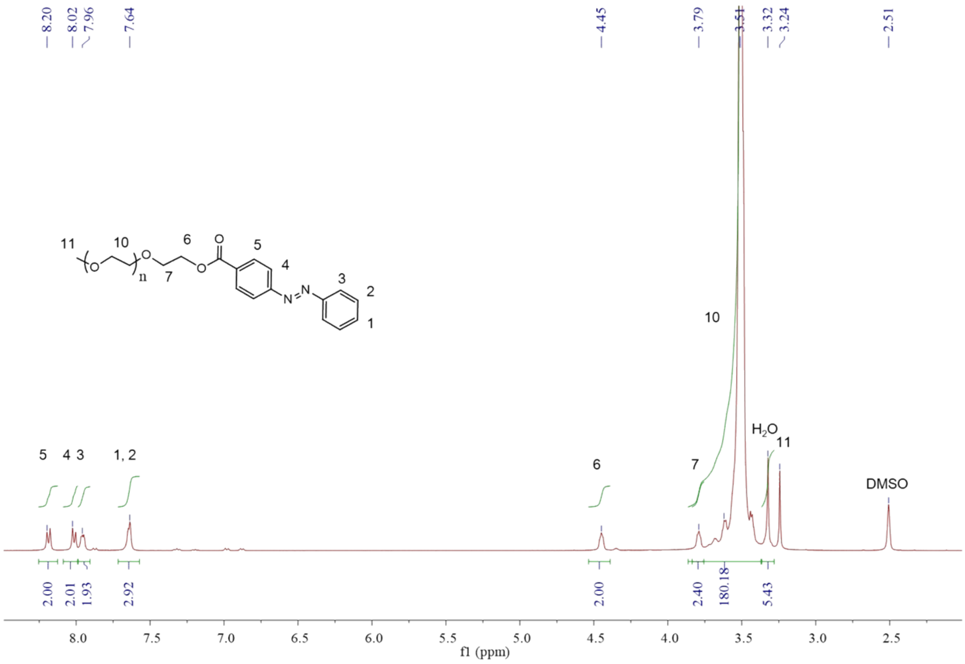


Figure S3. ^{1}H NMR spectrum of mPEG-Azo

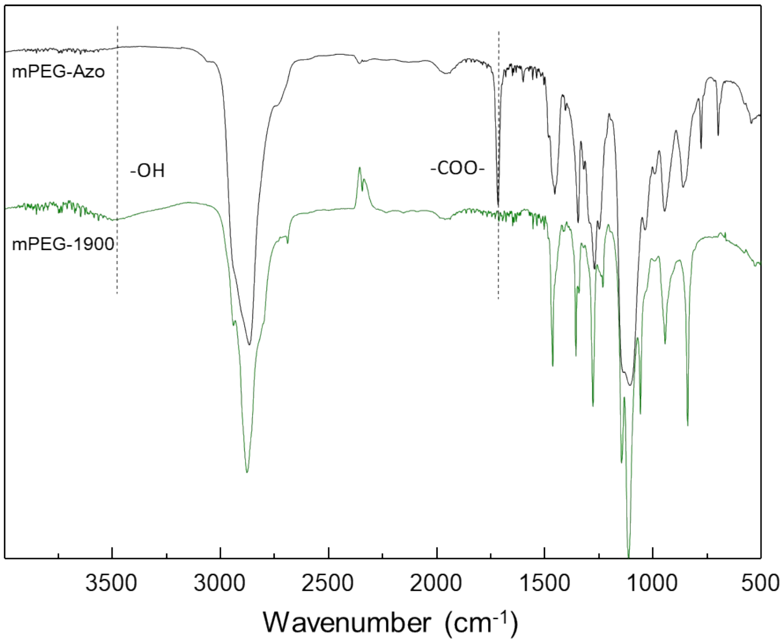
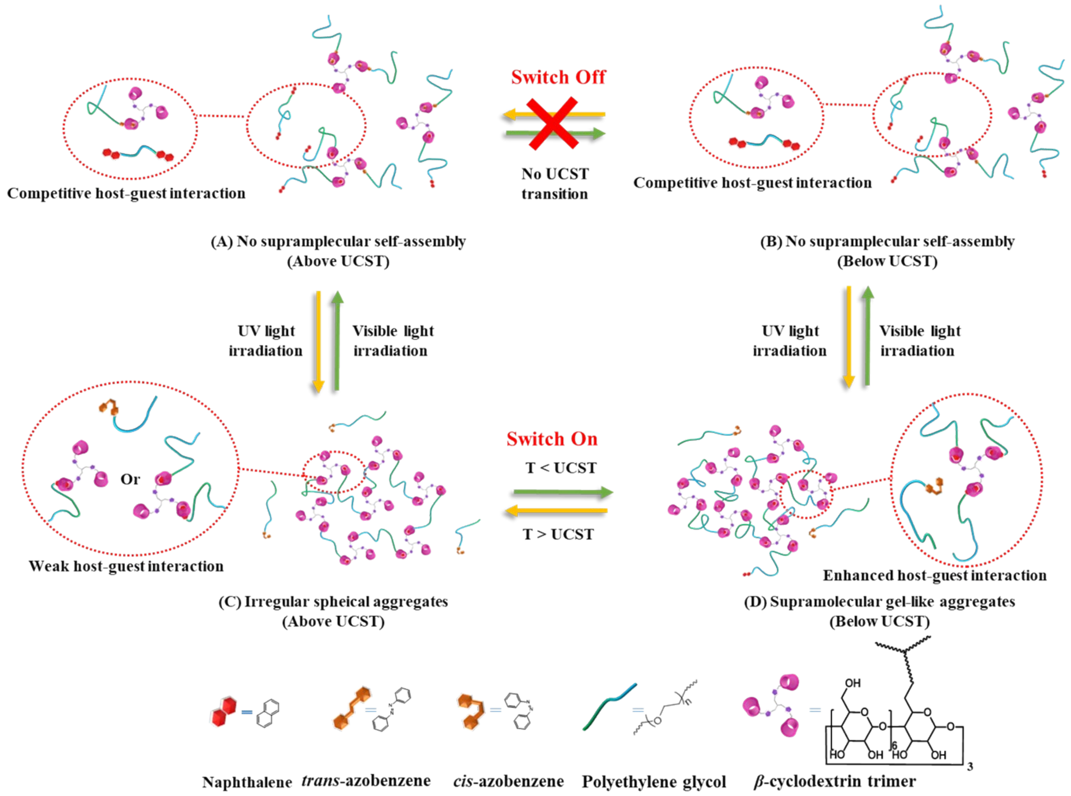


