Supplementary Information

Chiral Self-Assembly and Reversible Light Modulation of A Polyoxometalate Complex via Host-Guest Recognition

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Materials:

β-Cyclodextrin is the product of Aladdin Chemistry Co., Ltd. and recrystallized three times before use. $[N(C_4H_9)_4]_3\{MnMo_6O_{18}[(OCH_2)_3CNHCOCH_2OC_6H_4NNC_6H_5]_2\}$ and β-CD-OTs[S1] were prepared according to the literature. The remaining chemicals and solvents were purchased from Beijing Chemical Reagent Industry. Acetone and acetonitrile were distilled over P_2O_5 prior to use. DMSO was dried with CaH_2 for several days and distilled prior to use.

Measurements:

FT-IR spectra were carried out on a Bruker Vertex 80V FT-IR spectrometer equipped with a DTGS detector (32 scans) with a resolution of 4 cm^{-1} on a KBr pellet. The UV-Vis spectra were taken by using a spectrophotometer (Varian CARY 50 Probe). ^1H NMR spectra were recorded on a Bruker AVANCE 500 and 600 MHz spectrometer. Chemical shifts were referenced to the solvent values (δ = 2.50 ppm for DMSO-d_6 and δ = 4.79 ppm for D_2O). Matrix-assisted laser desorption / ionization time-off light mass spectrum (MALDI-TOF) was recorded on an autoflex MALDI-TOF/TOF (Bruker, Germany) mass spectrometer, equipped with a nitrogen laser (337 nm, 3 ns pulse). The mass spectrometer was operated in the positive ion reflector mode with a detector potential of –4.75 kV. X-ray diffraction (XRD) data were recorded on a Rigaku X-ray diffractometer using Cu $K\alpha_1$ radiation at a wavelength of 1.542 Å. Organic elemental analysis was carried out on a Flash EA1112 from Thermo-Quest Italia S.P.A. Circular dichroism (CD) spectra were carried out on a Bio-Logic MOS-450 spectropolarimeter in water with a step size of 1 nm and speed of 2 nm s^{-1} at 25 °C. Scanning electron microscope (SEM) images were acquired on a JEOL FESEM 6700F field emission scanning electron microscope, and high resolution transmission electron microscopy

(HRTEM) was conducted on JEOL JEM 2010 under an accelerating voltage of 200 kV without staining.

Synthesis of samples:

Synthesis of Mono-6-deoxy-6-pyridine-β-Cyclodextrin (**β-CD-Py**). β-CD-Py was prepared according to the modified procedure reported by Ikeda et al. Briefly, β-CD-OTs (1 g) was dissolved and heated in dry pyridine (100 mL) at 90°C for 48 h to obtain β-CD-Py. The reaction mixture was cooled to room temperature and added dropwise to anhydrous ether solution (500 mL), the precipitate was filtered off and washed with a large number of anhydrous ether for three times (0.7 g, 66%).^{1}H NMR (500 MHz, DMSO-d_6, 25 °C, δ): 9.02 (d, 2H, Ar H), 8.64 (s, 1H, Ar H), 8.14 (d, 2H, Ar H), 7.46 (d, 2H, Ar H), 7.12 (d, 2H, Ar H), 6.1–5.5 (m, 14H, OH), 4.90–4.72 (m, 7H, CH), 2.29 (s, 3H, CH_3). MALDI-TOF MS: *m/z*: calcd. for $C_{47}H_{74}O_{34}N$: 1197.07; found: 1196.5 [M^+].

Preparation of $Na_3\{MnMo_6O_{18}[(OCH_2)_3CNHCOCH_2OC_6H_4NNC_6H_5]_2\}$ **(Azo-POM)**. $[N(C_4H_9)_4]_3\{MnMo_6O_{18}[(OCH_2)_3CNHCOCH_2OC_6H_4NNC_6H_5]_2\}$ (0.1 g, 0.04 mmol) in MeCN (5 mL) was added dropwise into the vigorously stirred MeCN of $NaClO_4$ (0.10 g, 0.08 mmol, 5 mL) and then the mixed solution was keeping stirring for 30 min to obtain yellow precipitation. The precipitation was washed with MeCN and anhydrous methanol for two times respectively (0.036 g, 50%). ^{1}H NMR (500 MHz; DMSO-d_6, 25 °C, δ): 64.10 (br, 12H, CH_2), 7.91 (d, 4H, Ar H), 7.85 (d, 4H, Ar H), 7.57 (t, 6H, Ar H), 7.51 (t, 2H, Ar H), 7.15 (d, 4H, Ar H), 4.94 (br, 4H, CH_2). IR (KBr, cm^{-1}): v = 2943, 2918, 2870, 1684, 1636, 1601, 1541, 1501, 1441, 1319, 1244, 1153, 1119, 1067, 1028, 945, 924, 837, 770, 665, 569 cm^{-1}. Elemental analysis calcd. (%) for $C_{36}H_{36}N_6O_{28}Na_3MnMo_6$ (1700.24 g mol^{-1}): C 25.43, H 2.13, N 4.94; found C 25.01, H 2.23. N 4.73.

Preparation of pyridine-modified β-Cyclodextrin wrapping azobenzene (Azo) grafted polyoxometalate complexes (**CD-Azo-POM**). Azo-POM (10 mg, 0.006 mmol) in water (5 mL) was added dropwise into the stirred water solution of β-CD-Py (26.4 mg, 0.020 mmol, 1 mL) and then the mixed solution was keeping stirring for 3 h to obtain yellow precipitation. The precipitation was separated by centrifugation (10000 rpm, 15 min), then washed with

anhydrous ethanol for three times. (18.7 mg, 79.5%). ^{1}H NMR (500 MHz; DMSO-d_6, 25 °C, δ): 64.48 (br, 12H, CH_2), 9.02 (d, 4H, Ar H), 8.64 (t, 2H, Ar H), 8.14 (t, 4H, Ar H), 7.91 (d, 4H, Ar H), 7.85 (d, 4H, Ar H), 7.57 (t, 6H, Ar H), 7.51 (t, 2H, Ar H), 7.15 (d, 4H, Ar H), 6.1–5.5 (m, 28H, OH), 4.94 (br, 4H, CH_2), 4.90–4.72 (m, 14H). IR (KBr, cm^{-1}): v = 2924, 1686, 1634, 1601, 1543, 1499, 1406, 1368, 1331, 1302, 1229, 1155, 1105, 1078, 1055, 1032, 945, 924, 907, 847, 758, 673, 608, 579 cm^{-1}. Elemental analysis calcd. (%) for $(C_{47}H_{74}O_{34}N)_2NaC_{36}H_{36}O_{28}N_6MnMo_6 \cdot 10H_2O$ (4228.57 g mol^{-1}): C 36.93, H 4.86, N 2.65; found C 36.93, H 5.17, N 2.36.

