Supporting Information

Light-controlled smart nanotubes based on the orthogonal assembly of two homopolymers

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1. Materials

Acrylic acid (Acros, 99%), 4-pentynoic acid (Acros, 99%), dicyclohexylcarbodiimide (DCC, Alfa Aesar, 99%), 4-dimethylaminopyridine (DMAP, Alfa Aesar, 98%), 1-adamantanemethanol (Adam-OH, Acros, 99%), and stannous octoate ($Sn(Oct)_2$, Acros, 98%) were used as received. Azodiisobutyronitrile (AIBN, Beijing Chemical Technology Co., 98%) was recrystallization in $CHCl_3$ twice. Copper bromide (CuBr, Alfa Aesar, 99%, USA) was treated by stirring in acetic acid and washed with ethanol three times. Pentamethyldiethylenetriamine (PMDETA, Acros, 98%, USA) and ε-caprolactone (CL, Acros, 99%) were stirred overnight over CaH_2 and distilled under reduced pressure prior to use. All solvents were used as received. 2-Cyano-4-hydroxybutan-2-yl ethyl carbontrithioate (CTT) was supplied from Prof. Dr. Lei Tao who synthesized it according to the previous literature.[S1] 4-Ethoxy-azobenzyl carboxylic acid (Azo-COOH) and 6-mono-azido-α-cyclodextrin (α-CD-N_3) were prepared by the literature.[S2,S3]

2. Instruments and Methods

Fourier Transform Infrared Spectroscopy (FT-IR). The absorption spectra of all products were recorded on an AVATAR 360 ESP FT-IR spectrometer and the results were collected at 30 scans with a spectral resolution of 1 cm^{-1}.

Nuclear Magnetic Resonance Spectroscopy (NMR). ^1H NMR spectra for the polymer structural analysis were obtained from a JEOL JNM-ECA300 (300MHz) and JNM-ECA600 (600MHz) spectrometer with $CDCl_3$ as the solvent.

Gel Permeation Chromatography (GPC). The molecular weight ($M_{n,GPC}$) and the molecular weight distribution (M_w/M_n) were measured on a GPC system equipped with a Waters 515 pump, three columns and a 2410 differential refractometer detector. THF was used as the eluent at a flow rate of 1.0 mL/min at 30 oC. Monodisperse polystyrene was used as the standard to generate the calibration curve.

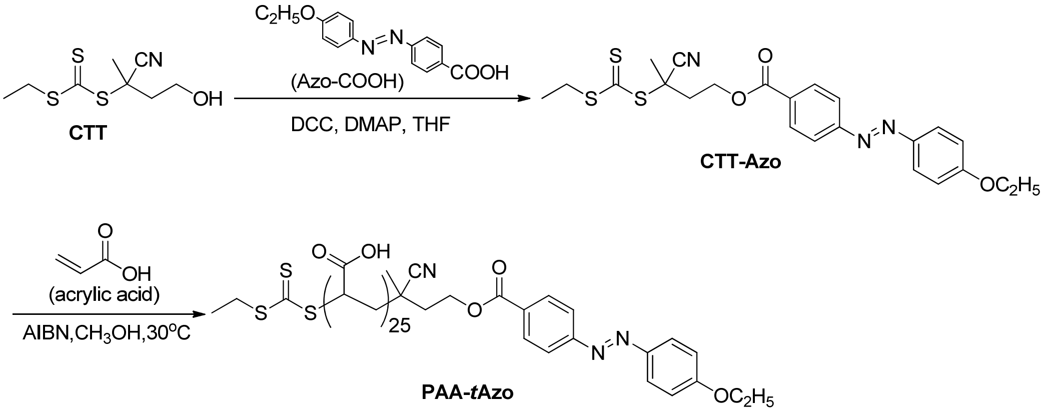
Surface Tension Measurement. Surface tension measurements were engaged on a high-sensitive micro-electromechanical balance system (Dataphysics DCAT21, Germany). The plate used to detect the surface tension is with a length of 19.9 mm and a width of 0.2 mm. The motor speed to drive the plate is 1.00 mm/s.