Figure S4. FTIR spectra of mPEG-1500 and mPEG-Azo

3. Confirmation of binary and ternary supramolecular systems



Scheme S2 General mechanism of the photo-reversible supramolecular switch based on the upper critical solution temperature (UCST) transitions in the ternary supramolecular system. (A-B) Supramolecular switch is completely kept in “off” state without UCST phase transition; (A-C, C-A) Reversible association and dissociation of irregularly spherical aggregates under alternative UV and visible light irradiation above UCST; (C-D, D-C) Supramolecular switch lies in “on” state with a reversible UCST phase transition; (B-D, D-B) Reversible association and dissociation of gel-like aggregates under alternative UV and visible light irradiation below UCST.

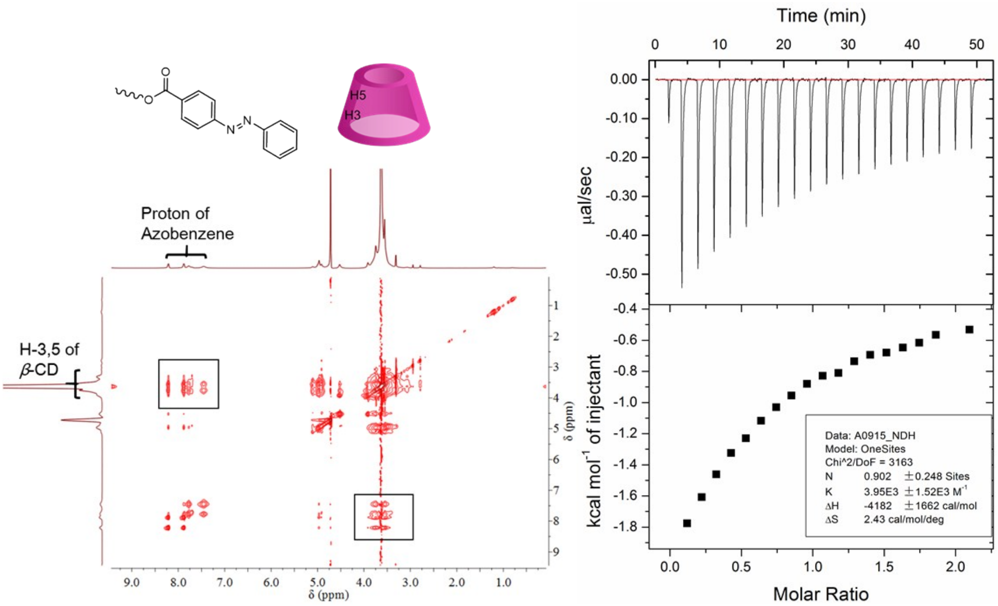


Figure S5. (A) 2D-NOESY NMR spectrum of the mixture solutions of Azo-PEG-Azo and β-CD_3 at 25 °C; (B) ITC data for the isothermal titration of Azo-PEG-Azo (0.1 mM) with β-CD_3 (0.033 mM) in aqueous solution.

