Electronic Supplementary Information for:

UV light- and thermo-responsive hierarchical assemblies based on the inclusion complexation of β-cyclodextrin and azobenzene

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1. Materials

PEG monomethyl ether (Fluka) with M_n = 1000 g/mol was dried by azeotropic distillation in the presence of toluene. β-Cyclodextrin (β-CD, Sigma-Aldrich) was dried 100 °C for 48 h in vacuum after recrystallization from water before use. 2-(2-Methoxyethoxy)ethyl methacrylate (MEO_2MA, M_n = 188 g/mol) and oligo(ethylene glycol) methacrylate (OEGMA, M_n = 475 g/mol) were purchased from Sigma-Aldrich and passed through a column of activated basic alumina to remove inhibitors. Copper bromide (CuBr, Alfa Aesar, 99%) was treated by stirring in glacial acetic acid and washed with ethanol several times. Methylene chloride (CH_2Cl_2, Sinopharm Chemical Reagent Co.), tetrahydrofuran (THF, Sinopharm), *N,N*-dimethylformamide (DMF, Sinopharm), and triethylamine (Et_3N, Sigma-Aldrich) were dried over CaH_2 and distilled before use. 4-Hydroxy-azo-benzene (Sigma-Aldrich), 6-chlorohexanol (Sigma-Aldrich), dicyclohexylcarbodiimide (DCC, Alfa Aesar), 4-dimethylaminopyridine (DMAP, Fluka), 2-bromoisobutyryl bromide (Sigma-Aldrich), *N,N',N'',N''*- pentamethyldiethylenetriamine (PMDETA, Acros), potassium carbonate (K_2CO_3, Sinopharm), potassium iodide (KI, Sinopharm) and sodium azide (NaN_3, Alfa Aesar) were used as received. Propargyl 3-carboxylic-propanoate was prepared according to the literature.[1]

2. Characterization

Attenuated total internal reflectance Fourier transform infrared (ATR FT-IR). ATR FT-IR spectra of samples were recorded on an EQUINOSS/HYPERION2000 spectrometer (Bruker, Germany).

Nuclear magnetic resonance (NMR). ^1H NMR spectra of samples were obtained from a Bruker AV 400 NMR spectrometer with $CDCl_3$, DMSO-*d6* or D_2O as the solvent. The chemical shifts were relative to tetramethylsilane.

Gel permeation chromatography (GPC). GPC analysis was carried out with a HLC-8320 (Tosoh, Japan) analysis system with two columns (TSK gel super AWM-H×2, R0091+R0093), using DMF with 10 mM LiBr as eluent at a flow rate of 0.6

mL/min at 40 ºC. Monodisperse poly(methyl methacrylate) (PMMA) calibration kit was used as the calibration standard.

Fluorescence spectroscopy (FS). The fluorescence measurements were conducted on an F-2500 (Hitachi, Japan) fluorescence spectrophotometer with a xenon lamp source. The excitation wavelength for critical aggregation concentration (CAC) measurement and Azo-P(MEO_2MA-*co*-OEGMA) fluorescence spectra is 335nm and 290 nm, respectively.

UV-visible (UV-vis) absorption measurements. UV-vis absorption studies were carried out using a U-3310 spectrophotometer (Hitachi, Japan) equipped with a temperature controller (0.1 ºC accuracy).

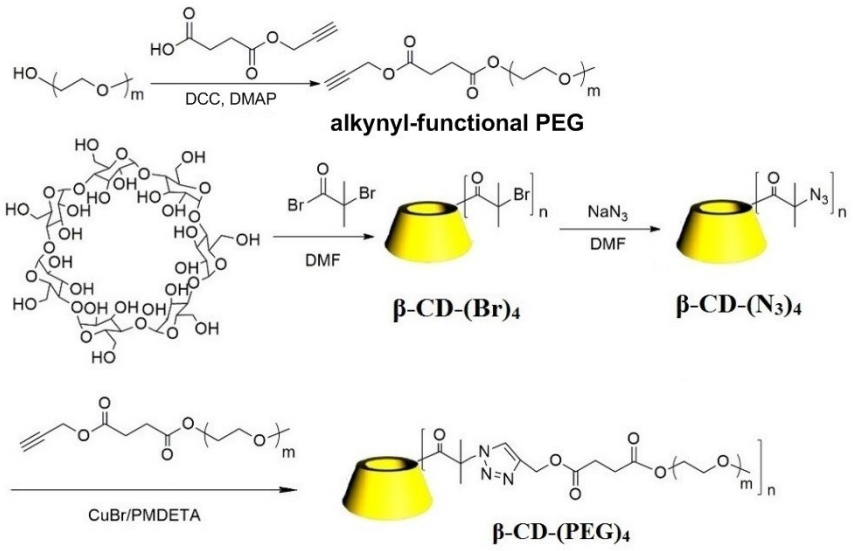
Dynamic light scattering spectrophotometry (DLS). The hydrodynamic radius (R_h) of the polymer aggregates was determined on a Malven Autosizer 4700 DLS spectrometer. The apparent R_h was obtained by a cumulant analysis.

Transmission electron microscopy (TEM). The morphology of polymer aggregates was observed with a JEOL JEM-2010 TEM at an accelerating voltage of 120 kV. The samples for TEM observation were prepared by dropping 10 μL of polymer solutions on copper grids coated with thin films and carbon.