Transmission electron microscopy (TEM). The visualized images of the assemblies were obtained from a JEM-2010 Microscope with an accelerating voltage of 120 kV and the sample was stained by 0.2% phosphotungstic acid hydrate before observation.

Dynamic Light Scattering (DLS). A commercial spectrometer (ALV/DLS/SLS-5022F) equipped with a multi-tau digital time correlator (ALV5000) and a 22 mW He-Ne laser (λ_0 = 632 nm) as the light source was used. In dynamic light scattering (DLS) experiments, scattering light was collected at a fixed angle of 90º for duration of ~10 min. Average radius ‹R_h› and particle size distributions ‹f_h› were computed using cumulants analysis and CONTIN routines.

UV-vis Spectroscopy (UV-vis). The optical transmittance of the aqueous solution was measured on a UV 2100 UV-visible spectrophotometer (Shimadzu, Japan) for responsible to the absorption measurement of the polymeric solutions.

3. Synthetic Procedures



Scheme S1. The Synthetic Route of the End-Decorated Homopolymer PAA-*t*Azo

3.1 Synthesis of poly(acrylic acid)-*trans*-azobenzyl carboxylic acid (PAA-*t*Azo).

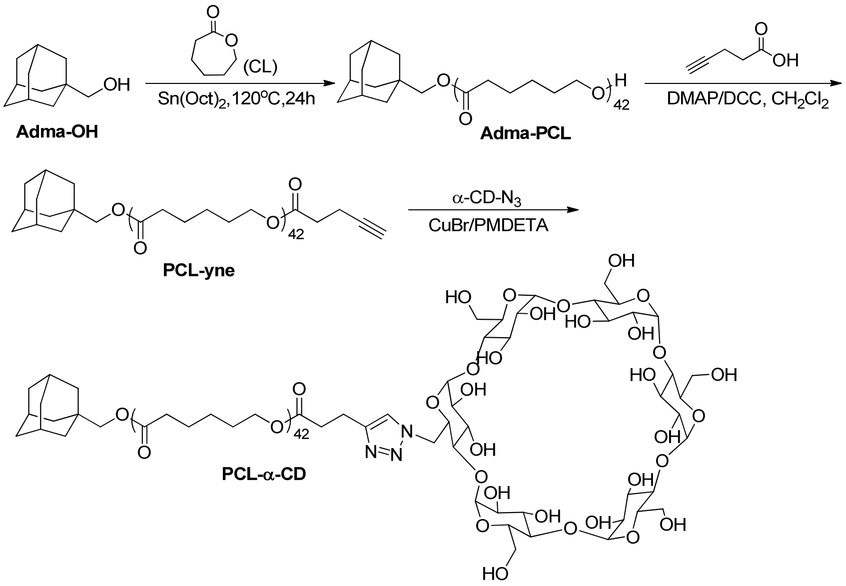
Synthesis of terminal functionalized chain transfer agent CTT-Azo

The chain transfer agent 2-cyano-4-hydroxybutan-2-yl ethyl carbontrithioate (CTT, 0.24 g, 1.0 mmol), 4-ethoxy-azobenzyl carboxylic acid (Azo-COOH, 0.32 g, 1.2 mmol), DCC (0.24 g, 1.2 mmol), DMAP (0.15 g, 1.2 mmol) were dissolved in 20 mL of anhydrous DMF solvent, and the reaction was performed at 0 °C for 48 h under nitrogen atmosphere. The byproduct solid dicyclohexylcarbodiurea (DCU) was removed by filtration, and the filtered solution was evaporated. The crude product was dissolved in THF twice to remove the insoluble Azo-COOH residues, and then the solution was recrystallized in methanol to obtain final product (0.39 g, yield: 76%). ^{1}H NMR (δ, ppm, d_6-DMSO): 8.30 (d, 2H, in azobenzene), 8.10 (q, 4H, in azobenzene), 7.32 (d, 2H, in azobenzene), 4.54 (d, 2H, $-CH_2C\boldsymbol{H_2}OCO-$), 4.34 (q, 2H, $-OC\boldsymbol{H_2}CH_3$), 4.23 (t, 2H, $CH_3C\boldsymbol{H_2}SCS-$), 2.12 (t, 2H, $-C\boldsymbol{H_2}CH_2OCO-$), 1.84 (s, 3H, $-C(C\boldsymbol{H_3})(CN)-$), 1.54 (t, 3H, $-OCH_2C\boldsymbol{H_3}$), 1.35 (t, 3H, $C\boldsymbol{H_3}CH_2SCS-$).