Photo-irradiation:

For UV irradiation, the CD-Azo-POM solution (1.0 mL) sealed in a quartz cell, WHF 203 UV lamp (365 nm) was used. For visible light irradiation, 200 W incandescent light bulb (> 440 nm) was applied. The UV/Visible light irradiation time is limited in 10 min for 0.024 μM and 2 h for 0.24 μM, and the distance between the light source and sample is kept at 5 cm.

Preparation of supramolecular assemblies:

In a typical example, CD-Azo-POM were dispersed in water (0.24 μM) after ultrasound 30 min, then the dispersion solution irradiated with UV light (365 nm) for 2 h, then solution becames clear and transparent as the initial *cis*-state for self-assembly. After standing in darkness for 7 days, the assemblies were formed as precipitation from solution. And the assemblies were separated and lyophilized for further measurements.

Preparation of assemblies for NMR studies:

All samples for NMR studies were prepared using D_2O as solvent. Due to the solubility limit of CD-Azo-POM in D_2O, NMR characterizations were carried out at the concentration of 0.22 μM. For 1D selective NOESY NMR experiment in D_2O/DMSO-d_6 (4:1 in *v/v*), the assemblies in darkness for 7 days was separated from D_2O and dissolved in D_2O/DMSO-d_6 (4:1 in *v/v*).

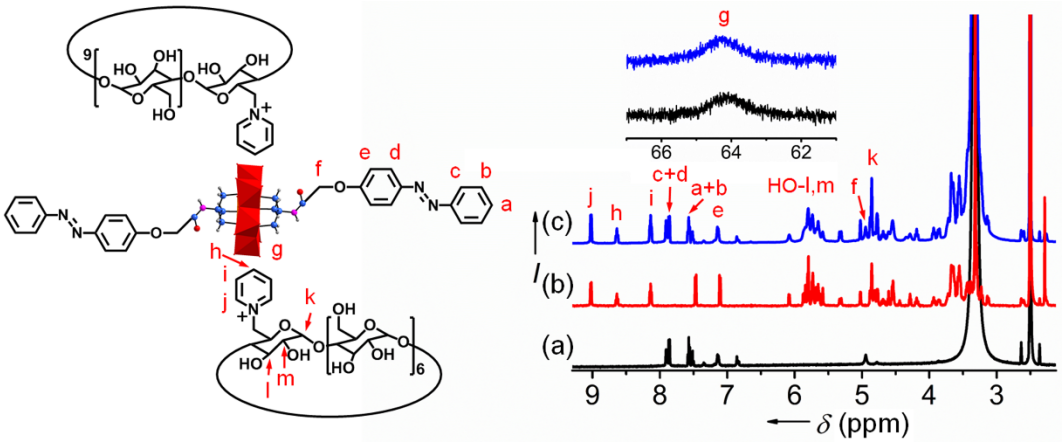

Fig. S1 ^{1}H NMR spectra of (a) Azo-POM; (b) β-CD-Py and (c) CD-Azo-POM (DMSO-d_6, 25 °C).

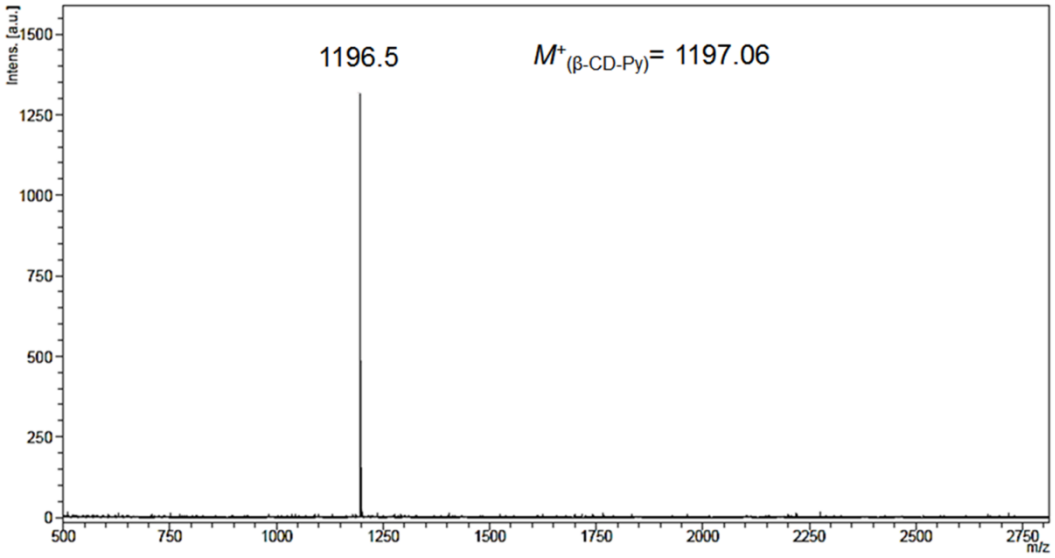

Fig. S2 MALDI-TOF mass spectrum of β-CD-Py.

