Supplementary Information

Light-Triggered Reversible "One-to-Two" Morphological Transition from A "Latent Double-Amphiphilic" Linear-Hyperbranched Supramolecular Block Copolymer

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1. Materials

4-(phenylazo)benzoic acid (TCI, >98%), thionyl chloride (Acros, 99.7%), boron trifluoride etherate (Acros, 48% BF_3), p-Toluenesulfonyl chloride (TsCl) (Alfa Aesar 99%), Sodium azide (Acros, 99+%), Copper Sulfate Pentahydrate (Acros, 98%) and Sodium ascorbate (Alfa Aesar, 99%) were used as received. Monomethyl poly(ethylene glycol) (Fluka, 99%, Mn~1100 Da), triethylamine (Acros, 99%), Tetrahydrofuran (Acros, 99.5%), propargyl alcohol (Alfa Aesar, 99%) were dried before used. 3-ethyl-3-oxetanemethanol (EHO) was synthesized according to our previous work.[1] *β*-Cyclodextrin (Sinopharm Chemical Reagent Co., Ltd, AR) was re-crystallized from deionized water 2 times and dried in vacuum at 70 °C for 48h. Dialysis bag (Shanghai green Bird Science & Technology Development Co., Ltd, MWCO: 1000Da and 3500Da).

2. Instruments and Measurements

^{1}H NMR, ^{13}C NMR spectra were recorded using a Varian Mercury Plus 400 (400 MHz) spectrometer with deuterated chloroform ($CDCl_3$), dimethylsulfoxide-d_6 (DMSO-d_6) or methanol-d (CD_3OD) as solvents at 298K. Two-dimensional nuclear Overhauser enhancement spectroscopy (2D-NOSEY) spectrum of sodium 4-phenylazophenol (AZO-Na) and CD-$_g$-HBPO in D2O was recorded using Bruker AVANCEIII 400 (400 MHz) spectrometer at 298K. $_1$H NMR results of adding D_2O to CD-*g*-HBPO or AZO-PEG DMSO-d_6 solution, as well as to the mixture of CD-*g*-HBPO and AZO-PEG DMSO-d_6 solution, were obtained in the following method: CD-*g*-HBPO (10.6 mg, 0.002 mmol) and AZO-PEG (2.2 mg, 0.002 mmol) were firstly dissolved in 0.5 ml DMSO-d_6 and D2O was then added gradually (0.025 ml for each time). After shaking and equilibrating for 20 min, the measurements were carried out and ^{1}H NMR spectra were recorded. A similar method was employed

for CD-*g*-HBPOs or AZO-PEGs, but the difference was that a capillary-sealed potassium hydrogen phthalate in D_2O was added into NMR tube as external standard when measuring AZO-PEGs.

DLS measurements were taken on a Malvern Zetasizer Nano S instrument equipped with a 4 mW He-Ne laser light, and samples (1 mL) were loaded into a quartz cuvette. All samples were performed by using a 633 nm laser at 25 ^{o}C with a scattering angle of 90^{o}.

SEM measurements were performed on a FEI NOVA NANOSEM 450 operating with an accelerating voltage of 5 kV, or on a FEI SIRION 200 instrument with an accelerating voltage of 5 kV. The samples for SEM observations were prepared by depositing several drops of the aggregates solutions onto the surface of cleaned silicon chips, and then air-dried or freeze-dried in vacuum at -50 ^{o}C for 24h. The samples observed on FEI NOVA NANOSEM 450 were coated with a thin film of platinum (Pt) before measuring, while those observed on FEI SIRION 200 were coated with gold (Au).

TEM measurements were carried out on a JEOL JEM-2100 instrument at a voltage of 200 kV, or on a Hitachi HT7700 instrument at a voltage of 80 kV. For conventional TEM imaging, grids were prepared by applying a droplet of aggregates solution onto a carbon-coated copper grid and dried after wicking away most of the solution. TEM samples stained with uranyl acetate were prepared by the following procedure: A droplet of aggregates solution was cast onto a carbon-coated copper grid and after wicking away most of the solution, waiting until the solution became invisible to naked eye and a droplet of 1% (w/v) aqueous uranyl acetate solution was immediately deposited onto the surface. After 3 minutes, the excess staining agent was taken away and the sample was dried before measurement. As for the deeply stained TEM sample, a thin uranyl acetate solution film was left on the grid instead

of totally taken away.

AFM measurements were performed on a Multimode Nanoscope-IIIa Scanning Probe Microscope (DigitalInstrument Co., Ltd. U.S.A.) equipped with a MikroMasch silicon cantilever, NSCII (radius < 10 nm, resonance frequency = 300 kHz, spring constant = 40 N/m) with tapping mode at room temperature. Samples for AFM measurements were prepared by applying a droplet of aggregates solution onto freshly cleaved mica disks and dried after removing the excess solution.

UV-vis absorption spectra were recorded by UV-1800PC (Shanghai Mapada Company). Samples of aggregates solutions were added to a quartz cell (path length: 1cm) and absorption spectra were recorded with the wavelength range from 200 to 550 nm.

3. Synthesis and Characterizations of AZO-PEG (Linear part).

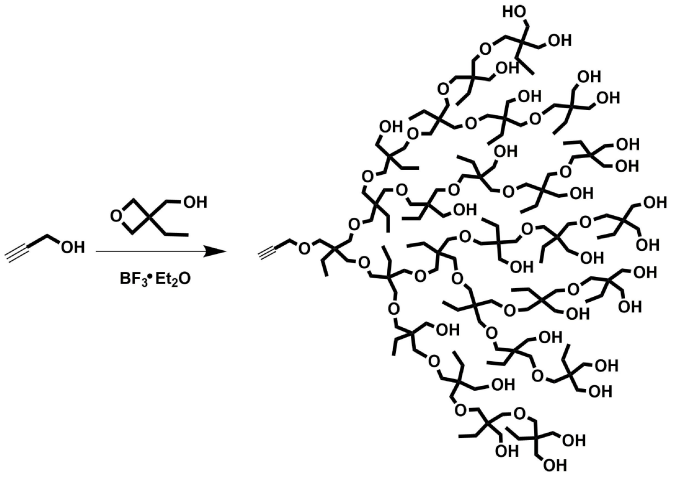
AZO-PEG was synthesized by the esterification reaction between 4-(phenylazo)benzoic acid and monomethyl poly(ethylene glycol). The synthesis route was as follows: Firstly, 4-(phenylazo)benzoic acid was activated via reacting with thionyl chloride by the following process: 4-(phenylazo)benzoic acid (1.13 g, 5 mmol) and thionyl chloride (25 mL, 344 mmol) were added to a dry two-neck flask, and then heated and refluxed at 85 ºC for 8h under the protection of argon. After removing the excess thionyl chloride by reduced pressure distillation, a crude product of red solid was obtained. This product was exactly 4-(phenylazo)benzoyl chloride and can be used directly without purification. Secondly, AZO-PEG was obtained by the following process: monomethyl poly(ethylene glycol) (5.51 g, 5 mmol) and triethylamine (2.17 mL, 15 mmol) were dissolved in dried THF(25 mL). After cooling the mixture with ice-bath to about 5 ºC, 4-(phenylazo)benzoyl chloride (all amount obtained above) in dried THF(10 mL), was dropwise added within 1h under argon atmosphere. The mixture was warmed

up slowly to room temperature and reacted overnight. Precipitate (salt of triethylammonium chloride) was observed in the solution during the reaction, indicating the proceeding of the esterification reaction. After reaction, the mixture was filtered and THF was removed through rotation evaporation. A crude product of reddish yellow solid was obtained and then purified by column chromatograph on silica gel ($CHCl_3$: Methanol = 10: 1, v/v, R_f= 0.52). The final product was reddish yellow and the yield is about 85% (5.51 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 1.6 Hz, 2H), 7.92 (d, J = 1.6 Hz, 2H), 7.51 (m, 3H), 4.50 (t, J = 4.9 Hz, 2H), 3.85 (t, J = 4.8 Hz, 2H), 3.50-3.75 (br, 96H), 3.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 155.4, 152.8, 131.9, 130.9, 129.4, 123.1, 70.5, 64.6, 59.2.