Synthesis of poly(acrylic acid)-trans-azobenzyl carboxylic acid (PAA-tAzo) via reversible addition-fragmentation chain transfer polymerization (RAFT).

The tailored chain transfer agent CTT-Azo (0.24 g, 0.5 mmol), AIBN (17 mg, 0.1 mmol), acrylic acid (2.16 g, 30.0 mmol), and 50 mL of methanol solvent were added in to a 150 mL round-bottom flask, followed by three freeze-vacuum-thaw cycles. The flask was immersed into an oil bath at 30 °C with magnetic stirring. After reaction for 6 h, the flask was cooled to room temperature and opened to the air. The polymer was diluted in 15 mL of methanol and then precipitated in 250 mL of diethyl ether three times for removal of unreacted acrylic acid monomer. The slight yellow polymer obtained was dried in vacuum oven for 24 h (conversion: 42%). $M_{n,GPC}$ = 2010 g/mol, M_w/M_n = 1.19. IR (KBr, cm^{-1}): 3250~3780 ($\nu_{O\text{-}H}$ and ν_{COOH}), 2886 ($\nu_{C\text{-}H}$), 1710 ($\nu_{C=O}$ in PAA), 1130, 1049 ($\nu_{S=C=S}$). ^{1}H NMR (d_6-

DMSO, ppm): 8.30 (d, 2H, in azobenzene), 8.11 (q, 4H, in azobenzene), 7.32 (d, 2H, in azobenzene), 4.52 (d, 2H, $-CH_2C\boldsymbol{H}_2OCO-$), 4.34 (q, 2H, $-OC\boldsymbol{H}_2CH_3$), 4.23 (t, 2H, $CH_3C\boldsymbol{H}_2SCS-$), 2.18 (t, 2H, $-C\boldsymbol{H}_2CH_2OCO-$), 1.57—1.91 (broad, $-[CH_2-C\boldsymbol{H}]_n-$ in PAA), 1.35 (t, 3H, $C\boldsymbol{H}_3CH_2SCS-$), 0.72—1.10 (broad, $-[C\boldsymbol{H}_2-CH]_n-$ in PAA).



Scheme S2. The Synthetic Route of the End-Decorated Homopolymer PCL-*α*-CD

3.2 Synthesis of poly(caprolactone)-*α*-cyclodextrin (PCL-*α*-CD).

Synthesis of poly(caprolactone) (PCL) via ring-opening polymerization.

A typical polymerization procedure was shown as follows: 1-adamantanemethanol (Adam-OH, 83 mg, 0.5 mmol), CL (2.85 g, 25.0 mmol), and a catalytic amount of $Sn(Oct)_2$ were dissolved in 25 mL of freshly anhydrous xylene in dried polymerization tube. The tube was followed three freeze-vacuum-thaw cycles, and then was immersed into an oil bath at 120 °C under nitrogen atmosphere with vigorous stirring for 24 h. After cooling to room temperature, the resultant was dissolved in 15 mL of chloroform and precipitated with cool methanol three times to afford the purified homopolymer. The product was dried in vacuum until constant weight (2.48 g, conversion: 84%). $M_{n,GPC}$ = 4910 g/mol, M_w/M_n = 1.05. IR (KBr, cm^{-1}): 3210—3360 (ν_{O-H}), 2920 (ν_{C-H}), 1730 ($\nu_{C=O}$ in PCL). ^{1}H NMR (δ, ppm, $CDCl_3$): 4.07 (t, $-OC\boldsymbol{H}_2CH_2CH_2CH_2CH_2COO-$ in PCL), 3.61 (t, terminal $-C\boldsymbol{H}_2OH$), 3.19 (s, Adam-$C\boldsymbol{H}_2O-$), 2.30 (t, $-OCH_2CH_2CH_2CH_2C\boldsymbol{H}_2COO-$ in PCL), 1.98 (s, $-C\boldsymbol{H}(CH_2)_3-$ in Adam), 1.68 (q, $-CH(C\boldsymbol{H}_2)_3-$ in Adam), 1.63 (m, $-OCH_2C\boldsymbol{H}_2CH_2C\boldsymbol{H}_2CH_2COO-$ in PCL), 1.50 (s, $-CH(C\boldsymbol{H}_2)_3-$ in Adam), 1.36 (m, $-OCH_2CH_2C\boldsymbol{H}_2CH_2CH_2COO-$ in PCL).