UV and visible light irradiation. A UV LED irradiator (UVATA, wavelength = 365 nm) and a Vis LED irradiator (CCS, wavelength = 500 nm) were used to induce the photoisomerization of the azobenzene moiety.

3 Experimental procedures

3.1 Synthesis of the host polymer β-CD-$(PEG)_4$



Scheme S1 Synthesis route of the host polymer β-CD-$(PEG)_4$.

Synthesis of bromide modified β-CD (β-CD-Br_4)

β-CD-Br_4 was synthesized according to the literature.[2] Briefly, β-CD (3.06 g, 3.38 mmol) and Et_3N (1.37 g, 13.52 mmol) were dissolved in anhydrous DMF (45 mL) under stirring. The mixture was stirred and cooled to 0 °C. Then 2-bromoisobutyric bromide (3.11 g, 13.52 mmol) in dry DMF (15 mL) was added dropwise to the mixture within 1 h in argon. The reaction mixture was stirred for 48 h at room temperature before precipitation in cold diethyl ether. The resulted powder was collected from filtration, washed with acetone (3×20 mL). Then the crude product was suspended in deionized water (90 mL) and the mixture was stirred overnight. The purified product was centrifuged, washed with acetone (3×20 mL), and dried in vacuum until a constant weight was reached.

The product was purified using the method based on the solubility difference of bromide modified β-CDs with different degrees of substitution in water and acetone.[2] ^{1}H NMR spectrum of the product is shown in Fig. S1b. Compared to β-CD (Fig. S1a), a new signal ascribed to methyl protons next to the terminal bromine at 1.90 ppm (peak a, Fig. S1b) appeared. The number of bromine groups was calculated to be 4 per β-CD molecule based on the integrated areas of peak a at 1.90 ppm and peak C(1)*H* at 4.86 ppm in Fig. S1b.

The detailed assignments of the ^{1}H NMR spectra for β-CD-Br_4 are shown as follows:

^{1}H NMR (δ, ppm, DMSO-d_6): 1.90 (m, 24H, -COOC(C***H***$_3$)$_2$Br), 3.42-6.15 (m, 66H, -O***H*** and -C***H***- of β-CD).

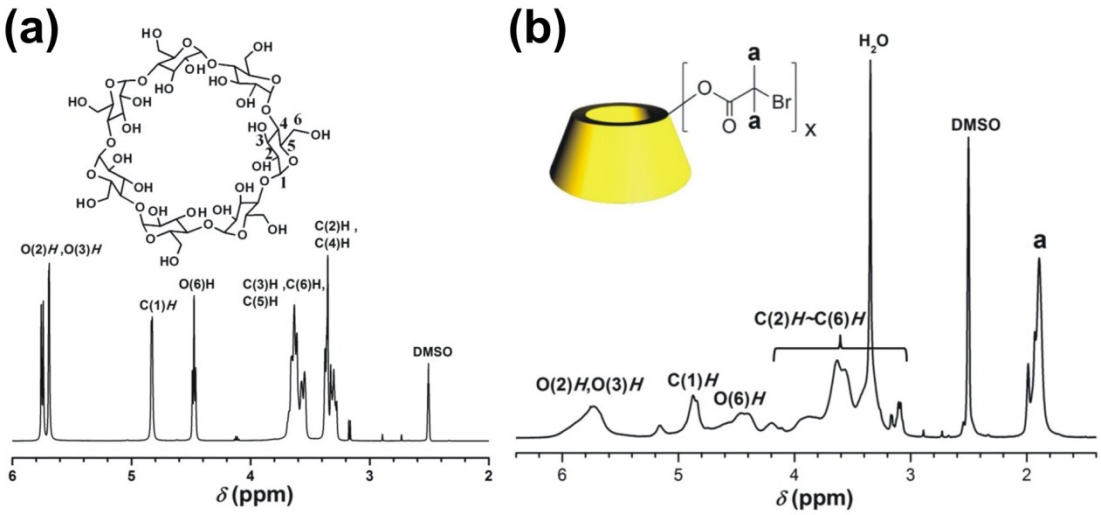


Fig. S1 ^{1}H NMR of (a) β-CD and (b) bromide modified β-CD (β-CD-Br_4).

Synthesis of azide modified β-CD (β-CD-$(N_3)_4$)

β-CD-$(N_3)_4$ was obtained from reacting β-CD-Br_4 with excess NaN_3. β-CD-Br_4 (2.50 g, 1.15 mmol), NaN_3 (2.95 g, 49.91 mmol), and 50 mL of dried DMF were charged in a 100 mL round-bottom flask. The reaction mixture was stirred for 48 h at room temperature. Unreacted NaN_3 was removed through filtration. Then the filtrate was rota-evaporated and precipitated into cold deionized water. The white powder of β-CD-$(N_3)_4$ was obtained after freeze-drying.

The ^{1}H NMR spectrum of β-CD-$(N_3)_4$ is shown in Fig. S2. It can be observed that the chemical shift of the methyl protons (-COOC(CH_3)$_2$-) shifted from 1.90 ppm in β-CD-Br_4 (Fig. S1b) to 1.42 ppm in β-CD-$(N_3)_4$ (Fig. S2), indicating that the bromide group was substituted by the azide group. The FT-IR spectra of β-CD-Br_4 and β-CD-$(N_3)_4$ in Fig. S3 further revealed the appearance of an absorbance peak at 2105 cm^{-1} for β-CD-$(N_3)_4$, which is characteristic of the azide group.[3,4]

The detailed assignments of the ^{1}H NMR spectra for β-CD-$(N_3)_4$ are shown as follows:

^{1}H NMR (δ, ppm, DMSO-d_6): 1.42 (m, 24H, -COOC(C***H*****$_3$**)$_2$N$_3$), 3.42-6.15 (m, 66H, -O***H*** and -C***H***- of β-CD).