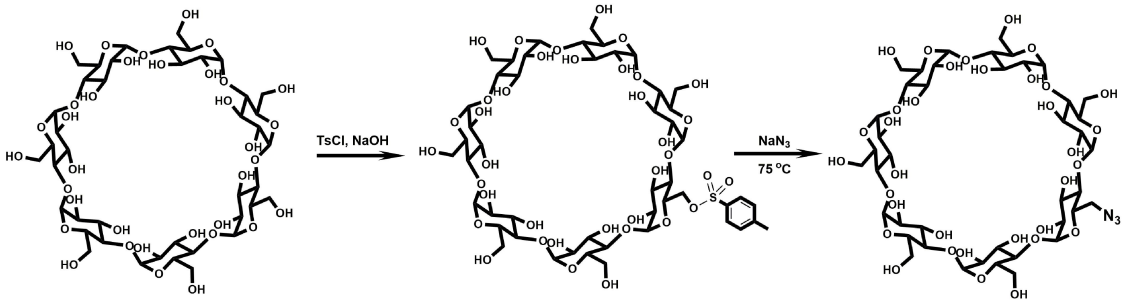
4. Synthesis and Characterization of CD-g-HBPO (Hyperbranched part).

CD-*g*-HBPO was synthesized by the following three steps (Fig. S1): Firstly, alkynyl-terminated HBPO (HBPO-yne) was synthesized through the cationic ring-opening polymerization of 3-ethyl-3-oxetanemethanol monomers by using propargyl alcohol as the initiator. Secondly, mono-6-deoxy-6-azido-*β*-Cyclodextrin (*β*-CD-N_3) was synthesized by using NaN_3 and mono-6-deoxy-6-(*p*-tolylsulfonyl)-*β*-cyclodextrin (*β*-CD-OTs, mono-esterification of 6-hydroxyl groups of *β*-CD with *p*-Toluenesulfonyl chloride). Thirdly, CD-*g*-HBPO was synthesized by click reaction between HBPO-yne and *β*-CD-N_3 using the copper (Ⅰ)-catalyzed azide-alkyne cycloaddition.

Step one: Synthesis of HBPO-yne



Step two: Synthesis of β-CD-N_3



Step three: Synthesis of CD-*g*-HBPO

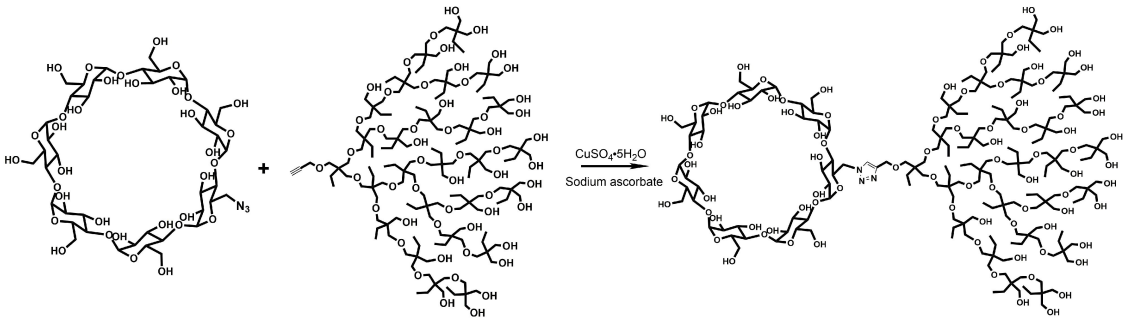


Fig. S1 Synthesis of CD-HPBO

A typical synthesis process was as follows:

Step one: Firstly, propargyl alcohol (280 mg, 5.0 mmol) dissolved in CH_2Cl_2 (50 mL) and $BF_3 \cdot OEt_2$ (6.28 mL, 50 mmol) were added into a dry, nitrogen-protected flask. After the mixture was heated to 35 °C, 3-ethyl-3-oxetanemethanol (11.6 g, 100 mmol) dissolved in dry CH_2Cl_2 (10 mL) was

dropwise added and the reaction was kept for 24h. Finally, a small amount of water was added to terminate the reaction. After dried by vacuum rotary evaporation, the crude product was dissolved in THF and then precipitated in water for 3 times. The precipitates was then dissolved and dialyzed (MWCO: 1000Da) in ethanol for 3 days to further remove unreacted porpargyl alcohol and other impurities. At last, solvents were removed and the final yellow solid of HBPO-yne was obtained (10.9 g, yields~90%).

^{1}H NMR (Fig. S2a) and ^{13}C NMR (Fig. S2b) are used to characterize the final product of HBPO-yne. All the protons or carbon atoms and their corresponding signals are clearly labeled in the following NMR spectra. Peaks f and g in ^{1}H NMR belong to protons of the terminal propargyl alcohol residue and peaks a~e belong to protons of HBPO part. Therefore, it is believed that HBPO part is initiated from propargyl alcohol and the degree of polymerization (DP) is supposed to be 35 calculated by Equation (1) using the area integration of peaks a~e and peaks f~g. Besides, the dendritic units, linear units and terminal units of HBPO can be clearly discerned in ^{13}C NMR spectrum. As a result, the degree of branching (DB) of HBPO part can be calculated by the integrated areas of signals around δ= 23.2 ppm according to Equation (2), which turns out to be 46.5%.