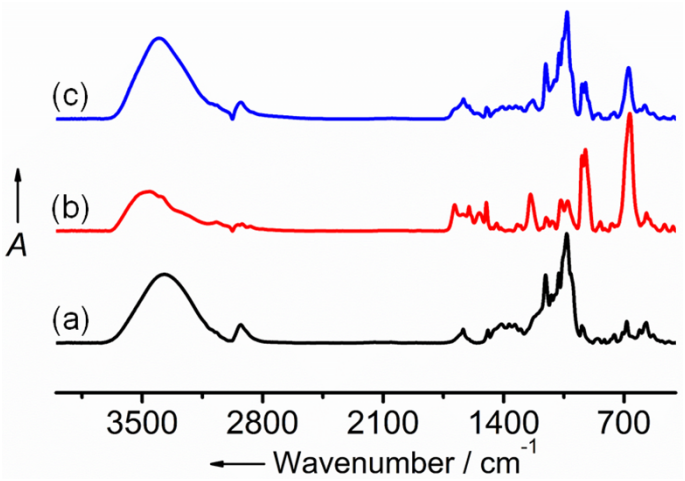

Fig. S3 FT-IR spectra of (a) β-CD-Py; (b) Azo-POM and (c) CD-Azo-POM.

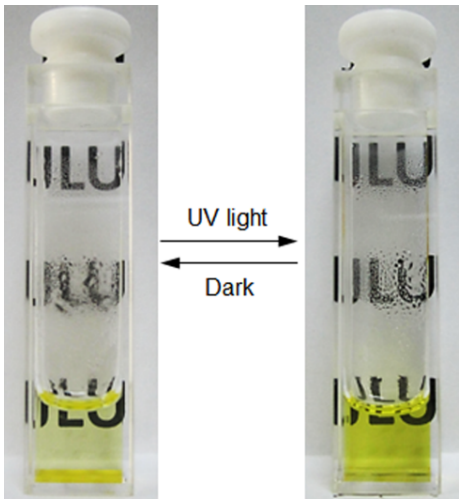

Fig. S4 Digital photographs of CD-Azo-POM alternating UV light irradiation for 2 h and aging in darkness for 7 days. (0.24 μM, 25 °C)

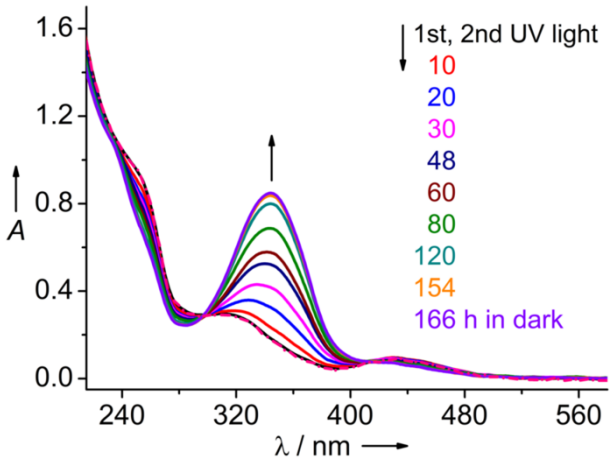

Fig. S5 UV-Vis spectra of CD-Azo-POM in water (0.024 μM) following the cycle of UV light irradiation and standing in darkness: black line: 1st UV light irradiation; pink dashed line: 2nd UV light irradiation.

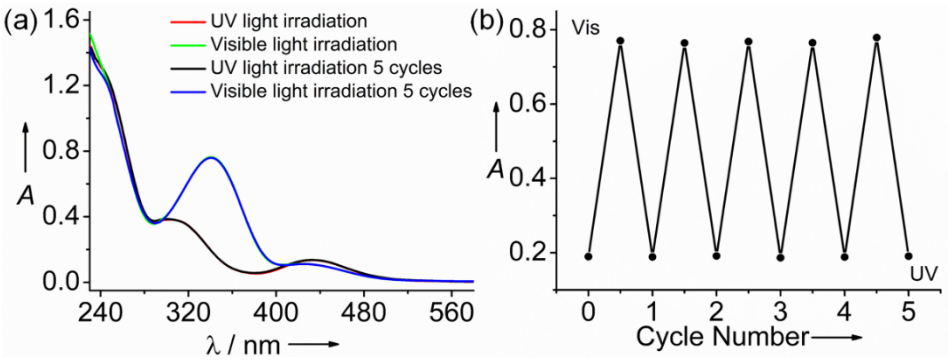

Fig. S6 (a) UV-Vis spectra of CD-Azo-POM and (b) plots of absorbance at 341 nm encountering five cycles of alternating UV (365-nm) and visible (450-nm) light irradiation. (0.024 μM, 25 °C)

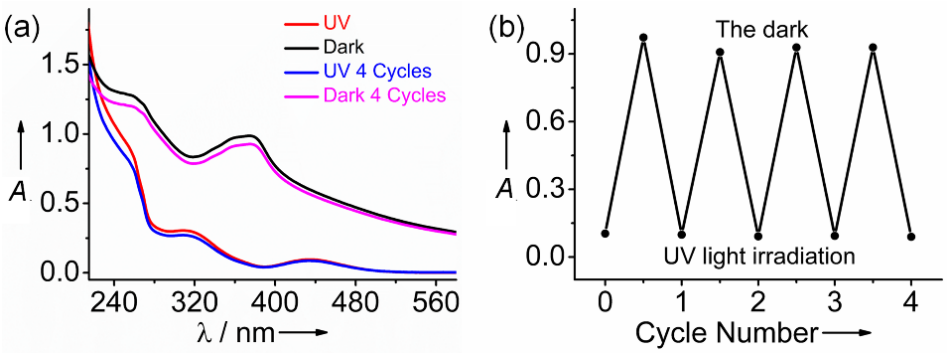

Fig. S7 (a) UV-Vis spectra of CD-Azo-POM and (b) plots of absorbance at 361 nm encountering four cycles of alternating UV light (365-nm) irradiation and standing in darkness. (0.24 μM, 25 °C)