Synthesis of alkynyl end-decorated poly(caprolactone) (PCL-yne).

The terminal condensation reaction was performed according to reported literature:[S4] PCL (1.20 g, 0.24 mmol), 4-pentynoic acid (0.24 g, 2.4 mmol), DCC (0.48 g, 2.4 mmol), and DMAP (29 mg, 0.24 mmol) were dissolved in 50 mL of anhydrous methylene chloride, and the reaction was at room temperature for 48 h under nitrogen atmosphere. The byproduct DCU was removed by filtration, and the filtered solution was evaporated to dryness. The crude product was re-dissolved in 30 mL of THF and precipitated into cool methanol three times. The purified product was dried in vacuum (0.98 g, yield: 79%). $M_{n,GPC}$ = 4970 g/mol, M_w/M_n = 1.05. FT-IR (KBr, cm^{-1}): 3291 (ν_{C-H} in terminal alkynyl), 2949 (ν_{C-H} in alkyl), 2118 ($\nu_{C\equiv C}$ in terminal alkynyl), 1728 ($\nu_{C=O}$ in PCL). ^{1}H NMR (δ, ppm, $CDCl_3$): 4.09 (t, $-OC\boldsymbol{H}_2CH_2CH_2CH_2CH_2COO-$ in PCL), 3.63 (t, terminal $C\boldsymbol{H}_2O$), 3.19 (s, Adam-$C\boldsymbol{H}_2O-$), 2.57 (s, 4H, $-COOC\boldsymbol{H}_2C\boldsymbol{H}_2C\equiv CH$), 2.30 (t, $-OCH_2CH_2CH_2CH_2C\boldsymbol{H}_2COO-$ in PCL), 1.99 (s, $-C\boldsymbol{H}(CH_2)_3-$ in Adam), 1.88 (s, 1H, $-COOCH_2CH_2C{\equiv}C\boldsymbol{H}$), 1.68 (q, $-CH(C\boldsymbol{H}_2)_3-$ in Adam), 1.63 (m, $-OCH_2C\boldsymbol{H}_2CH_2C\boldsymbol{H}_2CH_2COO-$ in PCL), 1.52 (s, $-CH(C\boldsymbol{H}_2)_3-$ in Adam), 1.35 (m, $-OCH_2CH_2C\boldsymbol{H}_2CH_2CH_2COO-$ in PCL).

Synthesis of α-cyclodextrin end-decorated poly(caprolactone) (PCL-α-CD) via "click chemistry".