$$DP = \frac{A(a \sim e)/12}{A(f-g)/3} \quad \text{..... (1)}$$

$$DB = \frac{2D}{2D+L} \quad \text{..... (2)}$$

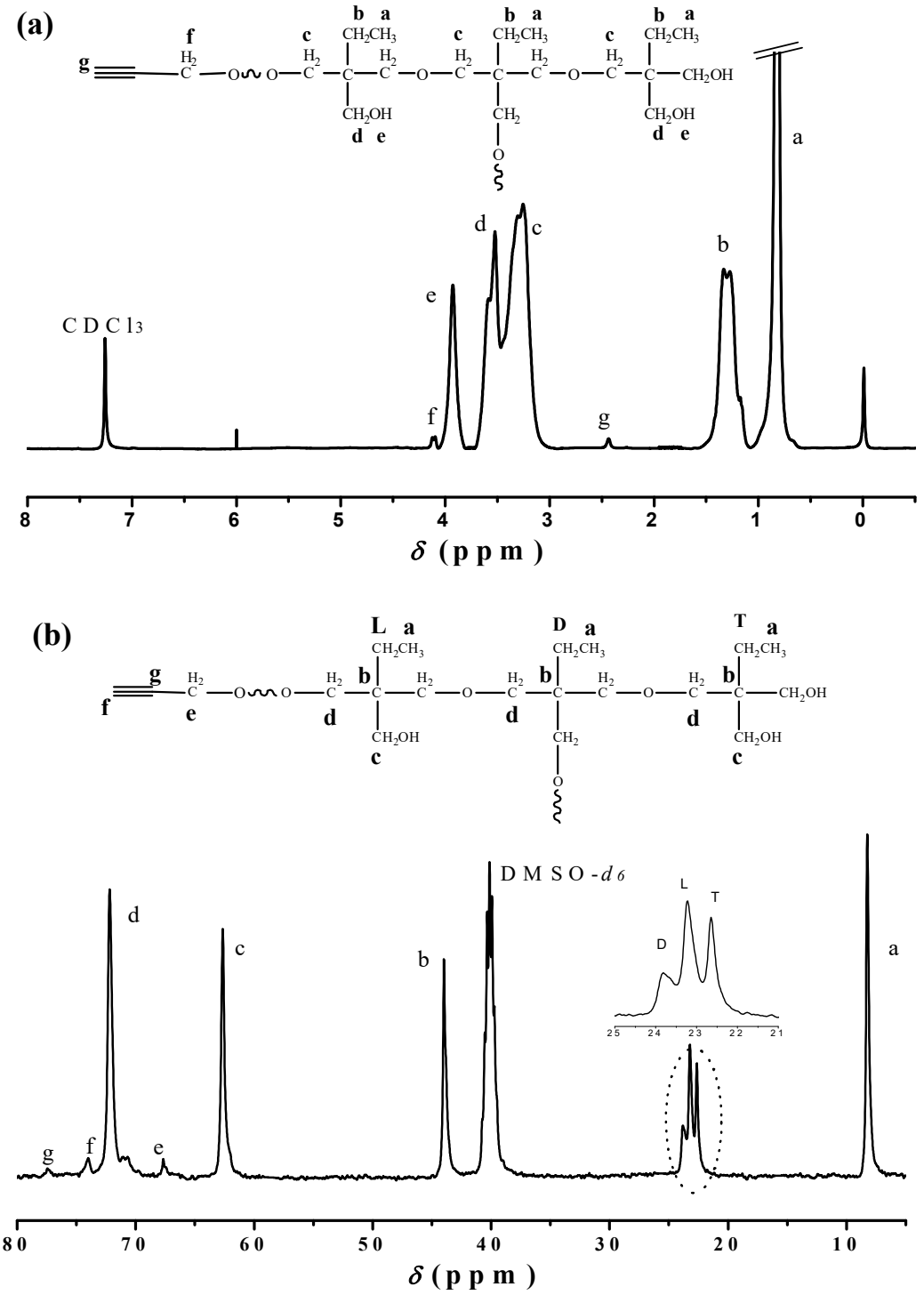


Fig. S2 (a) ^{1}H NMR spectrum of HBPO-yne ($CDCl_3$, 298K). (b) Quantitative ^{13}C NMR spectrum of HBPO-yne (DMSO-d_6, 298K), the inset shows the magnified three signals at δ= 23.2 ppm.

Step two: The synthesis of *β*-CD-N_3 was carried out as follows: *β*-CD (60g, 52.9 mmol) and 500 mL distilled water were put into a flask and then kept at 0 ºC. After that, NaOH (164 mmol, 6.57 g) dissolved in 20 mL water was added slowly with stirring, so as to dissolve *β*-CD. Then *p*-Toluenesulfonyl chloride (TsCl) (52.9 mmol, 10.08 g) dissolved in 30 mL acetonitrile was added slowly. The solution was heated to room temperature and reacted for 3h under stirring. Finally, pH was adjusted to 9 by HCl solution and the flask was kept at 4 ºC for 12h. Precipitates were filtered out before dried and the final white solid obtained was *β*-CD-OTs (15 g, yields: ~15%).

β-CD-OTs (2.57 g, 2 mmol) was dissolved in 25 mL dry DMF under stirring at 75 ºC. After that, NaN_3 (650 mg, 10 mmol) was added and the reaction was kept for 24h. Then the solution was dripped into a large amount of cold acetone and the precipitates were collected. After vacuum drying, *β*-CD-N_3 was obtained as a white solid powder (2.2 g, yields: >98%).

^{1}H NMR results of *β*-CD-N_3, *β*-CD-OTs and *β*-CD are shown in Fig. S3. All the protons and their corresponding peaks are labeled clearly in the figure. Comparing *β*-CD-OTs with *β*-CD, the appearance of peak a, b, c and d indicates the successful synthesis of *β*-CD-OTs. In addition, comparing *β*-CD-N_3 with *β*-CD-OTs, the disappearance of peak a, b, c and d indicates the removal of OTs groups and the appearance of peak e indicates the exits of *β*-CD-N_3. The integrated area ratio of proton peaks of *β*-CD, A (OH-2 & OH-3): A (H-1): A (OH-6): A (peak e) = 14: 7: 6: 2, reveals a pure product of *β*-CD-N_3 is obtained.

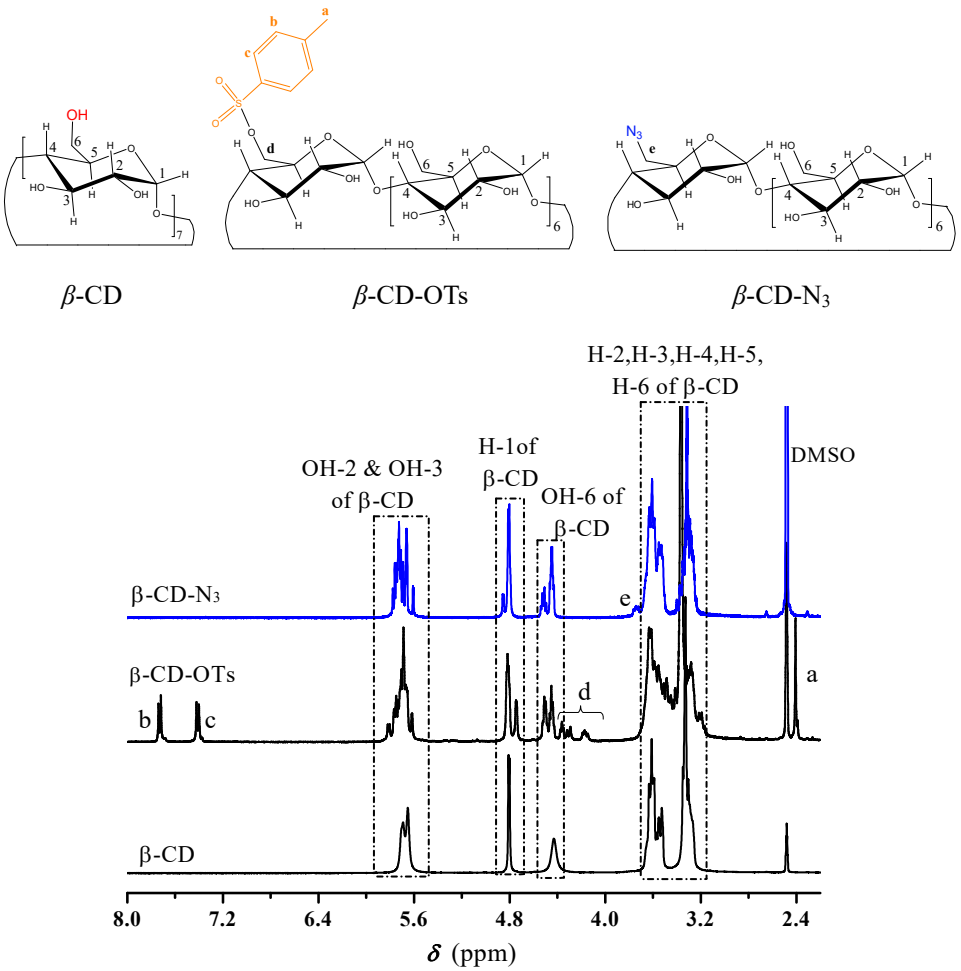
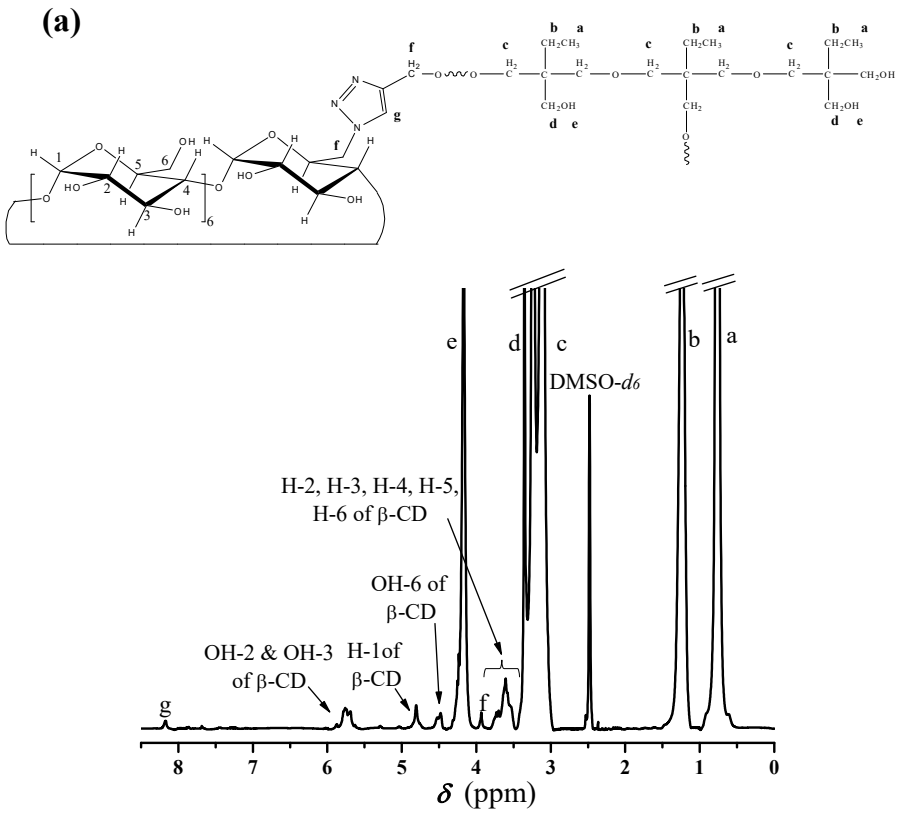