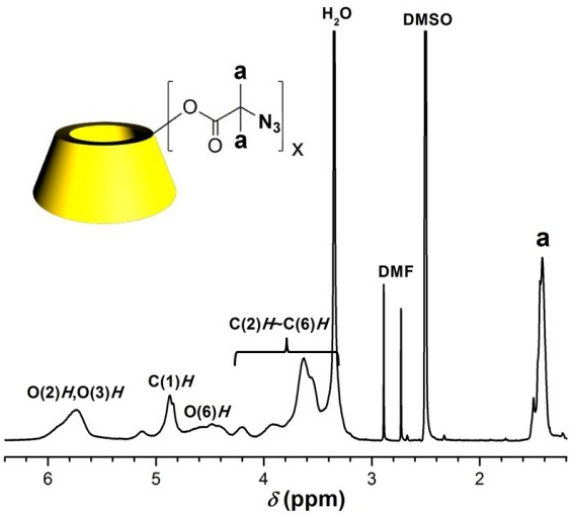


Fig. S2 ^{1}H NMR of azide modified β-CD (β-CD-(N$_3$)$_4$).

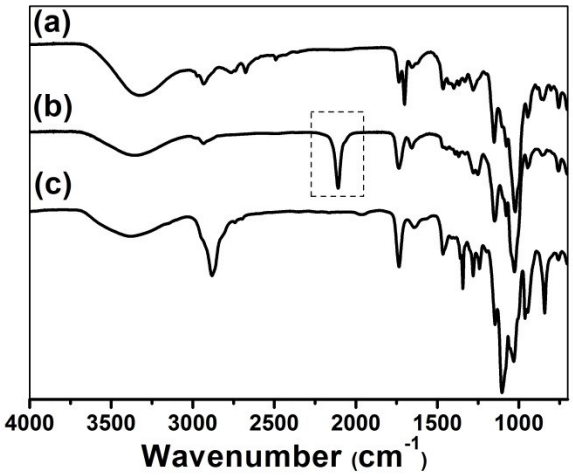


Fig. S3 FT-IR spectra of (a) β-CD-Br$_4$, (b) β-CD-(N$_3$)$_4$ and (c) β-CD-(PEG)$_4$.

Synthesis of alkynyl-functional PEG

The alkynyl-functional PEG was prepared by the reaction of PEG monomethyl ether with excess propargyl 3-carboxylic-propanoate. PEG monomethyl ether (5.00 g, 5.00 mmol), propargyl 3-carboxylic-propanoate (2.34 g, 15.00 mmol), DMAP (0.61 g, 5.00 mmol), and DCC (2.06 g, 10.00 mmol) were dissolved in 30 mL of anhydrous CH_2Cl_2. The reaction was carried out at room temperature for 48 h under vigorous stirring. The reaction byproduct dicyclohexylcarbodiurea (DCU) was removed

through filtration. Then the filtered solution was concentrated by a rotary evaporator. Diethyl ether was added to precipitate the polymer. The final product was obtained by filtration and dried in vacuum at room temperature until a constant weight was reached.

^{1}H NMR spectrum of alkynyl-functional PEG is shown in Fig. S4. New peaks at 2.51 ppm (peak g), 2.68 ppm (peak e), 4.25 ppm (peak d) and 4.70 ppm (peak f) can be seen. Moreover, the area ratio of the integration of the proton signals at 3.38 ppm (peak a) to 4.70 ppm (peak f) was 3:2, revealing that alkynyl-functional PEG was successfully prepared. The detailed assignments of the ^{1}H NMR spectra for alkynyl-functional PEG are shown as follows:

^{1}H NMR (δ, ppm, $CDCl_3$): 2.51 (s, -C≡C***H***), 2.68 (s, -COO-C***H$_2$***-C***H$_2$***-COO-), 3.38 (s, -OC***H$_3$***), 3.65 (m, -C***H$_2$***-C***H$_2$***-O-, -O-C***H$_2$***-C***H$_2$***-COO-), 4.25 (s, -O-CH_2-C***H$_2$***-COO-), 4.70 (s,-COO-C***H$_2$***-C≡CH).

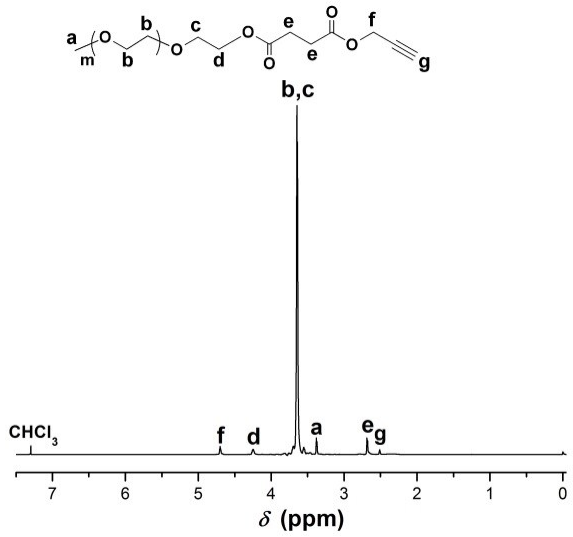


Fig. S4 ^{1}H NMR of alkynyl-functional PEG.