The coupling reaction between PCL-yne (0.55 g, 0.11 mmol) and *α*-CD-N_3 (0.11 g, 0.11 mmol) were conducted with 50 mL anhydrous DMF as solvent, followed by adding catalyst CuBr (15 mg, 0.11 mmol) and PMDETA (30 µL, 0.11 mmol) into the solution. Under the protection of argon atmosphere, the reaction was carried out at 35 °C with vigorous stirring for overnight. After removing the DMF solvent by reduced pressure distillation, the crude product was dissolved in chloroform and passed through neutral alumina to remove the copper catalyst. Water was added into the solution and extracted out the unreacted cyclodextrin, and then the organic phase was precipitated in methanol twice to obtain purified product (0.61 g, yield: 92%). $M_{n,GPC}$ = 5920 g/mol, M_w/M_n = 1.10. FT-IR (KBr, cm^{-1}): 3360~3580 ($\nu_{O\text{-}H}$ in *α*-CD), 2928 ($\nu_{C\text{-}H}$), 1728 ($\nu_{C=O}$), 1628, 1559 ($\nu_{C=C}$ and $\nu_{N=N}$ in triazole). ^1H NMR (*δ*, ppm, $CDCl_3$): 7.07 (s, $-C{=}C\boldsymbol{H}$), 5.65 (m, OH-2,3 in*α*-CD), 4.87 (m, H-1 in *α*-CD), 4.25 (m, OH-6 in *α*-CD), 4.09 (t, $-OC\boldsymbol{H}_2CH_2CH_2CH_2CH_2COO-$ in PCL), 3.19~3.78 (m, H-2,3,4,5,6 in *α*-CD, Adam-$C\boldsymbol{H}_2O-$, and $-OOCC\boldsymbol{H}_2C\boldsymbol{H}_2C$-triazole), 2.30 (t, $-OCH_2CH_2CH_2CH_2C\boldsymbol{H}_2COO-$ in PCL), 1.99 (s, $-C\boldsymbol{H}(CH_2)_3-$ in Adam), 1.68 (q, $-CH(C\boldsymbol{H}_2)_3-$ in Adam), 1.63 (m, $-OCH_2C\boldsymbol{H}_2CH_2C\boldsymbol{H}_2CH_2COO-$ in PCL), 1.52 (s, $-CH(C\boldsymbol{H}_2)_3-$ in Adam), 1.35 (m, $-OCH_2CH_2C\boldsymbol{H}_2CH_2CH_2COO-$ in PCL).

4. Characterization

4.1 The formation evidences of the supramolecular copolymer of PCL-*α*-CD/PAA-*t*Azo.

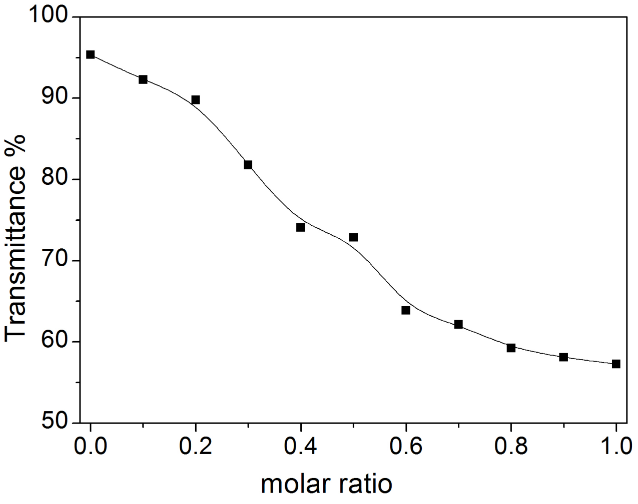


Fig. S1. The turbidity evidence for the formation of PCL-*α*-CD/ PAA-*t*Azo supramolecular copolymers

A 10 mL solution of 2.0 mg/mL PAA-*t*Azo in THF was slowly injected into 10 mL of PCL-*α*-CD THF solution (2.0 mg/mL) under sonication. When the PAA-*t*Azo solution was gradually added into the PCL-*α*-CD solution accompanied with turbid measurement by UV-vis, the transmittance of this binary colloidal mixture showed a dramatic transition from ~95% down to ~57%, indicating a typical formation of PCL-*α*-CD/PAA-*t*Azo supramolecular complex (See Fig. S1).