Fig. 3 ^{1}H NMR spectra of *β*-CD, *β*-CD-OTs and *β*-CD-N$_3$ (DMSO-*d*$_6$, 298K)

Step three: HBPO-yne (4.12 g, 1.0 mmol) and an excess amount of *β*-CD-N$_3$ (1.77 g, 1.5 mmol) were dissolved in 10 mL DMF and then injected into a microwave reactor. After $CuSO_4$ •$5H_2O$ (25 mg, 0.1 mmol) and sodium ascorbate (3.96 mg, 0.2 mmol) were added, the reaction was carried out under microwave irradiation at 100 °C for 30min. After cooling down, the solution was dialyzed against (MWCO: 3500Da) pure water for 3 days in order to remove the unreacted *β*-CD-N$_3$ and catalysts. At last the solvents were removed and the final product of CD-*g*-HBPO was obtained as a grey powder (4.56 g, yields: ~88%).

^{1}H NMR (Fig. S4a) and ^{13}C NMR (Fig. S4b) spectra are also used to characterize the product of CD-*g*-HBPO. All the protons and carbon atoms and their corresponding peaks are labeled clearly in the figure. Peaks f and g in ^{1}H NMR or peaks e and f in ^{13}C NMR spectrum, which correspond to protons or carbon atoms of the five-membered nitrogen-containing heterocycle, indicating the click reaction was carried out successfully and the objective compound CD-*g*-HBPO was obtained. The obtained CD-*g*-HBPO has a CD group and a hyperbranched HBPO part (DP= 35 according to NMR results mentioned above), thus a molecular weight to be about 5300 Da.



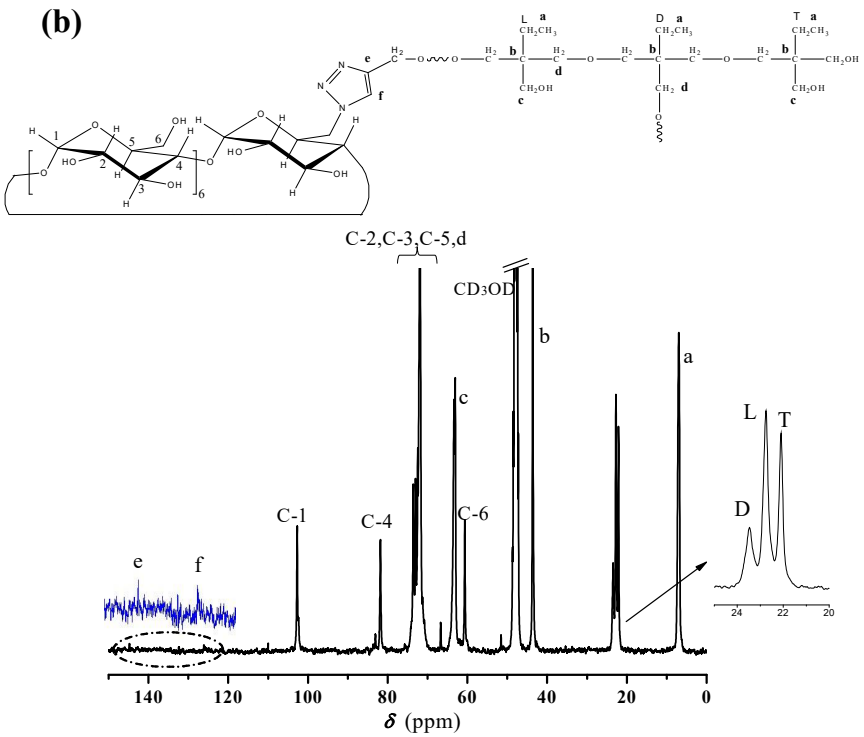


Fig. S4 (a) ^{1}H NMR spectrum of CD-*g*-HBPO (DMSO-d_6, 298K). (b) Quantitative ^{13}C NMR spectrum of CD-*g*-HBPO (CD_3OD, 298K), the inset shows the magnified three signals at δ= 22.7 ppm.

5. Preparation of self-assemblies of PEG-b-HBPO, AZO-PEG and CD-g-HBPO.

Self-assembly of PEG-*b*-HBPO: Equal molar ratio of AZO-PEG (6.6 mg, 0.005 mmol) and CD-*g*-HBPO (26.5mg, 0.005 mmol) were firstly dissolved in DMF (5 mL) for 3h under stirring. Subsequently, 1.75 mL water was added slowly to the solution by syringe pump within 5h under strong stirring. After being stirred for 3h, the solution was dialyzed against pure water for 3 days to remove DMF. The obtained solution was set to 32 mL and a polymer concentration of 1 mg/mL can be calculated. The final solution had a faint yellow turbidity without any precipitate, indicating the formation of self-assemblies. The PEG-*b*-HBPO aggregates sample with a polymer concentration of 0.2 mg/mL was prepared in the same procedure.

Self-assembly of AZO-PEG: AZO-PEG (100 mg, 0.076 mmol) was dissolved in DMF (5 mL) and

then water was added slowly by syringe pump with strong stirring until the solution processed a clear Tyndall effect. After being stirred for 3h, the solution was dialyzed against water to remove DMF for 3 days. The obtained solution was about 15 mL and the polymer concentration of AZO-PEG is calculated to be 7 mg/mL. The final solution had a yellow turbidity without any precipitates, indicating the formation of AZO-PEG self-assemblies.

Self-assembly of CD-*g*-HBPO: CD-*g*-HBPO (10.6 mg, 0.002 mmol) was dissolved in DMF (5 mL) and water was added slowly by syringe pump with strong stirring until the solution processed a clear Tyndall effect. After being stirred for 3h, the solution was dialyzed against water to remove DMF for 3 days. The obtained solution was about 20 mL and the polymer concentration of CD-*g*-HBPO is calculated to be 0.5 mg/mL. The final solution had a white turbidity without any precipitates, indicating the formation of CD-*g*-HBPO self-assemblies.

6. The capacity of CD-*g*-HBPOs to host guest groups of AZOs

Supramolecular block copolymer PEG-*b*-HBPO was constructed by the non-covalent coupling between AZO-PEG and CD-*g*-HBPO through the specific AZO/CD host-guest interactions. In order investigate the host capability of CD-*g*-HBPOs, 2D-NOESY spectrum was used by exploring if the water soluble sodium 4-phenylazophenol (AZO-Na) can complex with CD-*g*-HBPO. Fig. S5 shows strong signals (in green squares) of the intermolecular correlations among the internal H3 and H5 protons of *β*-CD and the protons of AZO groups, indicating the formation of AZO/CD host-guest inclusion complexes..