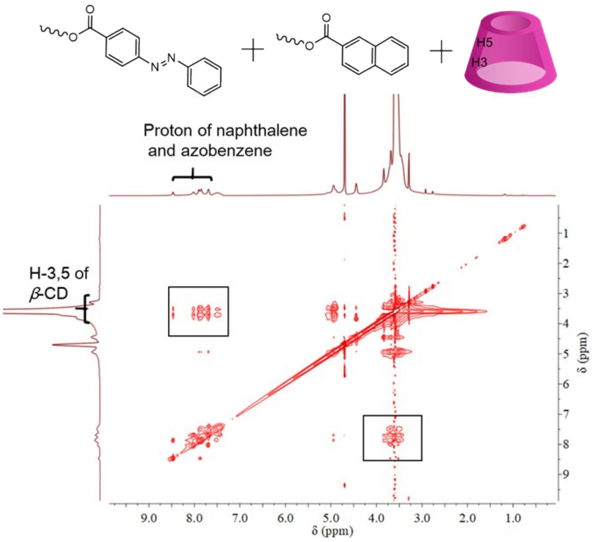


Figure S6. 2D-NOESY NMR spectra of the mixture solutions of NP-PEG-NP, Azo-mPEG and β-CD_3 at 25 °C.

4. Reversibility of UCST phase transitions

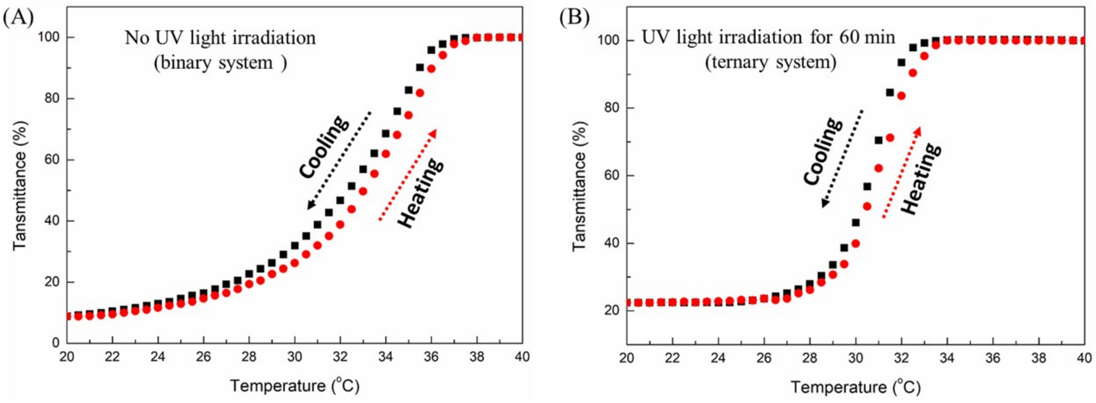


Figure S7. Turbidity-temperature curves upon cooling or heating of binary system without UV light irradiation (A) and ternary system under UV light irradiation for 60 min (B), respectively.