4.2 Macromolecular adduct's association constant between PCL-*α*-CD and PAA-*t*Azo.

The association constant between PCL-*α*-CD and PAA-*t*Azo in aqueous solution was determined by following UV absorption at 348 nm, which is the characteristic absorption of *trans*-Azo species, as shown in Fig. S2. The concentration of PAA-*t*Azo was kept at 1×10^{-5} M. Upon gradual addition of the PCL-*α*-CD species, the absorption of PAA-*t*Azo increased remarkably. With formation of a simple 1:1 macromolecular adduct, the inclusion complexation of PCL-*α*-CD/PAA-*t*Azo is expressed by the following equation:

$$\mathbf{H + G \xrightleftharpoons{K_t} H{\bullet}G}$$

We employed the usual double reciprocal plot according to the modified Hidebrand-Benesi equation:

$$\boxed{\frac{1}{\Delta A} = \frac{1}{K\mathrm{t}\Delta\varepsilon[H][G]} + \frac{1}{\Delta\varepsilon[H]}}$$

Where H, G, K_t represents host (PAA-*t*Azo), guest (PCL-*α*-CD), association constant respectively. Δ*A* denotes the absorbance difference before and after addition of PCL-*α*-CD species. Δε, which denotes the difference of the molar extinction coefficient between the host and host-guest complex at the same wavelength, is 5.68×10^{3} M^{-1}cm^{-1} in our work. The association constant K_t calculated by the equation is 1.32×10^{4} M^{-1}, which is a half smaller than simple molecular complex such as Azo/*α*-CD (2.8×10^{4} M^{-1}). It is reasonably ascribed that the presented complex is orthogonal assembly by two homopolymers.

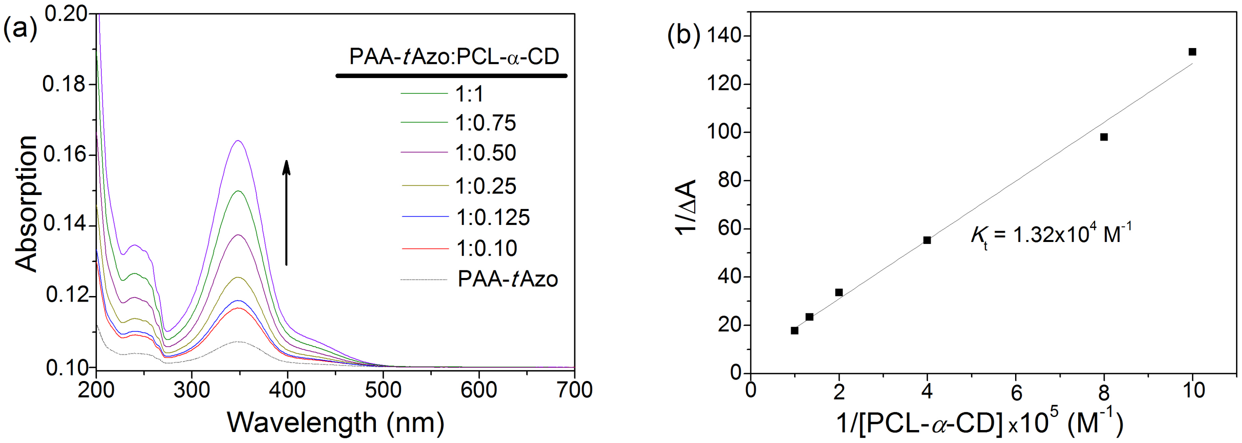


Fig. S2. The UV absorption of PAA-*t*Azo upon stepwise addition of PCL-*α*-CD, the concentration of PAA-*t*Azo keeps 1×10^{-5} M.

4.3 The CAC experiment of PCL-*α*-CD/PAA-*t*Azo aggregates in water.

The critical aggregate concentration (CAC) of PCL-*α*-CD/PAA-*t*Azo supramolecular aggregates was measured by the surface tension measurement. According to the Langmuir model for surface adsorption, below the CAC, some of the surfactants adsorb at the water-air interface, and the others disperse into the bulk solution without aggregation; but above the CAC, for the interface is fully covered by the surfactants, the surfactants cannot adsorb at the interface anymore, and instead, they will aggregate spontaneously in solution by self-assembly.[S5] Fig. S3 showed the change of surface tension with the variation of concentration of PCL-*α*-CD/PAA-*t*Azo complex at room temperature. For formation of the stable supramolecular aggregated structure in solution, there is a gradual decrease in the surface tension with the increase of concentration. The CAC of PCL-*α*-CD/PAA-*t*Azo supramolecular assemblies in aqueous solution is at the concentration of ~0.56 mg/mL, corresponding to the turbidity measurement.