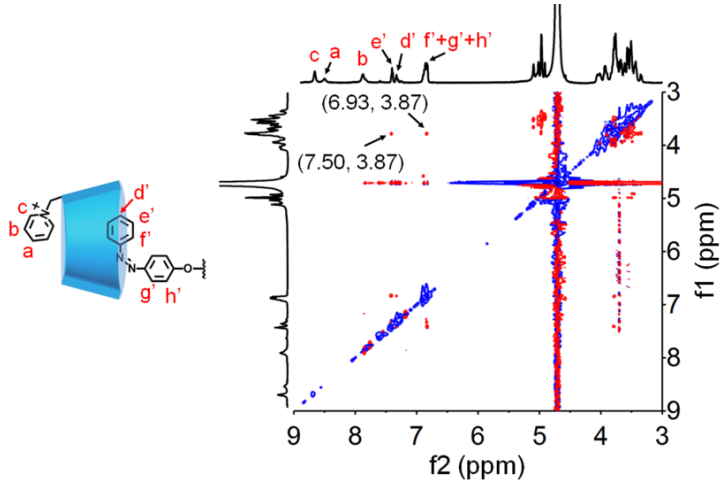

Fig. S8 2D ROESY NMR spectrum of *cis*-form CD-Azo-POM under UV light (365 nm) irradiation (0.22 μM, D_2O, 25 °C). Two cross-correlation peaks appear in ROESY NMR spectrum, implying the formation of the inclusion complex between β-CD-Py and *cis*- Azo-POM.

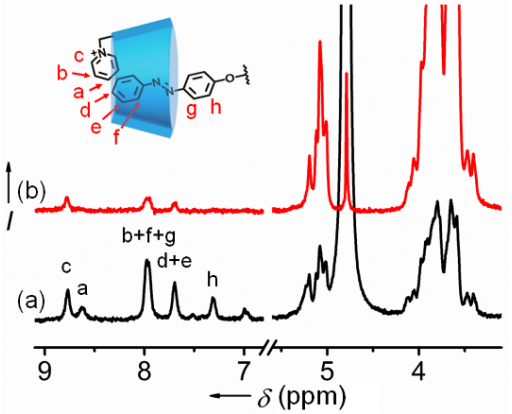

Fig. S9 (a) ^{1}H NMR spectrum of *trans*-form CD-Azo-POM aging in darkness for 7 days (0.22 μM, 25 °C) in D_2O/DMSO-d_6 (4:1 in v/v) and (b) the corresponding 1D selective NOESY NMR spectrum. In this 1D selective NOESY NMR experiment, the overlapped peaks (δ = 3.80 ppm) belonging to the cyclodextrin ring of *trans*-form CD-Azo-POM were irradiated. The NOE signals appear in the peaks of pyridine and *trans*- Azo groups (δ = 8.78, 7.95 and 7.68 ppm), indicating the formation of inclusion interactions of β-CD-Py with pyridine and *trans*- Azo groups.[S2]

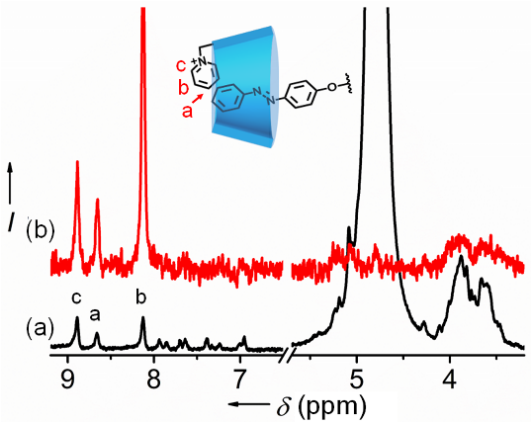

Fig. S10 (a) ^{1}H NMR spectrum of *trans*-form CD-Azo-POM in darkness for 7 days (0.22 μM, D_2O) and (b) the corresponding 1D selective NOESY NMR spectrum. In this 1D selective NOESY NMR experiment, the peak belonging to pyridine group of *trans*-form CD-Azo-POM (δ = 8.13 ppm) is irradiated. The NOE signals appear in the region of β-CD-Py ring (δ = 3.2–4.2 ppm), indicating the existence of intramolecular inclusion interaction between pyridine group and β-CD-Py.[S2]

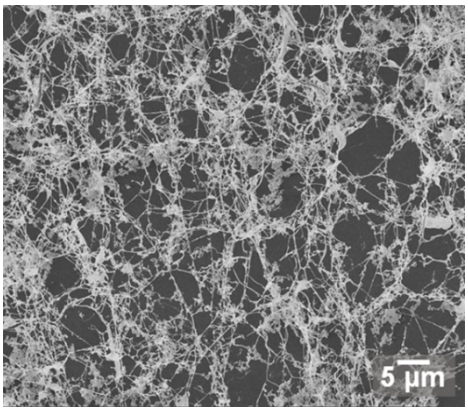

Fig. S11 SEM image of pure β-CD-Py in water.

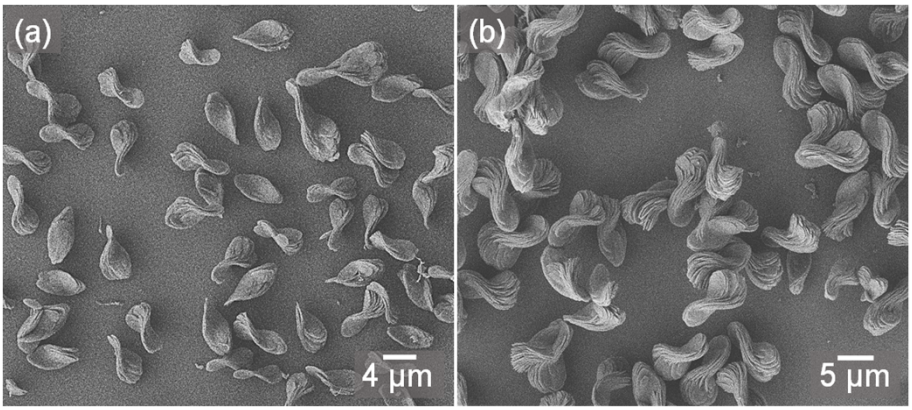

Fig. S12 SEM images of CD-Azo-POM (0.24 μM) after aging in dark for (a) 3 d and (b) 5 d.