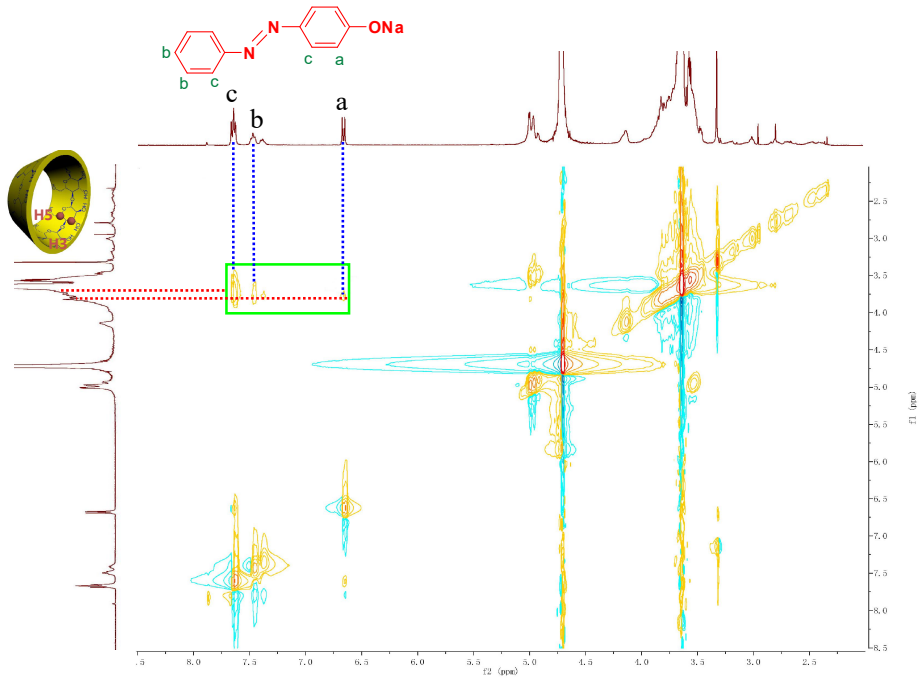


Fig. S5 2D-NOESY spectrum of CD-*g*-HBPO and AZO-Na (molar ratio: 1:1) in D_2O at 298K.

7. Molecular size of supramolecular block copolymer of PEG-*b*-HBPO

The hyperbranched CD-*g*-HBPOs are three-dimensional highly branched globular molecules, thus the size of CD-*g*-HBPOs is estimated by *Chem 3D*. The result is 3.1 nm. Given that PEG chains are random coils in water, therefore, in order to obtain an accurate size of the AZO-PEGs, we use full atomistic simulations to calculate the radius of gyration (R_g) of PEG domains.

Full atomistic simulations were performed in water as an explicit solvent for the PEG molecule at neutral using Gromacs 4.6.5 MD software package by employing OPLS_AA force field. The PEG structure with 24 repeat units was then loaded and immersed in a cubic water box using the TIP4P water model by choosing a 9 Å solvation shell around the PEG structure in all directions.

The solvated structures were then subjected to 5000 steps of steepest descent minimization of the potential energy. Subsequently, 8 ns long constant pressure-constant temperature (NPT) equilibrium

dynamics was carried out with Berendsen barostat and V-rescale thermostat (0.5 ps for pressure relaxation time and 0.1 ps time constant for heat bath coupling). Last 2 ns equilibrated trajectory was further used to calculate the radius of gyration. All calculations were performed at a pressure P= 1.0 atm and a temperature T= 298.0 K.

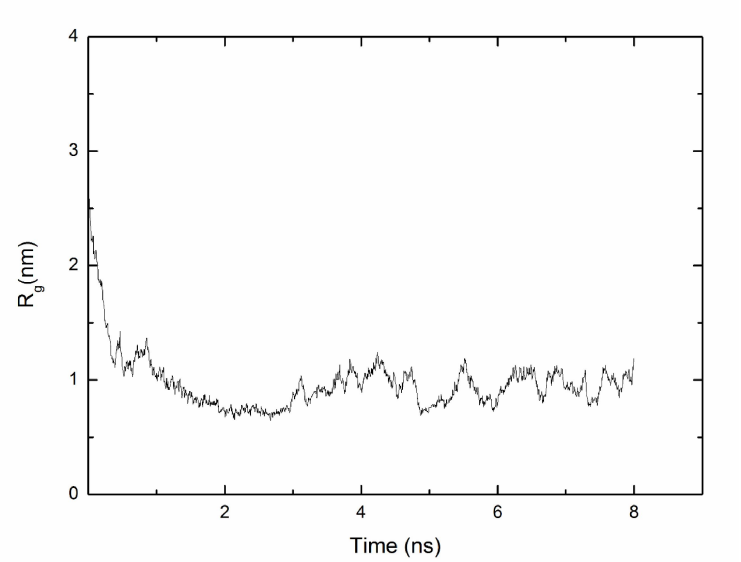


Fig. S6 Variation of the radius of gyration with the simulation time (ns).

The final R_g is 0.97 ± 0.089 nm (Fig. S6). Therefore, the D_g of PEG domains is about 2 nm. As the molecular size of AZO groups is about 1 nm, the total size of AZO-PEGs is supposed to be 3 nm (Fig. S7).

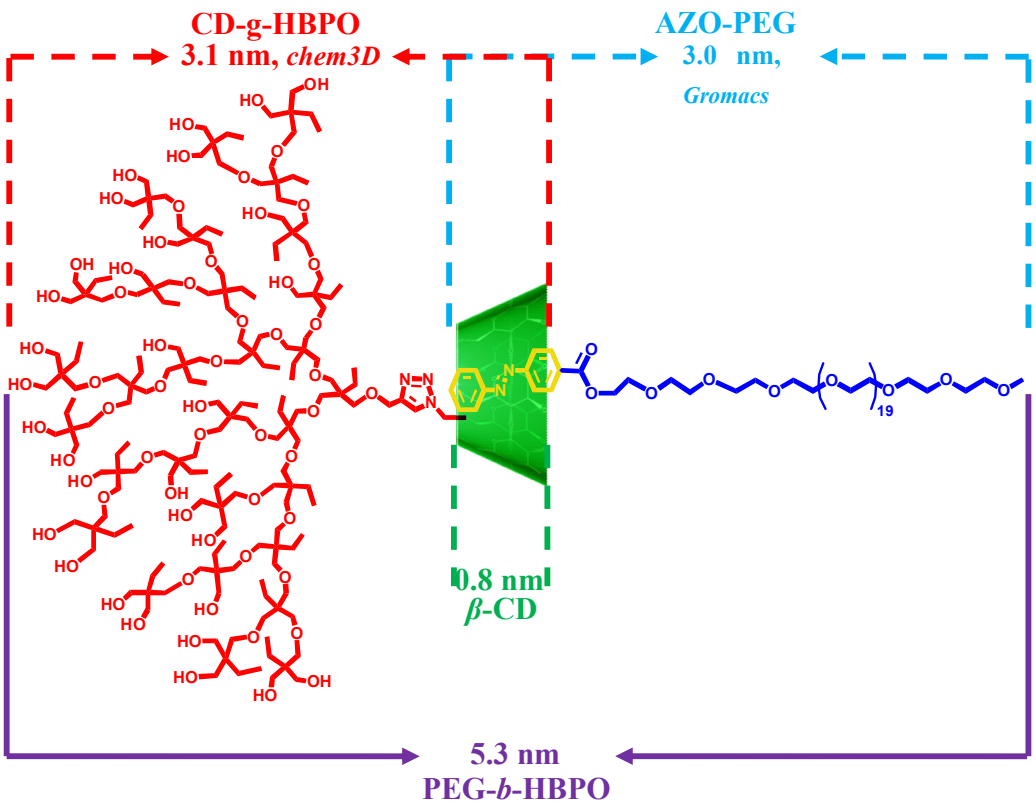


Fig. S7 Estimating the size of a PEG-*b*-HPBO molecule by Chem 3D and GROMACS software.