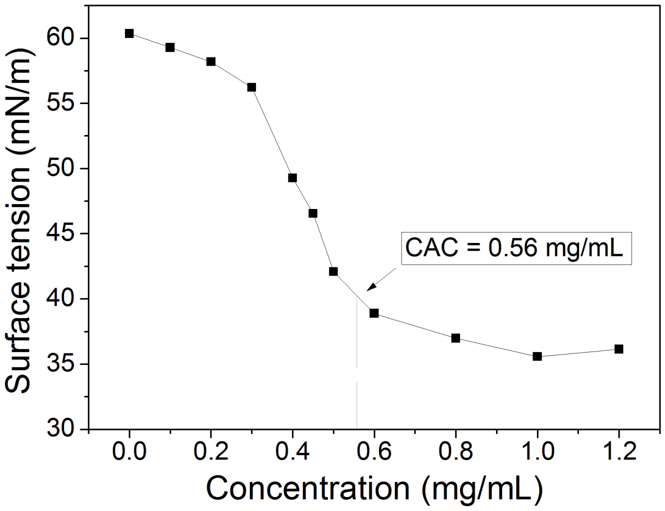


Fig. S3. Dependence of the surface tension on PCL-*α*-CD/PAA-*t*Azo supramolecular complex solution and the CAC of these supramolecular aggregat is ~0.56 mg/mL

4.4 The hydrodynamic size of the PCL-*α*-CD/PAA-*t*Azo aggregation.

As shown in Fig. S4, the average hydrodynamic size <D_h> of the PCL-*α*-CD/PAA-*t*Azo complex in aqueous media is characterized by DLS. It is observed that the <D_h> of the supramolecular aggregates is approximately 188 nm in water. In contrast to their tubular structure with ~220 nm length and ~90 nm in diameter, the equivalent hydrodynamic size (188 nm) is corresponding to the TEM results.[S6]

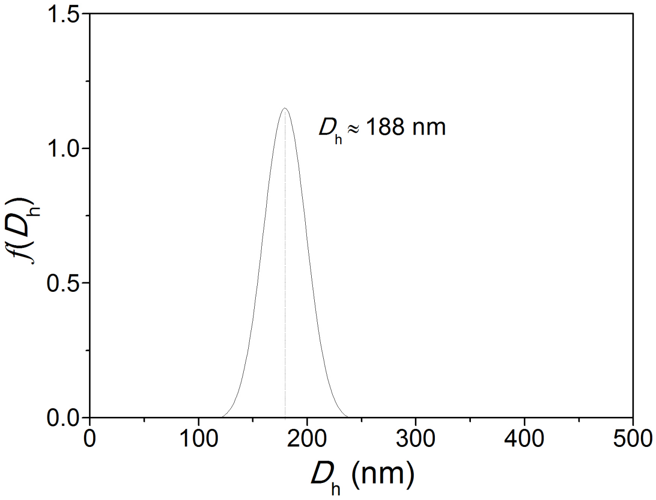


Fig. S4. The hydrodynamic diameter <D_h> distribution of the PCL-*α*-CD/PAA-*t*Azo supramolecular nanotubes in aqueous solution and the average <D_h> is ~188 nm.

4.5 Light-Responsive Nanotubes and their controlled assembly and disassembly.

The reversible host-guest interaction on the end-group of two homopolymers between PCL-*α*-CD and PAA-*t*Azo is further confirmed by UV-vis spectroscopy. A 5 mL PCL-*α*-CD/PAA-*t*Azo supramolecular tubular solution was performed UV detecting (Fig. S5a). The profiles show that the binary complex in water has a diagnostic and strong absorption (at 348 nm) of *trans*-Azo groups, which indicates that the formation of PCL-*α*-CD/PAA-*t*Azo aggregates in terms of terminal host-guest interaction between *α*-CD and *trans*-Azo species. However, upon an external UV light at 365 nm to this solution, the isomerization happens. Thus the absorption at 348 nm dramatically decreases concomitancy with a new peak at 433 nm ascribed to *cis*-Azo groups was obtained, indicating an obvious disassembly process of