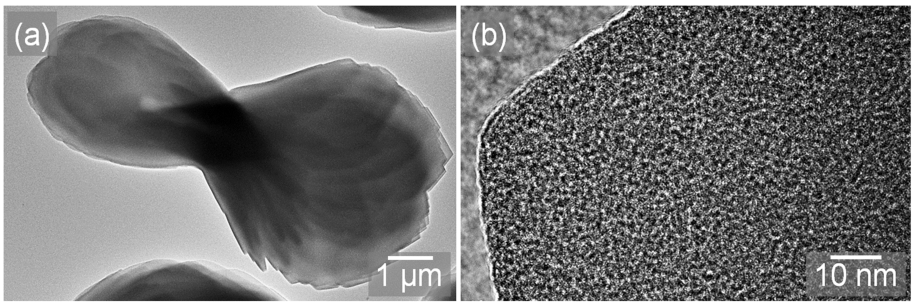

Fig. S13 (a) HRTEM image of single right-handed twisted assembly aging in darkness for 5 days. (b) Enlarged HRTEM image of the right-handed twisted assembly.

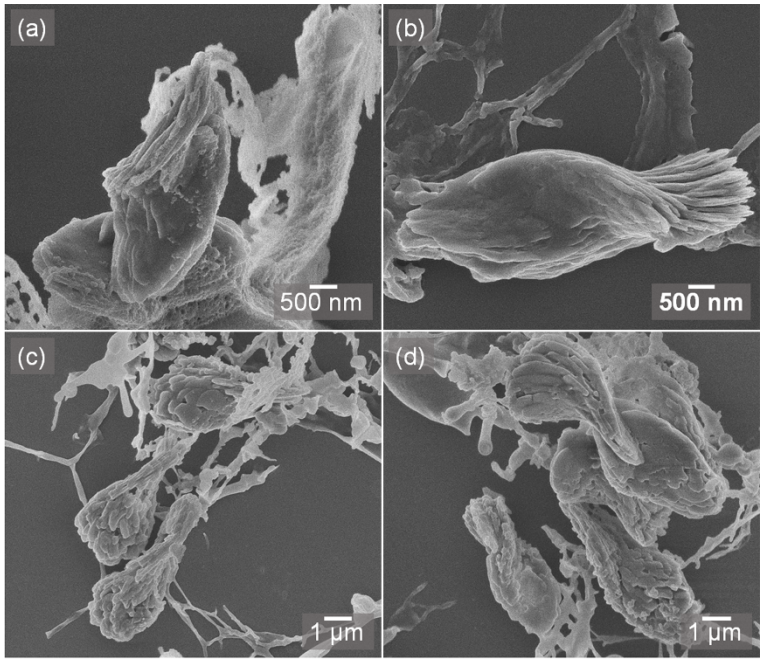

Fig. S14 SEM images of (a, b) the assembly process of right-handed twisted assemblies in darkness and (c, d) disassembly process of right-handed twisted assemblies under UV light irradiation.

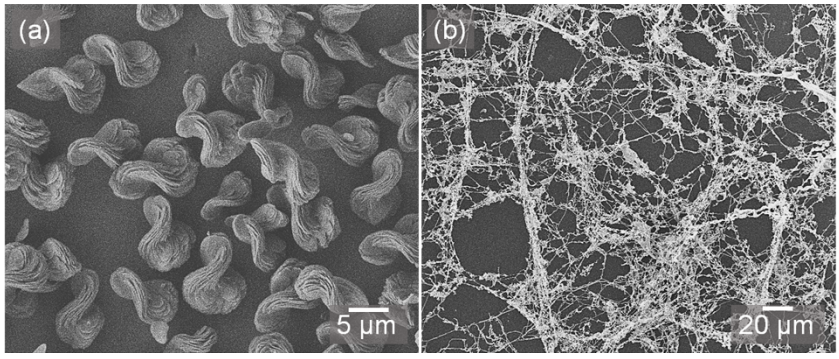

Fig. S15 SEM images of CD-Azo-POM after four cycles of alternating UV light irradiation and standing in darkness: (a) right-handed twisted assemblies in dark and (b) irregular nanofiber structures under UV light irradiation.

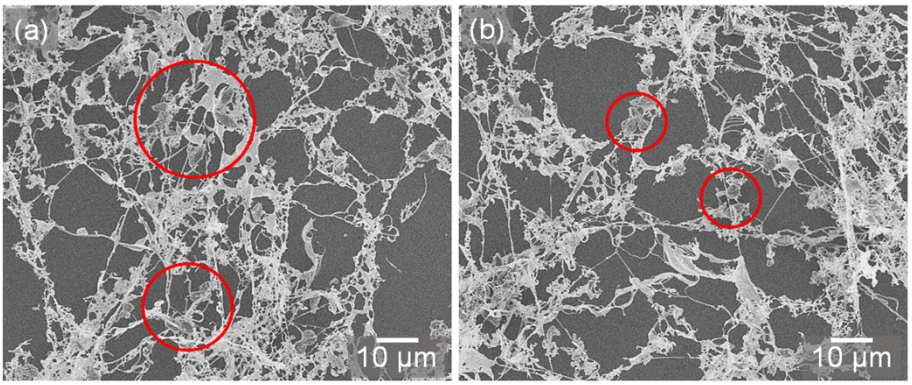

Fig. S16 SEM images of the assembly process of right-handed twisted assemblies aging in darkness for 2 days (red cycles: small assemblies).

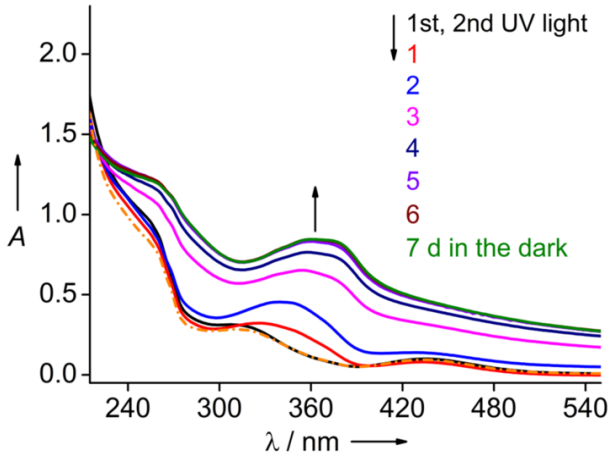

Fig. S17 UV-Vis spectra of CD-Azo-POM (0.24 μM) following a cycle of alternating UV light irradiation and standing in darkness for different time.