8. Characterizations of the PEG-*b*-HBPO vesicles

8.1 Size characterizations

The characterizations of self-assemblies prepared from PEG-*b*-HBPO are investigated by DLS, SEM, TEM and AFM. As shown in Fig. S8, the DLS results show that the aggregates have a nearly monodisperse size distribution with a PDI to be 0.013, and the D_h is about 600 nm.

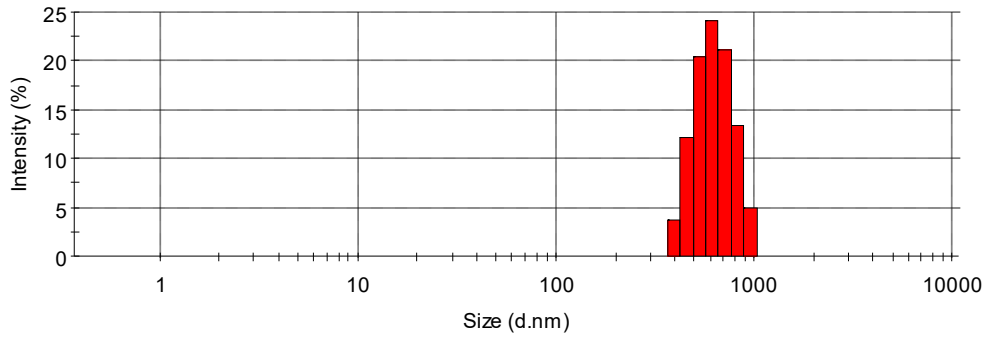


Fig. S8 DLS result of distribution of PEG-*b*-HBPO aqueous solution by intensity. The polymer concentration is 1mg/mL

8.2 Morphological characterizations

Figure S9 shows the TEM and AFM images of supramolecular PEG-*b*-HBPO self-assemblies. A sample stained with uranyl acetate for a longer time shows broken particles with some holes (pointed by black arrows in Fig. S9a). This further provides solid evidence to the hollow vesicular structure, and it is attributed to the osmotic pressure exerted by the massive salts onto vesicle membranes. In addition, budding or fusion, both of which are typical deformation behaviors of vesicles, were also observed (indicated by red arrows in Fig. S9b) in the vesicle sample without staining. All these evidences prove that the linear-hyperbranched supramolecular polymers of PEG-*b*-HBPOs self-assemble into vesicles in water. The vesicle wall thickness is measured to be about 10 nm by AFM (The height of the collapsed vesicles is around 19.9 nm, which is equal to the thickness of two stacked vesicle membranes as shown in the cartoon in Figure S9d, and thus the wall thickness is half of 19.9 nm, *i.e.*, about 10 nm), which agrees well with the measurement from TEM images (the distance between the two white arrows in Fig. S9c is measured to be about 10 nm). The wall's thickness is just 2 times of PEG-*b*-HBPO molecular size (Fig. S7), indicating a vesicle with a bilayer structure.

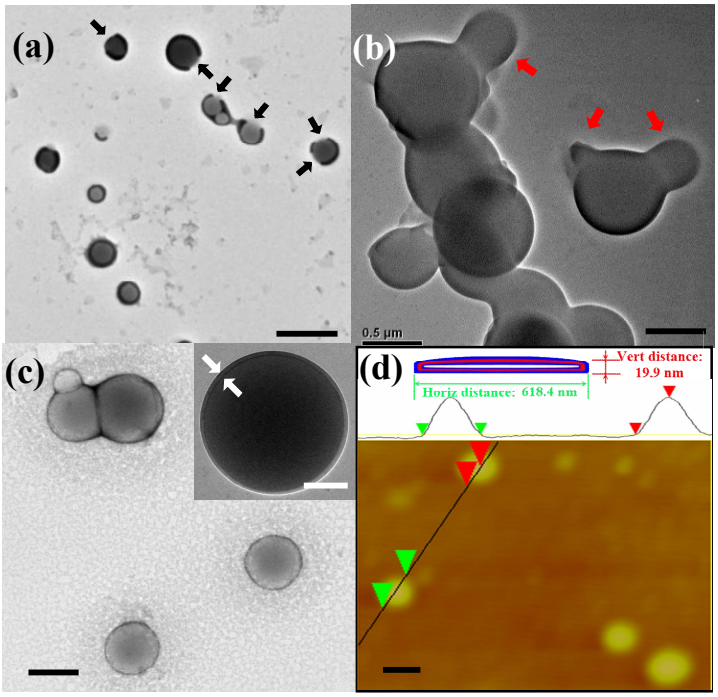


Fig. S9 Morphological characterizations of PEG-*b*-HBPO self-assemblies. (a) TEM image of aggregates deeply stained with uranyl acetate. Black arrows show the broken holes of the particles. Scale bar = 1 μm. (b) The TEM images of aggregates without staining. Budding and/or fusion behaviors of the particles can be observed (red arrows). Scale bar = 0.5 μm. (c) TEM images of aggregates stained with uranyl acetate. Inset in (c) shows a freeze-dried particle without staining, Scale bar = 0.2 μm. (d) AFM images of aggregates, Scale bar = 0.5 μm.

8.3 Core-shell structure in the vesicles

^{1}H NMR was used to monitor the molecular packing model in the vesicles by sequentially adding D_2O into the DMSO-*d6* solution of AZO-PEGs and CD-*g*-HBPOs (Fig. S10). As DMSO is a good solvent for both AZO-PEG and CD-*g*-HBPO, the proton signals of PEGs and HBPOs are both strong at the beginning. After D_2O was added into the polymer solution, the host-guest complexation of AZO-PEGs and CD-*g*-HBPOs into the supramolecular polymers of PEG-*b*-HBPOs as well as the

self-assembly into vesicles happened. In the meanwhile, the proton signals for HBPOs were gradually decreased and almost disappeared when 50% (water/DMSO, volume ratio) D_2O was added, while those for PEGs were still strong. Generally, the intensity of the proton signals in ^1H NMR measurements is highly dependent on the mobility of the groups in the solvent. Therefore, the results indicate during the vesicular self-assembly process, HBPOs aggregate together into a hydrophobic solid-like phase with less mobility, while the PEG chains are still well-solvated and have a good mobility. In other words, the vesicles have a core shell structure consisting of hydrophobic HBPO cores and hydrophilic PEG shells. Thus, based on the abovementioned morphological characterizations and the ^1H NMR data here, PEG-*b*-HBPO vesicles have a structure as shown in Scheme 1.

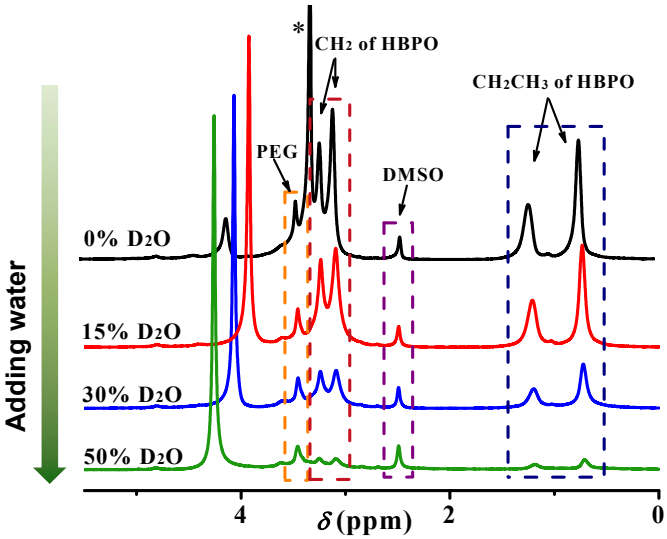


Fig. S10 ^1H NMR spectra (298 K, 400 MHz) of the mixed 1:1 (molar ratio) AZO-PEG and CD-g-HBPO DMSO-d_6 solutions by adding different volume of D_2O (D_2O: DMSO-d_6, v/v). The spectra are normalized by picking residual DMSO as internal standard to exclude the dilution effect. (Peak * in the spectrum with 0% D_2O is a water peak.)