Synthesis of the host polymer β-CD-(PEG)$_4$

The host polymer β-CD-$(PEG)_4$ was synthesized through the click chemistry between β-CD-$(N_3)_4$ and an excess of alkynyl-functional PEG. A dried 25 mL round-bottom flask with a magnetic stirrer was charged with β-CD-$(N_3)_4$ (0.47 g, 0.30 mmol), alkynyl-functional PEG (3.00 g, 2.64 mmol), CuBr (0.17 g, 1.20 mmol), PMDETA (250 μL, 1.20 mmol), and anhydrous DMF (25 mL). The flask was

degassed with three freeze-evacuate-thaw cycles and back filled with argon. Then, the reaction was performed for 24 h at 50 °C. After being cooled to room temperature, the reaction flask was exposed to air, and the crude product was purified by dialysis (molecular weight cut-off: 3500 g/mol) against water to remove the catalyst and unreacted alkynyl-functional PEG. The final product was collected by freeze-drying.

Fig. S5 shows the ^{1}H NMR spectrum of β-CD-(PEG)$_4$ with resonance shifts attributed to all the protons in the structure. In comparison with the ^{1}H NMR spectrum of β-CD-(N$_3$)$_4$ in Fig. S2, the chemical shift of the methyl protons shifted from 1.42 ppm (peak a, Fig. S2) to 1.88 ppm for β-CD-(PEG)$_4$ (peak a, Fig. S5). Meanwhile, a new resonance signal appeared at ~8.18 ppm, which is characteristic of the formation of 1,2,3-triazole linkages.[5,6] All these results suggested that the click reaction between β-CD-(N$_3$)$_4$ and alkynyl-functional PEG was accomplished, and the host polymer β-CD-(PEG)$_4$ was successfully prepared. This conclusion was further confirmed by the disappearance of the characteristic absorption peak of the azide group at 2105 cm^{-1} after the reaction from the FT-IR spectrum of β-CD-(PEG)$_4$ in Fig. S3c.

The $M_{n,NMR}$ of β-CD-(PEG)$_4$ can be calculated according to equation (1).

$$M_{n,NMR} = 1579 + 1138 \times 4 \qquad (1)$$

Here, 1579 is the molecular weight of β-CD-(N$_3$)$_4$, 1138 is the molecular weight of alkynyl-functional PEG, and 4 is the number of the PEG arms in the host polymer β-CD-(PEG)$_4$. The $M_{n,NMR}$ of β-CD-(PEG)$_4$ is 6131 g/mol. The GPC trace of β-CD-(PEG)$_4$ is shown in Fig. S6 and the M_n measured by GPC is 5400 g/mol.

The detailed assignments of the ^{1}H NMR spectra for β-CD-(PEG)$_4$ are shown as follows:

^{1}H NMR (δ, ppm, DMSO-d_6): 1.88 (s, -COOC(C***H*****$_3$**)$_2$-), 2.60 (s, -COO-C***H*****$_2$**-C***H*****$_2$**-COO-), 3.24 (s, -OC***H*****$_3$**), 3.42-4.83 (m, O(6)*H* and -C***H***- of β-CD, overlapped with methylene proton in the repeating unit in PEG), 3.50 (s, -C***H*****$_2$**-C***H*****$_2$**-O-), 5.13 (s, -C***H*****$_2$**- next to the 1, 2, 3-triazole group), 5.54-6.1 (s, O(2)***H*** and O(3)***H*** of β-CD), 8.18 (s, -C***H***- of the 1, 2, 3-triazole group).

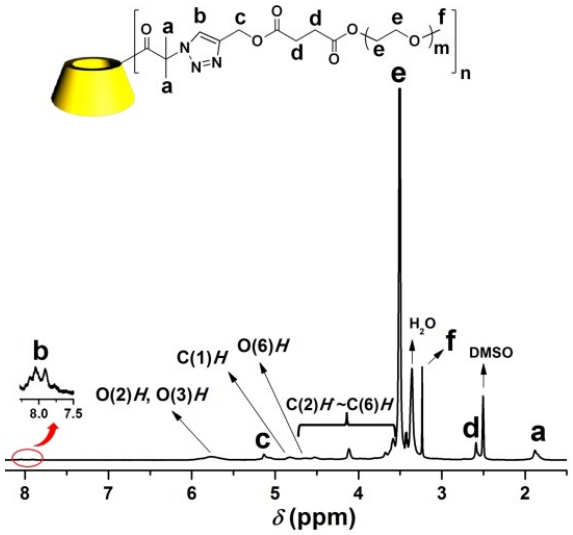


Fig. S5 ^{1}H NMR of β-CD-$(PEG)_4$.