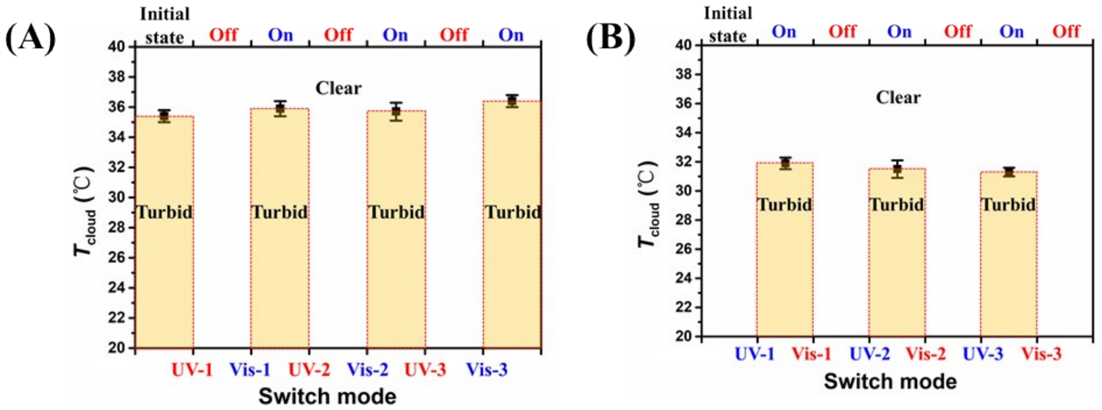


Figure S8. T_{cloud} change in the UCST phase transition process for three cycles of binary system (A) and ternary system (B), respectively.

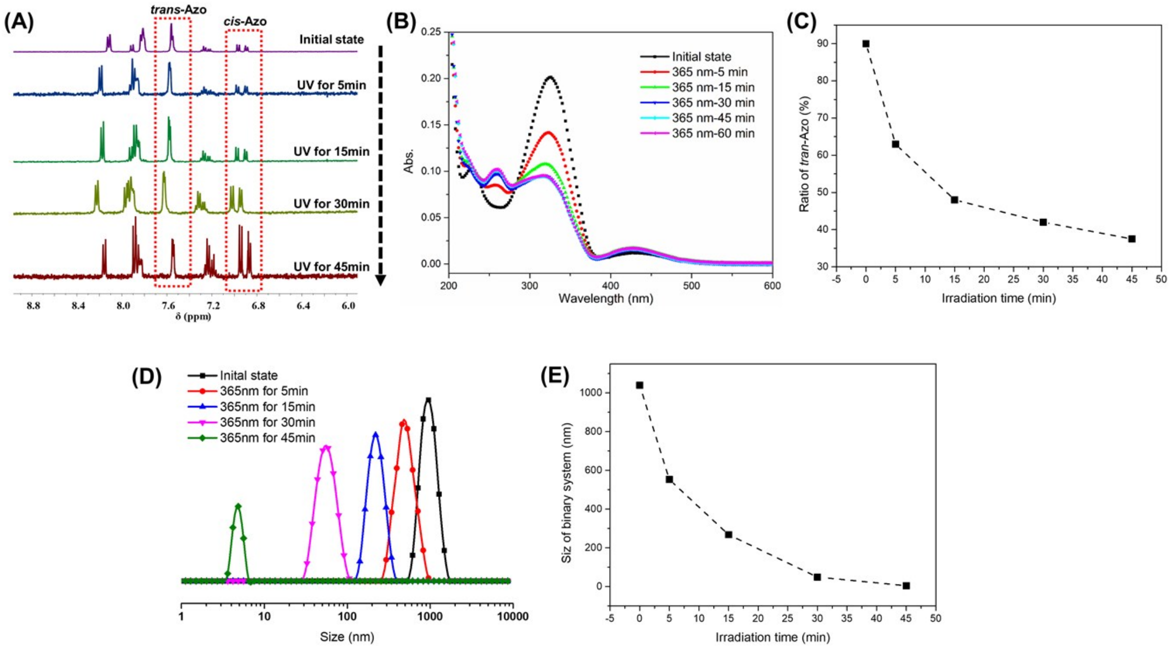
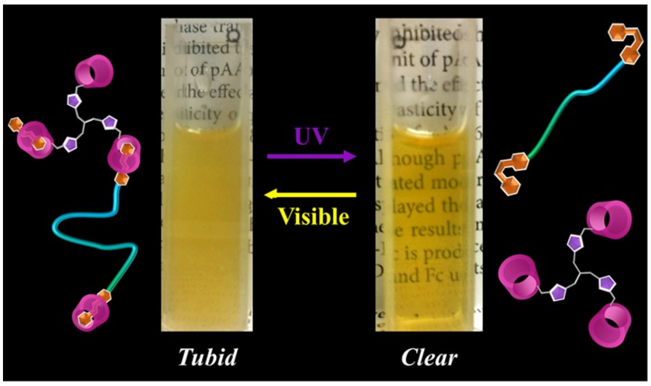


Figure S9 (A) ^{1}H NMR spectra recorded for the photoisomerization of the azobenzene group of azo-PEG by UV light irradiation. (B) UV−visible absorption spectra recorded for the photoisomerization of the azobenzene group in various azo-PEG solutions at 20 °C by UV light irradiation. (C) Change tendency of trans-Azo ratios upon different time of UV irradiation calculated by 1H NMR spectra. (D) DLS results of β-CD_3/Azo-PEG-Azo supramolecular system at 20 °C (below the UCST) upon different irradiation time with UV light. (E) Size change tendency of β-CD_3/Azo-PEG-Azo supramolecular system at 20 °C (below the UCST) upon different time of UV irradiation calculated by DLS.