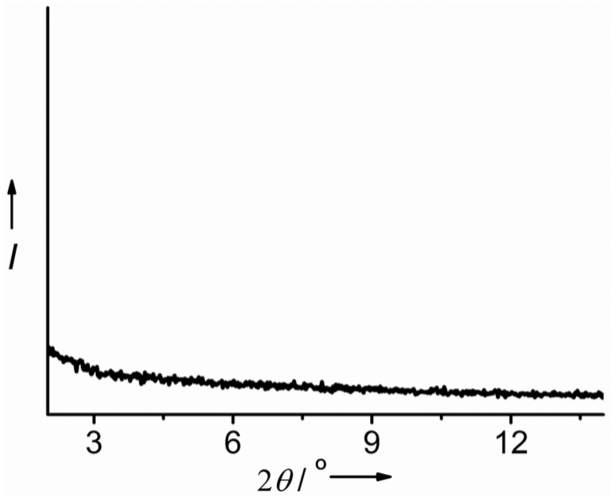

Fig. S18 XRD pattern of the irregular nanofiber structures prepared from UV light irradiation for 2 h.

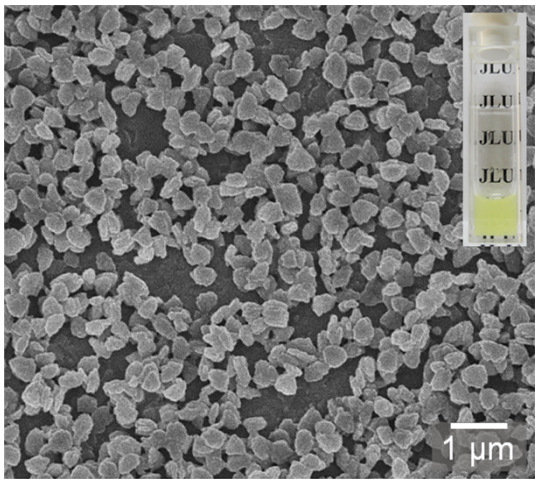

Fig. S19 SEM image of *trans*-form CD-Azo-POM upon visible light irradiation for 2 h; inset: the corresponding digital photograph of *trans*-form CD-Azo-POM after visible light irradiation.

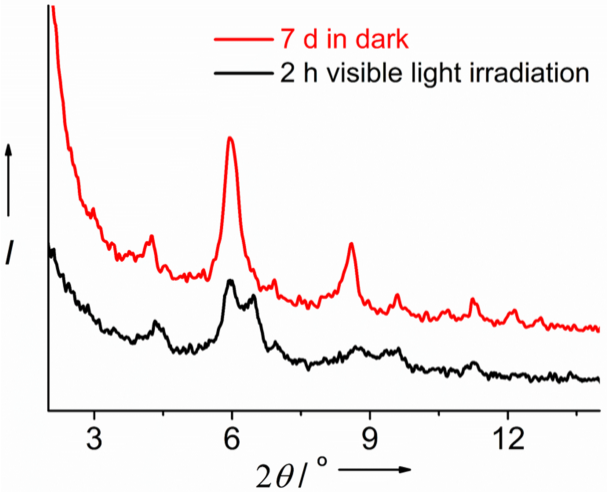

Fig. S20 XRD patterns of the CD-Azo-POM assemblies prepared under different conditions: red line: aging in darkness for 7 days; black line: under visible light irradiation for 2 h.

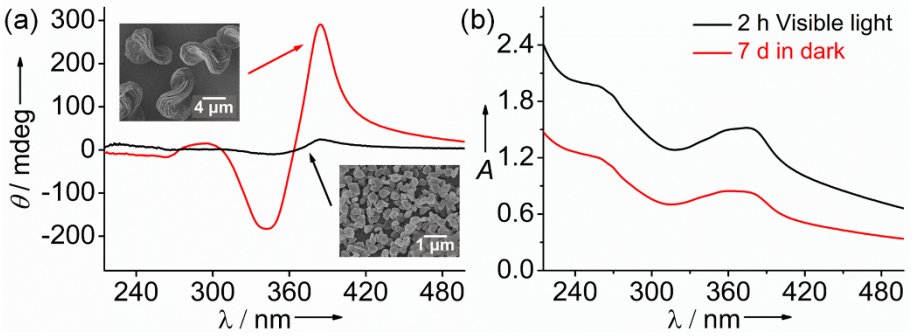

Fig. S21 (a) Circular dichroism and (b) UV-Vis spectra of the CD-Azo-POM assemblies prepared from different conditions: red line: aging in darkness for 7 days; black line: under visible light irradiation for 2 h. Inset SEM images in Figure S21a: right-handed twisted structures standing in darkness for 7 days (top one); block assemblies under visible light irradiation for 2 h (bottom one).

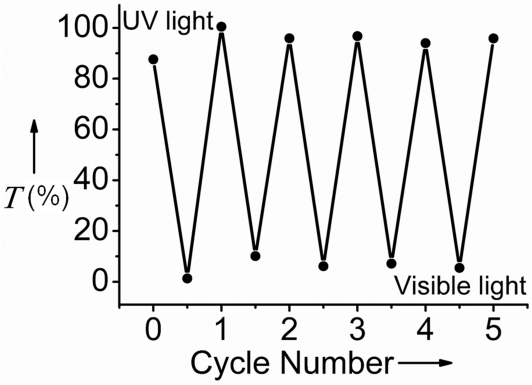

Fig. S22 Transmittance test of CD-Azo-POM (0.24 μM) encountering five cycles of alternating UV and visible light irradiation.