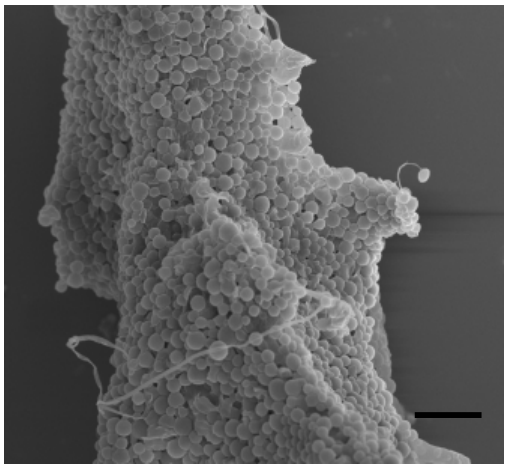


Fig. S11 SEM image of colloidal crystal-like vesicle aggregates prepared from PEG-*b*-HBPO aqueous solution with a higher polymer concentration of 1mg/mL. Scale bar = 2 μm.

9. Characterizations of the self-assemblies after UV/vis irradiation

9.1 Quantitative evaluation of *trans-to-cis* transition of AZO groups when exposed to UV light

To better understand the quantitative information of *trans*- to *cis*- transition of AZO groups when exposed to UV light, formation rate for *cis*-AZO groups and residual rate for *trans*-AZO groups (R) were calculated by comparing the absorbance of the AZO peak at any time (A_t) to that at the beginning ($A_{t=0}$) and at t=24 h ($A_{t=24}$). For *cis*-AZO groups, the absorbance peak is at λ=424 nm. The formation rate of *cis*-AZO groups (R_{cis}) is calculated according to Equation (3):

$$R_{cis} = \frac{A_t - A_{t=0}}{A_{t=24} - A_{t=0}} \times 100\% \quad \text{..... (3)}$$

To clearly show the decrease of absorbance peak of *trans*-AZO groups (λ=325 nm) under UV light, the residual rate of *trans*-AZO groups (R_{trans}) is used and the R_{trans} at the beginning of UV irradiation is set to be 100%. R_{trans} value at any time is calculated according to Equation (4):

$$R_{trans} = (1 - \frac{A_t - A_{t=0}}{A_{t=24} - A_{t=0}}) \times 100\% \quad \text{..... (4)}$$

Equation (3) and Equation (4) can be unified by Equation (5) (A_{max} and A_{min} represent the maximum and minimum peak value at λ=424 nm or λ=325 nm, respectively):

$$R = \frac{A_t - A_{\min}}{A_{\max} - A_{\min}} \times 100\% \quad \text{..... (5)}$$

The results as shown in Figure S12 display that the decrease of *trans*-AZO's absorbance and increase of *cis*-AZO's absorbance are both monotonic with time prolonging and then undergo an inflection point at the same time, which proves that AZO groups gradually isomerize from *trans*- to *cis*- form under UV irradiation within 24 hrs.

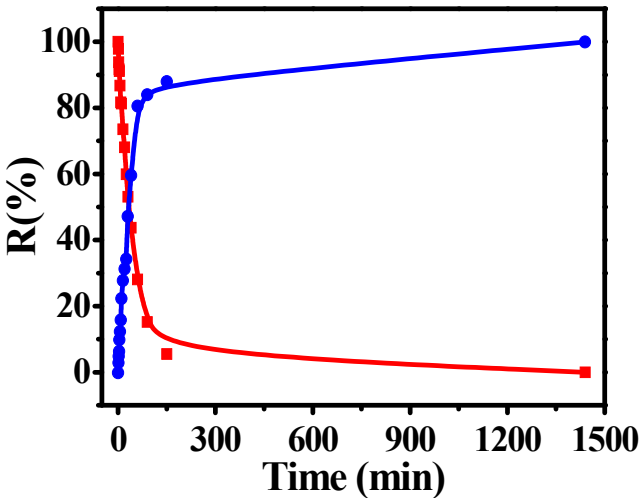


Fig. S12 Normalized formation rate for *cis*-AZO groups (blue) and residual rate for *trans*-AZO groups (red) as a function of UV irradiation time.

9.2 Morphology observations of self-assemblies during the disassembly process

The disassembly experiments were carried out by placing the vesicle solution under UV light (ZF-I, λ=365 nm, 8W) with stirring. The UV-vis spectra of the vesicle solution under UV irradiation for different time up to 24 hrs were recorded. The DLS results of the vesicle solution under UV irradiation for 0h, 2h and 12h were shown in Fig. 1e. The UV-vis irradiation cycles were performed by exposing

the vesicle solution to UV light for 24 hrs and then to visible light for another 24 hrs with stirring. UV-vis spectra of the solution were obtained after each irradiation and the peak values at λ=325 nm were shown in Fig. 1d. It is obvious that the *trans*- to *cis*- transformation of AZO groups can repeat many times.

TEM and SEM are used to capture the structure of aggregates in PEG-*b*-HBPO solution after UV irradiation for 24 hours and further visible light irradiation for another 24 hours (Fig. S13). After a day's UV irradiation, the vesicles of PEG-*b*-HBPO disappeared, and a mixture of long nanofibers and nanosheets appeared (Fig. S13a). After further visible light irradiation, however, spherical particles are observed instead of nanofibers or nanosheets according to the SEM observations (Fig. S13b). The TEM image shows these particles are vesicles (Fig. S13c), suggesting vesicles are regained reversibly after exposed to visible light. The vesicles disassembled into nanofibers and nanosheets under UV light and re-formed under visible light, indicating a totally light-triggered reversible morphological transition behavior.

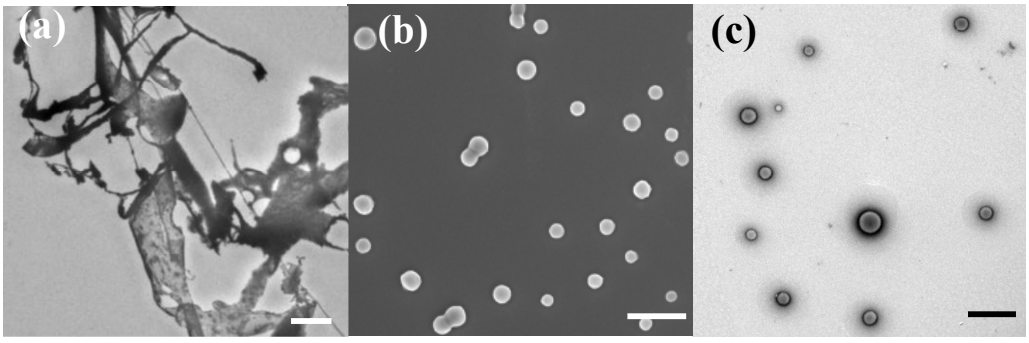


Fig. S13 TEM (a) images of aggregates in PEG-*b*-HBPO aqueous solution after UV irradiation for 24 hours. SEM (b) and TEM (c) images of aggregates prepared from the above solution after further 24 hours' visible light irradiation. TEM samples are both stained with uranyl acetate. Scale bars = 2 μm.