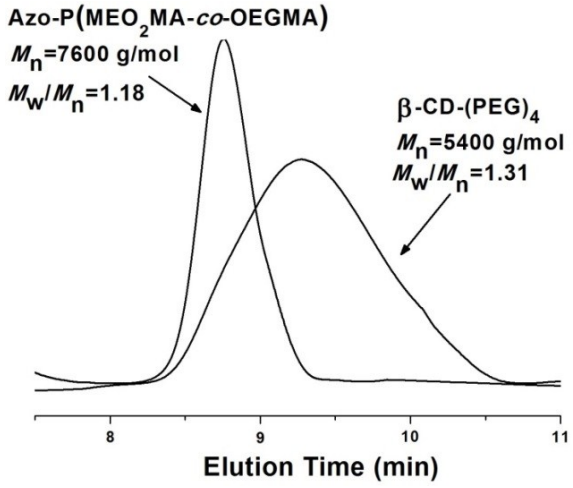
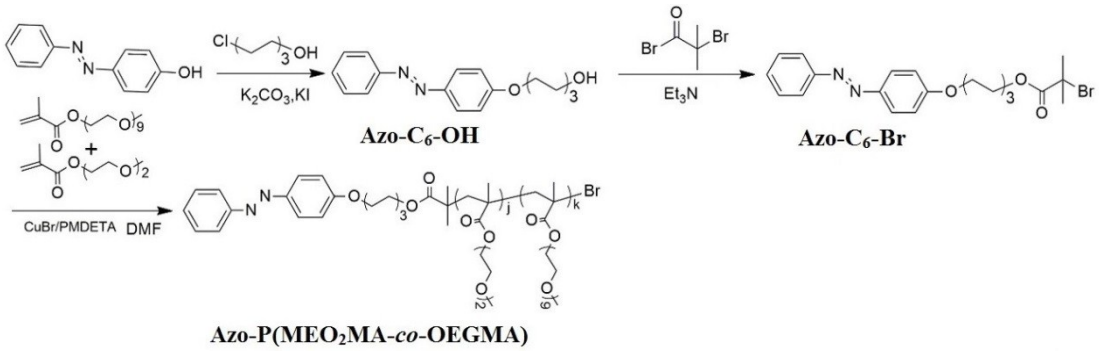


Fig. S6 GPC traces of the host polymer β-CD-$(PEG)_4$ and the guest polymer Azo-P(MEO_2MA-*co*-OEGMA).

3.2 Synthesis of the guest polymer Azo-P(MEO_2MA-*co*-OEGMA)



Scheme S2 Synthesis route of the guest polymer Azo-P(MEO_2MA-*co*-OEGMA).

Synthesis of Azo-C_6-OH

Azo-C_6-OH was synthesized by the Williamson etherification of 4-hydroxy-azo-benzene with 6-chlorohexanol, as described below. 4-hydroxy-azo-benzene (10.50 g, 53.03 mmol), 6-chloro-1-hexanol (10.82 g, 79.54 mmol), K_2CO_3 (10.98 g, 79.54 mmol) and a trace amount of potassium iodide were added into DMF (200 mL). The reaction was carried out at 90 °C for 12 h under stirring. The reaction mixture was poured into a large amount of deionized water, and then extracted with chloroform. The organic phase was collected and $MgSO_4$ were added into the chloroform solution. After being stirred overnight, the chloroform solution was collected after filtration. The crude product was received from rota-evaporation. The final product was obtained after recrystallization in ethanol and dried completely in vacuum at room temperature.

Fig. S7 shows the ^{1}H NMR spectrum of Azo-C_6-OH with all the protons detected. The integral area ratio of peak e at 4.05 ppm to peak c at 7.93 ppm was 1: 2, indicating the successful synthesis of Azo-C_6-OH. The detailed assignments of the ^{1}H NMR spectra for Azo-C_6-OH are shown as follows:

^{1}H NMR (δ, ppm, $CDCl_3$): 1.40-1.58 (m, 4H, -C***H₂***-C***H₂***-CH_2-CH_2-OH), 1.62 (m, 2H, -C***H₂***-CH_2-OH), 1.84 (m, 2H, -Ph-O-CH_2-C***H₂***-), 3.67 (t, 2H, -C***H₂***-OH), 4.05 (t, 2H, -Ph-O-C***H₂***-), 7.00-7.93 (m, 9H, -C***H***- of the azobenzene group).

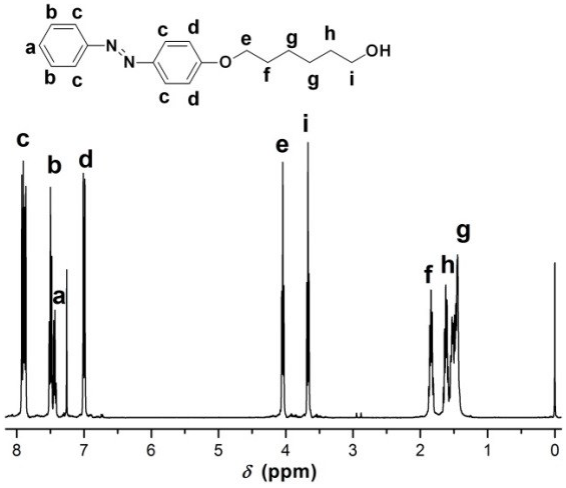


Fig. S7 ^{1}H NMR of Azo-C_6-OH.