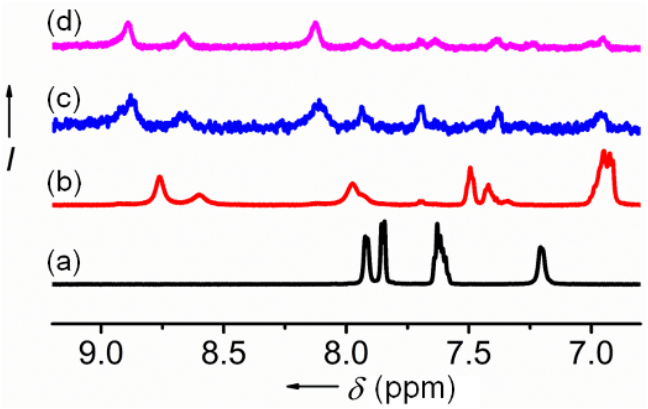

Fig. S23 ^{1}H NMR spectra of (a) isolated *trans*- Azo-POM; (b) *cis*-form CD-Azo-POM upon UV light irradiation for 2 h initially; (c) *trans*-form CD-Azo-POM upon visible light irradiation for 2 h and (d) *trans*-form CD-Azo-POM standing in darkness for 7 days. (0.22 μM, D_2O, 25 °C)

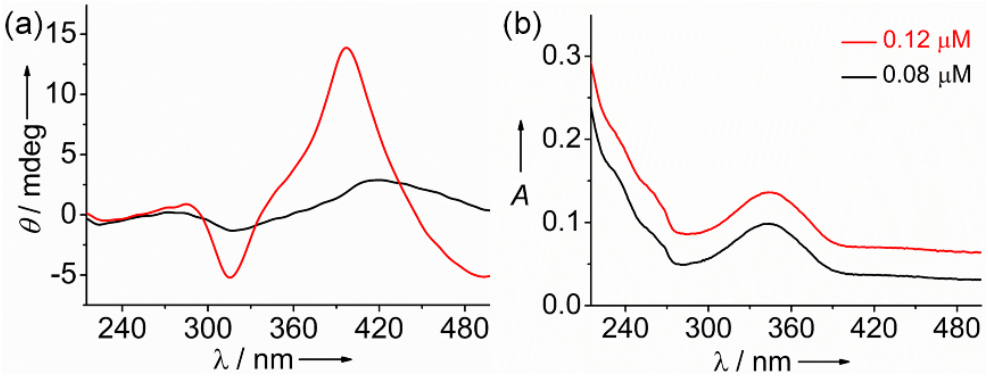

Fig. S24 (a) Circular dichroism and (b) UV-Vis spectra of CD-Azo-POM standing in darkness for 7 days at different concentrations: red line: 0.12 μM; black line: 0.08 μM.

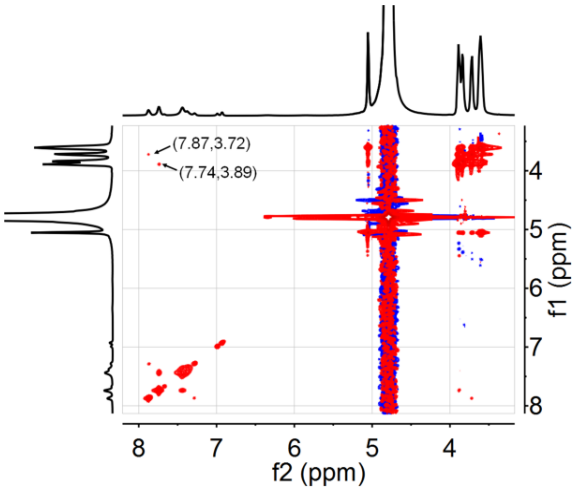

Fig. S25 2D ROESY NMR spectrum of β-CD and *trans*- Azo-POM (D_2O, 25 °C). Two cross-correlation peaks appear in ROESY spectrum, implying the formation of the inclusion complex between β-CD and *trans*- Azo-POM.

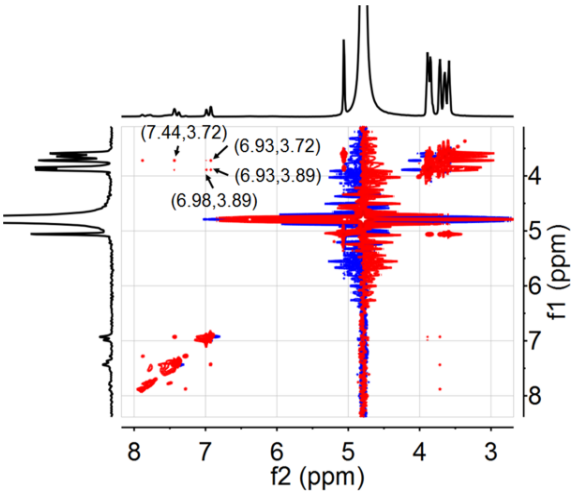

Fig. S26 2D ROESY NMR spectrum of β-CD and *cis*- Azo-POM under UV light irradiation (D_2O, 25 °C). Four cross-correlation peaks appear in ROESY spectrum, implying the formation of the inclusion complex between β-CD and *cis*- Azo-POM.

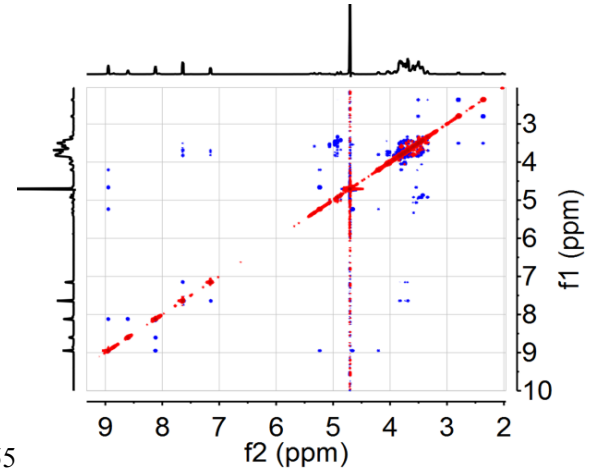

Fig. S27 2D ROESY NMR spectrum of β-CD-Py (D_2O, 25 °C). None of cross-correlation peaks between pyridine group and the cavity of β-CD appear in ROESY spectrum.