Scheme S3 Photographs for β-CD_3/Azo-PEG-Azo supramolecular system at 20 ^{o}C (below the UCST) with alternating UV or visible light irradiation.

5. Mechanism confirmation of supramolecular switch

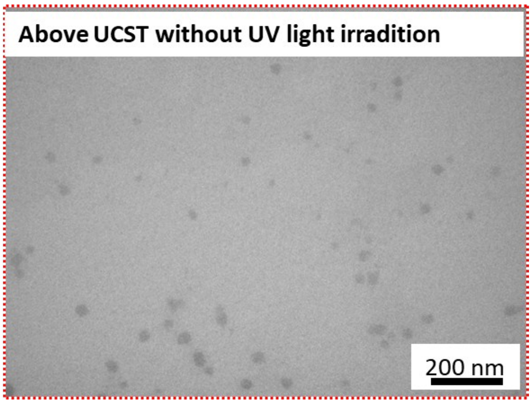


Figure S10. TEM images of the mixed solutions of β-CD_3/Azo-PEG-Azo above UCST (recovering from 20 °C) without UV light irradition.

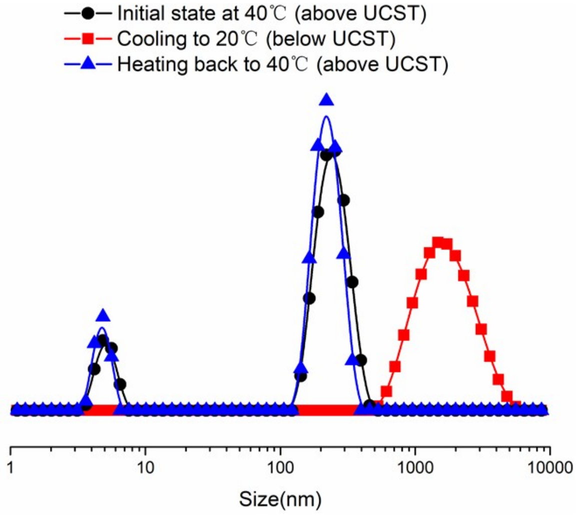


Figure S11. DLS results of the mixed solutions of β-CD_3/Azo-PEG-Azo at 40 °C (black) and cooling to 20 °C (red), after then heating back to 40 °C

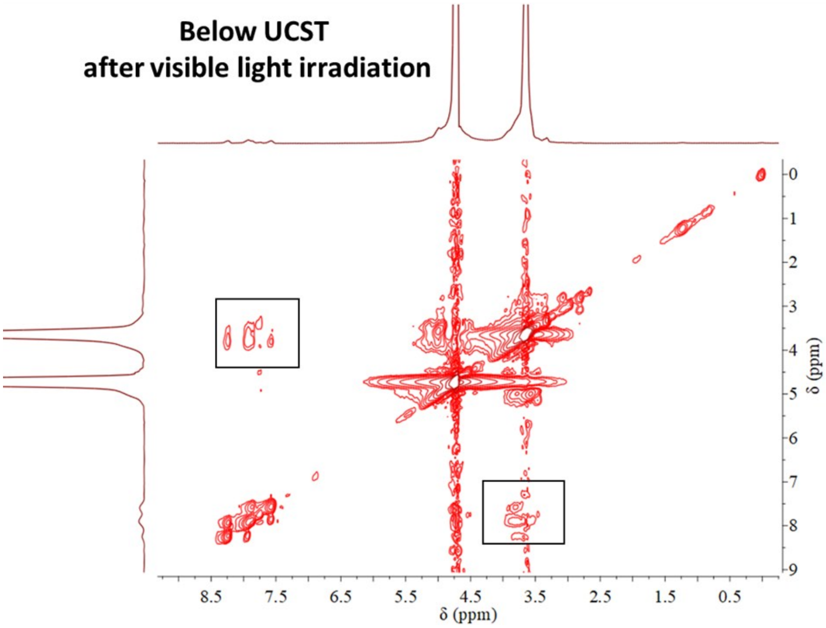


Figure S12. 2D NOESY spectra of *β*-CD$_3$/Azo-PEG-Azo self-assemblies after visible light irradiation.