Synthesis of Azo-C_6-Br

The Azo-C_6-Br was synthesized from the reaction between Azo-C_6-OH and excess of 2-bromoisobutyryl bromide. Azo-C_6-OH (4.00 g, 13.42 mmol) and Et_3N (1.36 g, 13.45 mmol) were dissolved in anhydrous CH_2Cl_2 (50 mL) under an argon atmosphere. The mixture was stirred and cooled to 0 °C in an ice bath. 2-bromoisobutyryl bromide (15.41 g, 67.03 mmol) in anhydrous CH_2Cl_2 (30 mL) was added dropwise to the mixture within 1 h at 0 °C. The reaction was carried out for 2 h at 0 °C and then stirred for 48 h at room temperature. The reaction mixture was rota-evaporated and then precipitated in cold ethanol. The product was obtained after filtration and dried completely in vacuum at room temperature.

The ^{1}H NMR spectrum of Azo-C_6-Br is shown in Fig. S8. In comparison with that of Azo-C_6-OH in Fig. S7, a new chemical shift at 1.94 ppm corresponding to the methyl protons in the bromoethyl group (-C(C***H***$_3$)$_2$Br) of Azo-C_6-Br and another new shift at 4.20 ppm (peak i, Fig. S8) can be detected in Fig. S8 while the shift at 3.67 ppm (peak i, Fig. S7) disappeared completely, revealing that the terminal hydroxyl groups in Azo-C_6-OH completely reacted with 2-bromoisobutyryl bromide. The detailed assignments of the ^{1}H NMR spectra for Azo-C_6-Br are shown as follows:

^{1}H NMR (δ, ppm, $CDCl_3$): 1.46-1.59 (m, 4H, -C***H***$_2$-C***H***$_2$-CH_2-CH_2-COO-), 1.74 (m, 2H, -C***H***$_2$-CH_2-COO-), 1.85 (m, 2H, -Ph-O-CH_2-C***H***$_2$-), 1.94 (s, 6H, -COO-C(C***H***$_3$)$_2$Br), 4.05 (t, 2H, -Ph-O-C***H***$_2$-), 4.20 (t, 2H, -COO-C***H***$_2$-), 7.00-7.93 (m, 9H, -C***H***- of the azobenzene group).

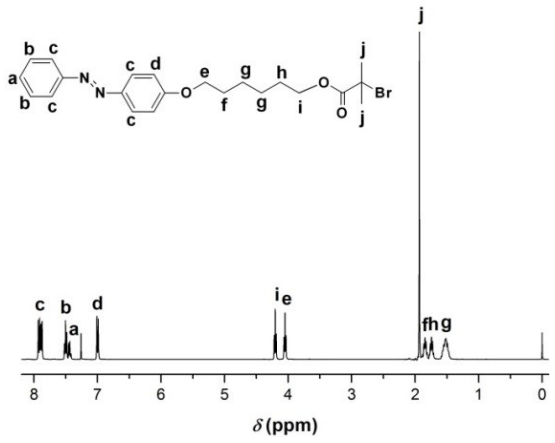


Fig. S8 ^{1}H NMR of Azo-C_6-Br.

Synthesis of the guest polymer Azo-P(MEO_2MA-co-OEGMA)

The guest polymer Azo-P(MEO_2MA-*co*-OEGMA) was synthesized via ATRP of MEO_2MA and OEGMA monomers using Azo-C_6-Br as the initiator, with a typical procedure described below. A dried reaction flask with a magnetic stirrer was charged with Azo-C_6-Br (0.60 g, 1.34 mmol), MEO_2MA (7.99 g, 42.55 mmol), OEGMA (1.76 g, 3.70 mmol), PMDETA (283 μL, 1.34 mmol), CuBr (0.19 g, 1.34 mmol), and DMF (20 mL). The flask was degassed with three freeze-evacuate-thaw cycles and backfilled with argon. Then, the polymerization was performed for 8 h at 60 °C under stirring. After being cooled to room temperature, the reaction flask was exposed to air. The reaction mixture was purified through dialysis (molecular weight cut-off: 3500 g/mol) against water to remove the catalyst and unreacted monomers. The final product was collected from freeze-drying.

The ^{1}H NMR spectrum of Azo-P(MEO_2MA-*co*-OEGMA) is shown in Fig. S9. All the resonance signals can be attributed to the protons in the polymer. The feed molar ratio of MEO_2MA and OEGMA was 92:8. And the virtual molar ratio of MEO_2MA and OEGMA calculated from ^{1}H NMR analysis by comparing the integral areas of peak h at 3.52-3.75 ppm and peak i at 3.40 ppm was 92.1:7.9, consistent with the feed ratio. The degree of polymerization was calculated from ^{1}H NMR spectrum by comparing the integral areas of peak g (4.11 ppm) and peak d (7.0 ppm) in Fig. S9. The $M_{n,NMR}$ of Azo-P(MEO_2MA-*co*-OEGMA) can be calculated according to equation (2).

$$M_{n,NMR} = \left(\frac{I_g}{I_d} \times 92.1\% \times 188 + \frac{I_g}{I_d} \times 7.9\% \times 475\right) + 447 \qquad (2)$$

Here, 92.1% is the mole fraction of MEO_2MA in Azo-P(MEO_2MA-*co*-OEGMA), 7.9% is the mole fraction of OEGMA in Azo-P(MEO_2MA-*co*-OEGMA), 188 is the molecular weight of MEO_2MA monomer, 475 is the molecular weight of OEGMA monomer, and 447 is the molecular weight of the initiator Azo-C_6-Br. The $M_{n,NMR}$ of Azo-P(MEO_2MA-*co*-OEGMA) is 7336 g/mol. The GPC trace of Azo-P(MEO_2MA-*co*-OEGMA) is shown in Fig. S6 and the M_n value measured by GPC is 7600.