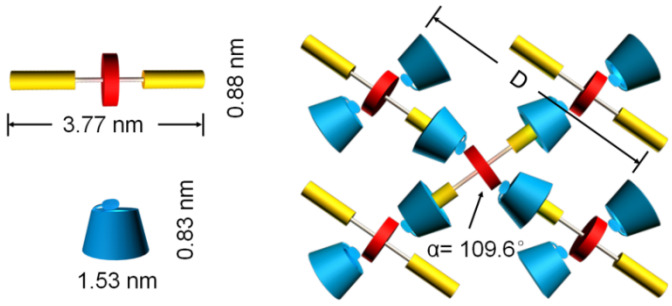

Fig. S28 The calculation of the size of self-crosslinked structure formed by *trans*-form CD-Azo-POM. D = 3.77 + 0.83 × 2 + 0.88 × cos(109.6° – 90°) + 0.28 × 2 – 0.8 × 2 ≈ 5.2 nm; 0.28 nm: the distance between β-CD-Py cations and anionic Azo-POM; 0.8 nm: the length of Azo groups into cyclodextrin cavity.

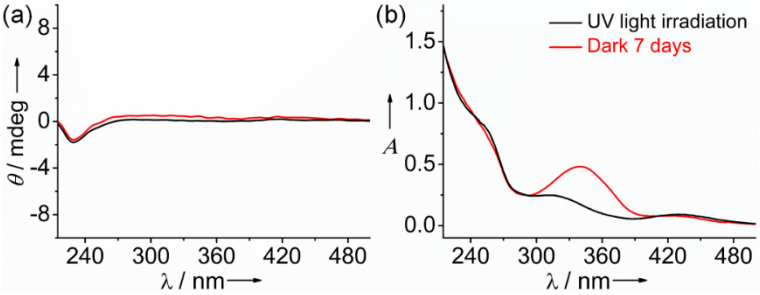

Fig. S29 (a) Circular dichroism and (b) UV-Vis spectra of CD-Azo-POM (0.24 μM) after adding adamantyl carboxylic acid alternating UV light irradiation for 2 h (black line) and aging in darkness for 7 days (red line). After adding adamantyl carboxylic acid, no chiral signal derived from Azo group is found, which is indicative of no self-inclusion of *trans*-form CD-Azo-POM due to the formation more stronger inclusion complex between β-CD-Py and adamantyl carboxylic acid.

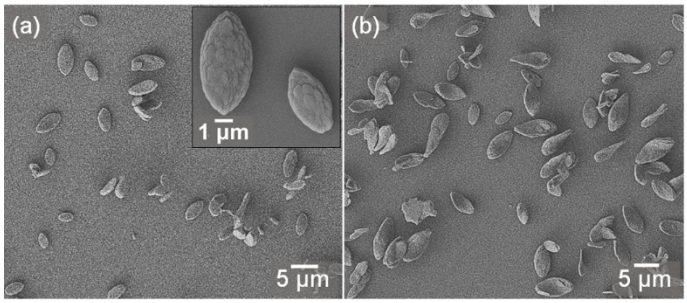

Fig. S30 SEM images of CD-Azo-POM after standing in darkness for 7 days at concentrations of (a) 0.08 and (b) 0.12 μM. The morphologies of CD-Azo-POM at lower concentrations further identify the formation process of right-handed twisted self-assemblies. At the concentration of 0.08 μM, a mass of flat assemblies are clearly observed in the scale of several micrometers. From an amplified image, it is seen that the self-assemblies are composed of a lot of elliptic sheets. When the concentration increases up to 0.12 μM, the flat assemblies tend to grow up and twist dextrally along the long axis of assemblies. This concentration-dependent morphological evolution implies that the sufficient superposition of the lamellar structure is a preliminary requirement for the twisted structure of self-assemblies.

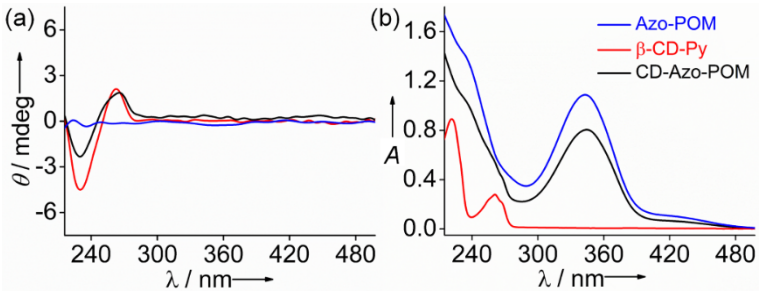

Fig. S31 (a) Circular dichroism and (b) UV-Vis spectra of CD-Azo-POM (0.024 μM, black line); pure β-CD-Py (0.024 μM, red line) and pure Azo-POM (0.024 μM, blue line) standing in darkness for 7 days. At a much lower concentration, no chiral signal derived from Azo group is found, which is indicative of no visible self-inclusion of *trans*-form CD-Azo-POM. A possible reason is that the concentration of the complex is too low to generate the intermolecular inclusion.[s3]

Table S1 Summary of elemental analysis for Azo-POM and CD-Azo-POM.

Sample		C/%	H/%	N/%
Azo-POM	Found	25.01	2.23	4.73
	Calcd.	25.43	2.13	4.94
CD-Azo-POM	Found	36.93	5.17	2.36
	Calcd.	36.93	4.86	2.65

Table S2 Summary of Miller indices and comparison of observed diffraction patterns of right-handed twisted assemblies with calculated diffractions from the body-centered cubic structure.

Measured diffraction [Å]	Predicted diffraction [Å]	Fitted Miller indices		
		h	*k*	*l*
21.03	20.79	1	1	0
14.73	14.70	2	0	0
10.31	10.39	2	2	0
9.23	9.30	3	1	0
8.30	8.49	2	2	2
7.86	7.86	3	2	1
7.32	7.35	4	0	0
		4	1	1
6.98	6.93		or	
		3	3	0

Reference:

[1] R. C. Petter, J. S. Salek, C. T. Sikorski, G. Kumaravel, F. Lin, *J. Am. Chem. Soc.*, **1990**, *112*, 3860.

[2] Y. Zhao, K. Guo, C. Wang, L. Wang, *Langmuir*, **2010**, *26*, 8966.

[3] M. Miyauchi, Y. Takashima, H. Yamaguchi, A. Harada, *J. Am. Chem. Soc.*, **2005**, *127*, 2984.