PCL-α-CD and PAA-*c*Azo.[S7] In the presence of an external visible light at 450 nm for changing the *cis*-Azo to *trans*-Azo, analogous absorption curve at 348 nm can revert back. Furthermore, applied an alternative UV/visible light to this supramolecular tubular solution, the reversible assembly and disassembly process can repeat many times, as evidenced by the strong and weak absorption in turns at 348 nm belonged to *trans*-Azo species (Fig. S5b).

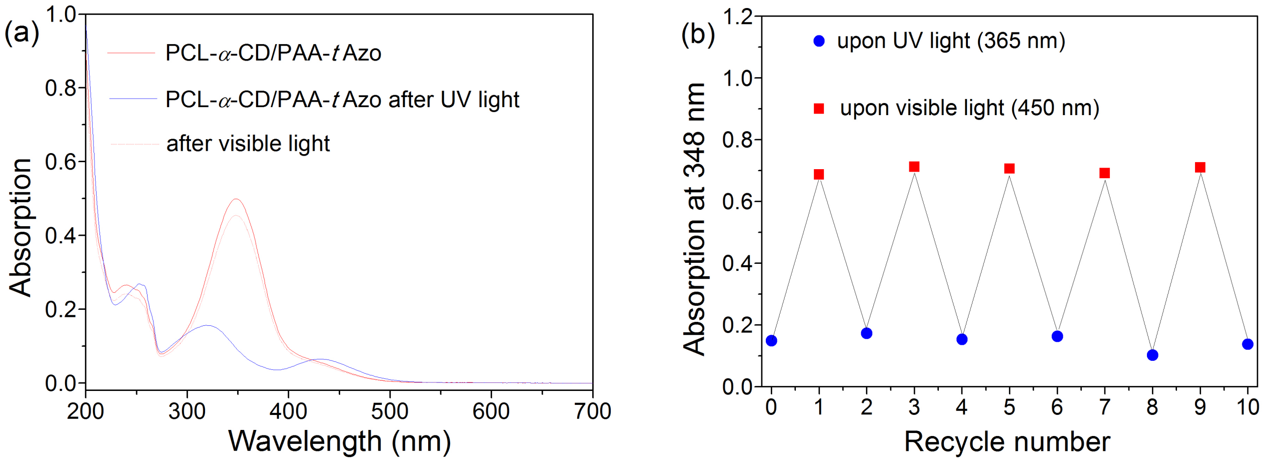


Fig. S5. (a) The absorption changes of PCL-α-CD/PAA-*t*Azo supramolecular nanotubes upon UV light and visible light, (b) the characteristic trans-Azo group absorption variation at 348 nm upon alternative UV/visible light stimuli

References

[S1] Lowe, A. B.; McCormick, C. L. *Prog. Polym. Sci.* **2007**, *32*, 283-351.

[S2] Hamasaki, K.; Ikeda, H.; Nakamura, A.; Ueno, A.; Toda, F.; Suzuki, I.; Osa, T. *J. Am. Chem. Soc.* **1993**, *115*, 5035-5040.

[S3] Melton, L. D.; Slessor, K. N. *Carbohydr. Res.* **1971**, *18*, 29-38.

[S4] Yan, Q.; Yuan, J. Y.; Cai, Z. N.; Xin, Y.; Kang, Y.; Yin, Y. W. *J. Am. Chem. Soc.* **2010**, *132*, 9268-9270.

[S5] Omar, A. –A. M. A.; Abdel-Khalek, N. A. *J. Chem. Eng. Data* **1998**, *43*, 117-122.

[S6] Lim, Y-B.; Lee, E; Lee, M. *Angew. Chem. Int. Ed.* **2007**, *46*, 9011-9014.

[S7] Wang, Y. P.; Ma, N.; Wang, Z. Q.; Zhang, X. *Angew. Chem. Int. Ed.* **2007**, *46*, 2823-2826.