The detailed assignments of the ^{1}H NMR spectra for Azo-C_6-Br are shown as follows:

^{1}H NMR (δ, ppm, $CDCl_3$): 0.70-1.11 (m, -$CH_2C(CH_3)$-), 1.72-2.15 (m, -$CH_2C(CH_3)$-), 3.40 (s, -$OCH_2CH_2OCH_3$), 3.52-3.75 (m, -$COOCH_2CH_2OCH_2CH_2O$-), 4.11 (s, -$COOCH_2CH_2O$-), 7.00-7.93 (m, 9H, -C*H*- of the azobenzene group).

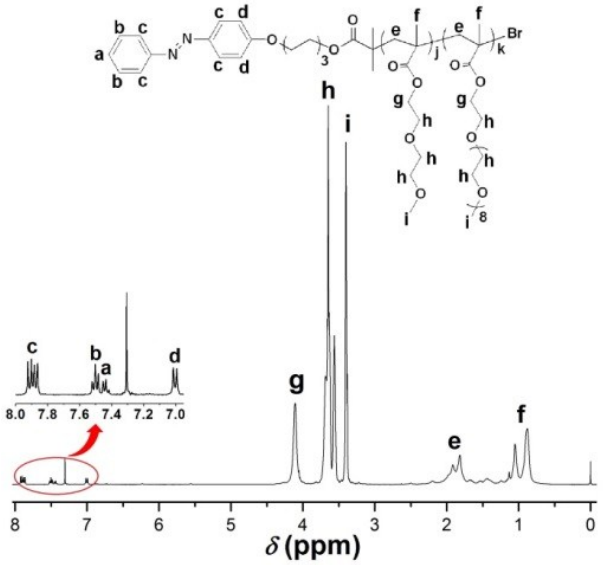


Fig. S9 ^{1}H NMR of Azo-P(MEO_2MA-*co*-OEGMA).

3.3 Preparation of the host and guest polymer aggregates, and the hierarchical assemblies

β-CD-$(PEG)_4$ and Azo-P(MEO_2MA-*co*-OEGMA) aggregates were obtained by dissolving the host and guest polymers in the deionized water separately. The procedure for the preparation of β-CD-$(PEG)_4$ aggregates was typically as follows. 10 mg of β-CD-$(PEG)_4$ was dissolved in in 20 mL of deionized water. The solution was stirred for 48 h and then equilibrated for 24 h at 25 ºC. The preparation of Azo-P(MEO_2MA-*co*-OEGMA) aggregates was the same as that of the β-CD-$(PEG)_4$ aggregates.

The hierarchical assemblies were prepared by mixing the host and guest polymer aqueous solutions together with a molar ratio of β-CD to azobenzene group being 1:1. After sonication for 10 min, the mixtures were stirred for 48 h to ensure the formation of supramolecular complexes.

4. Critical aggregation concentration (CAC) measure of the host, guest, and supramolecular polymers in aqueous solutions

The CACs of the host, guest, and supramolecular polymer assemblies in aqueous solutions were measured using pyrene as a fluorescent probe. The CAC measurement for the host polymer β-CD-$(PEG)_4$ was performed as follows. Pyrene (4.9 mg, 0.024mmol) was dissolved in 12 mL of acetone and then 10 μL of the solution was added into each cuvette. The acetone was allowed to evaporate. Then 2.0 mL of β-CD-$(PEG)_4$ aqueous solutions with concentrations ranging from 0.488 to 1000 mg/L were added into the pyrene-containing cuvette separately. Upon sonication for 10 min, the solutions were kept at room temperature and equilibrated for 24 h before fluorescent emission measurements with an excitation wavelength of 335 nm. The emission spectra were recorded in the 340-600 nm wavelength range. For each spectrum obtained, the intensity ratio of the first and third peaks, I_1/I_3, was calculated. The CAC was estimated as the concentration at which I_1/I_3 began to drop, suggesting that polymer aggregation occurred. The results show that the CAC of the host polymer β-CD-$(PEG)_4$ was 124.8 mg/L (Fig. S10a). The CAC measurement procedures for the guest polymer Azo-P(MEO_2MA-*co*-OEGMA) and supramolecular polymer β-CD-$(PEG)_4$/Azo-P(MEO_2MA-*co*-OEGMA) are the same as that for the host polymer. And the CACs of the guest and supramolecular polymers were 86.8 mg/L (Fig. S10b) and 110.7 mg/L (Fig. S10c), respectively.