10. Characterizations of the CD-*g*-HBPO Nanosheets

10.1 Morphology observations

Figure S14 shows the SEM, TEM and AFM images of self-assemblies of CD-*g*-HBPO. CD-*g*-HBPO self-assembles into nanosheets. Some nanosheets are curved or wrinkled (inset in Fig. S14b), indicating they are flexible. The size of the nanosheets is around 400 nm, which is a little greater than the DLS data (Fig. 1f, D_h~300 nm) and is probably due to the irregular and nonspherical structure. The nanosheets are homogeneous in thickness, which is about 6.1 nm by measuring the vert distance between the nanosheet plane and mica surface (Fig. S.14c)

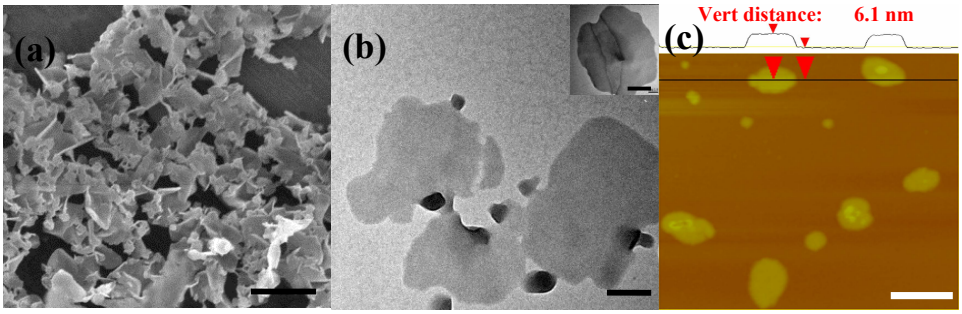


Fig. S14 The SEM (a), TEM (b) and AFM (c) images of the CD-g-HPBO nanosheets. Scale bar = 2, 0.2 and 0.5 μm, respectively.

10.2 Core-shell structure in the nanosheets

The arrangements of molecules in nanosheets are further proved with ^{1}H NMR spectra. As shown in Figure S15, proton signals of HBPO diminished significantly with the volume percentage ratio of D_2O/DMSO-d_6 increases from 0% to 60%, while signals of β-CD remained almost unchanged. This indicates the formation of a continuous hydrophobic HBPO phase, which is surrounded by the solvent-soluble β-CDs.

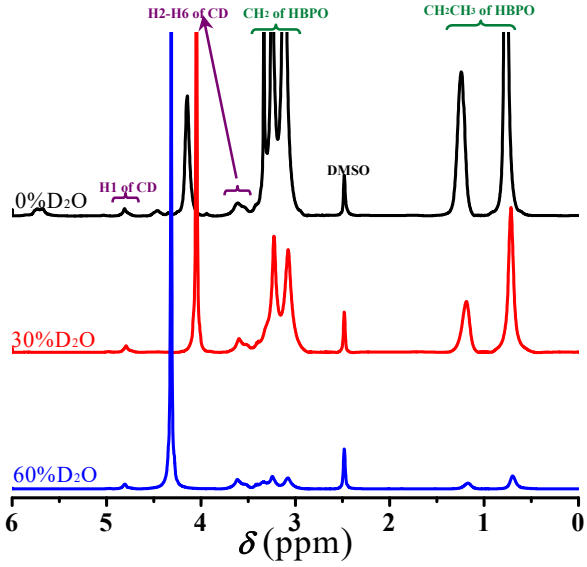


Fig. S15 ^{1}H NMR spectra (298 K, 400 MHz) of CD-*g*-HBPOs with different D_2O/DMSO-*d6* volume percentage ratios (v/v).

11. Characterization of the AZO-PEG Nanofibers

11.1 Morphology observations

Figure S16 shows the TEM and AFM images of AZO-PEG self-assemblies. Except for the majority of uniform thin nanofibers, thick nanofibers (Fig. S16a, indicated by white arrows) and a ball of nanofibers (Fig. S16b) were also observed, indicating the nanofibers have a tendency to aggregate. The diameter of the uniform thin fibers is measured to be about 10 nm.

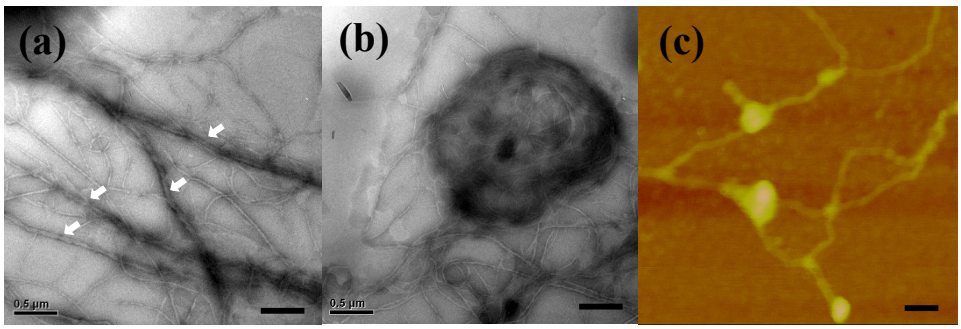


Fig. S16 The TEM (a, b) and AFM (c) images of AZO-PEG aggregates. (a) and (b) are prepared from AZO-PEG aqueous solution and stained with uranyl acetate. Scale bars = 0.5 µm, 0.5 µm and 0.2 µm, respectively.

11.2 Core-shell structure in the nanofibers

The arrangements of molecules in nanofibers were further investigated with ^{1}H NMR spectra. As shown in Figure S17, compared with the external standard, proton signals for PEG domains decreases (44%), half of those for AZO groups (85%), with the volume percentage ratio of D_2O/DMSO-d_6 increasing from 0% to 60%, indicating the AZO groups arranged into the core of the nanofibers while the PEG domains stretched towards the outside on the shell (the decrease of PEG signals might be mainly due to the dilution effect). In addition, the gradually broadened peaks for AZO groups also suggests they form a solid-like phase in the core where the mobility of AZO groups is greatly limited.

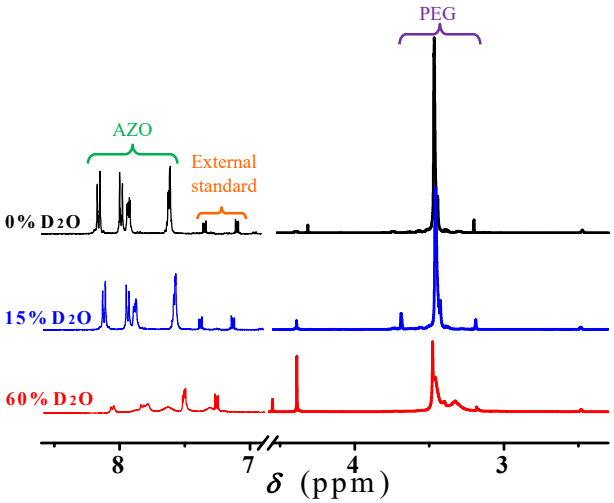


Fig. S17 ^{1}H NMR spectra (298 K, 400 MHz) of AZO-PEG with different D2O/DMSO-d_6 volume percentage ratios (v/v). External standard is potassium hydrogen phthalate dissolved in D_2O.

12. Characterizations of aggregates obtained by mixing CD-*g*-HBPO nanosheets and AZO-PEG nanofibers:

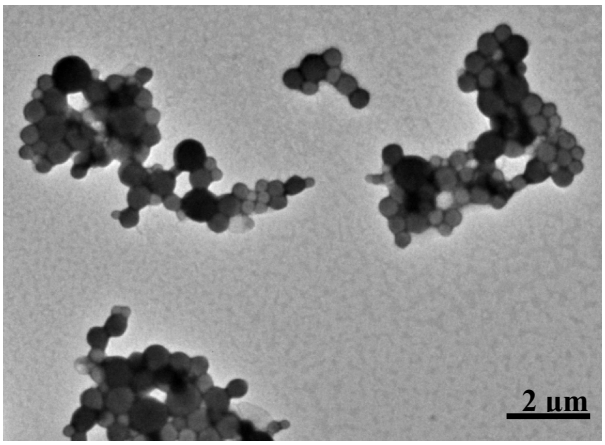


Fig. S18 The TEM images of aggregates after mixing CD-*g*-HBPO nanosheets and AZO-PEG nanofibers together for 5 hrs, the sample is stained with uranyl acetate. The darker wall and lighter inner pool and background suggest the spherical particles are vesicles. Scale bar = 2 μm.

References

(1) D. Y. Yan, Y. F. Zhou and J. Hou, *Science,* 2004, **303**, 65.

(2) Y. Liu, C. Yu, H. Jin, B. Jiang, X. Zhu, Y. Zhou, Z. Lu and D. Y. Yan, *J. Am. Chem. Soc.*, 2013, **135**, 4765.