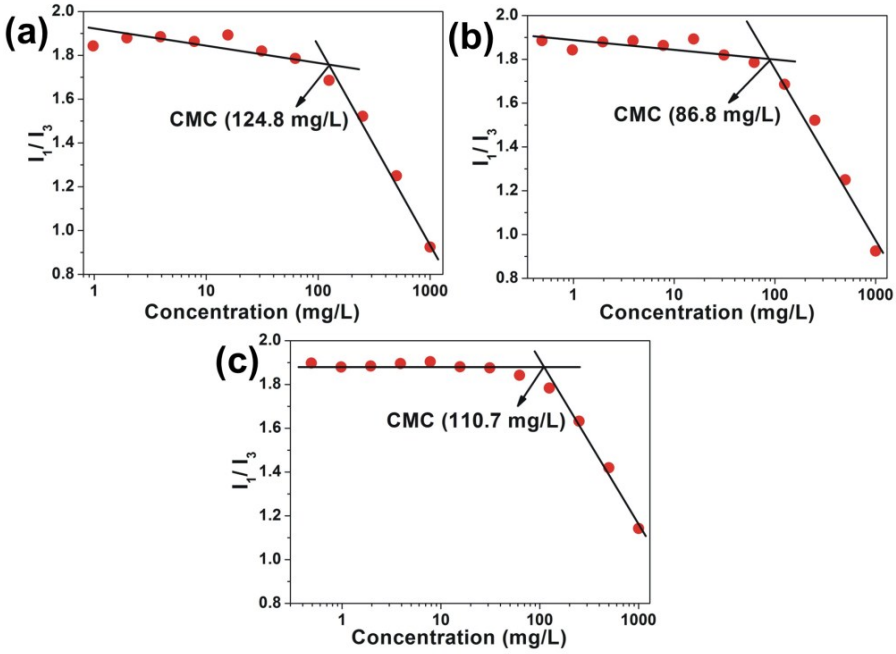


Fig. S10 CACs of (a) the host polymer β-CD-$(PEG)_4$, (b) the guest polymer Azo-P(MEO_2MA-*co*-OEGMA), and (c) the supramolecular polymer $(PEG)_4$/Azo-P(MEO_2MA-*co*-OEGMA.

5. Other Supplementary Results

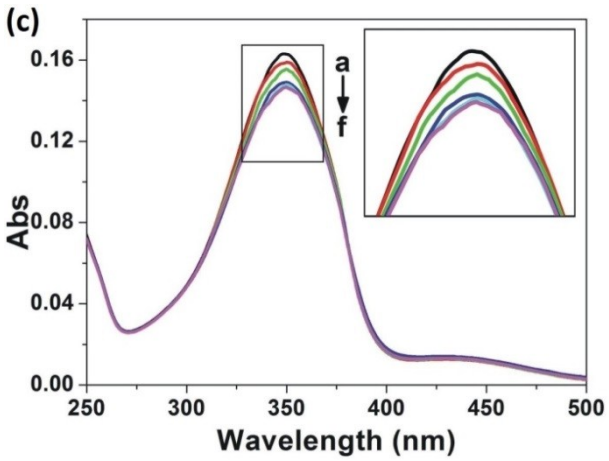


Fig. S11 UV-vis spectra of Azo-P(MEO_2MA-*co*-OEGMA) (0.0068 mM) at different times after the addition of β-CD-$(PEG)_4$ (0.0068 mM).

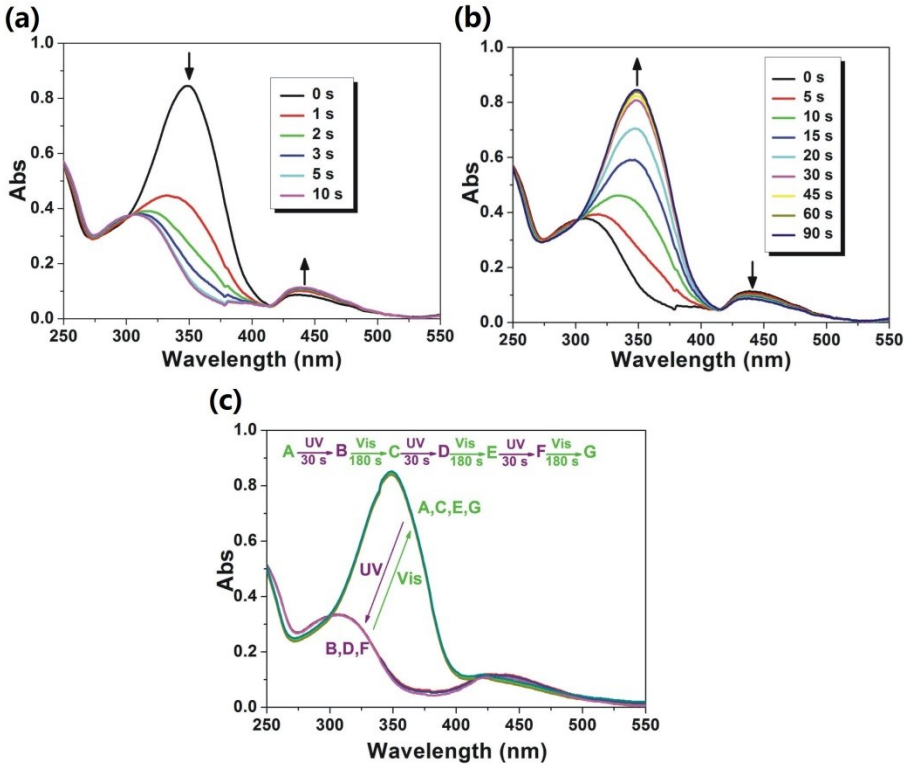


Fig. S12 UV-vis spectra of the supramolecular polymer β-CD-$(PEG)_4$/Azo-P(MEO_2MA-*co*-OEGMA) aqueous solutions upon (a) irradiation at 365 nm for different times, (b) subsequent irradiation at 500 nm for different times, and (c) periodical change of UV-vis spectroscopy under the control of light for the β-CD-$(PEG)_4$/Azo-P(MEO_2MA-*co*-OEGMA) aqueous solutions (Concentration: 0.5 mg/mL).

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