Electronic Supplementary Information

for

Light-Controlled Reversible Formation and Dissociation of Nanorods via Interconversion of Pseudorotaxanes

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Experimental Section

General Method. All chemicals were commercially available and were used without further purification unless noted otherwise. Compounds **1**, **2** and **3** were synthesized according to the previous reports.[1,2,3] The synthesis of 4,8-dimethoxy-naphthalene-1,5-disulfonate sodium (DNDS) was described in the following, and it was identified by NMR spectroscopy in D_2O, performed on a Varian 400 spectrometer, mass spectrometry, performed on an IonSpec QFT-ESI MS, which were listed in Figures **S1**–**S3**, respectively. RPMI-1640 culture solution purchased Gibco company and the HGC-27 gastric cells were provided by Beijing tumor biology test center.

Preparation of stocks solution

A predetermined amount of **1**, **2**, **3** and α-CD were dissolved in aqueous phosphate-buffered saline (PBS) buffer to gain 1 mM stock solutions. Corresponding bulk of the above stock solutions were mixed for each measurement.

UV-Vis Spectra and Optical Transmittance

UV-Vis spectra and optical transmittance were recorded in a quartz cell (light path 10 mm) on a Shimadzu UV-3600 spectrophotometer equipped with a PTC-348WI temperature controller.

TEM and SEM Experiments

TEM images were recorded on a Philips Tecnai G2 20S-TWIN microscope operating at an accelerating voltage of 200 keV. The sample for TEM measurements was prepared by dropping the solution onto a copper grid. The grid was then air-dried. SEM images were recorded on a Hitachi S-3500N scanning electron microscope. The

sample for SEM measurements was prepared by dropping the solution onto a coverslip, followed by evaporating the liquid in air.

Zeta Potential measurements

Zeta Potential experiment was carried out on a Zetasizer Nano ZS from Brookhaven Instruments equipped with a 10 mW HeNe laser at a wavelength of 633 nm.

Synthesis of 4,8-dimethoxy-naphthalene-1,5-disulfonate sodium (DNDS). We have synthesized host **1** building subunit according our previous article.[S1] The process of synthesis was as follows: 2.33 g (20.00 mmol) chlorosulfonic acid was added dropwise over a period of 2 h to a stirred solution of 1,5-dimethoxynaphthalene (0.38 g, 2 mmol) in dry 150 mL $CHCl_3$ at -5 °C. After additional 4 h reaction at -5 °C, a white precipitate was obtained. The precipitate was carefully collected by filtration and washed with 50 mL dry $CHCl_3$ at once. The residue was taken up into 100 mL H_2O, and 5% NaOH solution was added until pH = 7. The solvate was envapoured and the residue was recrystallized from acetonitrile-acetone for three times and dried by vacuum, the target compound was obtained as white solid (731 mg, 91%).

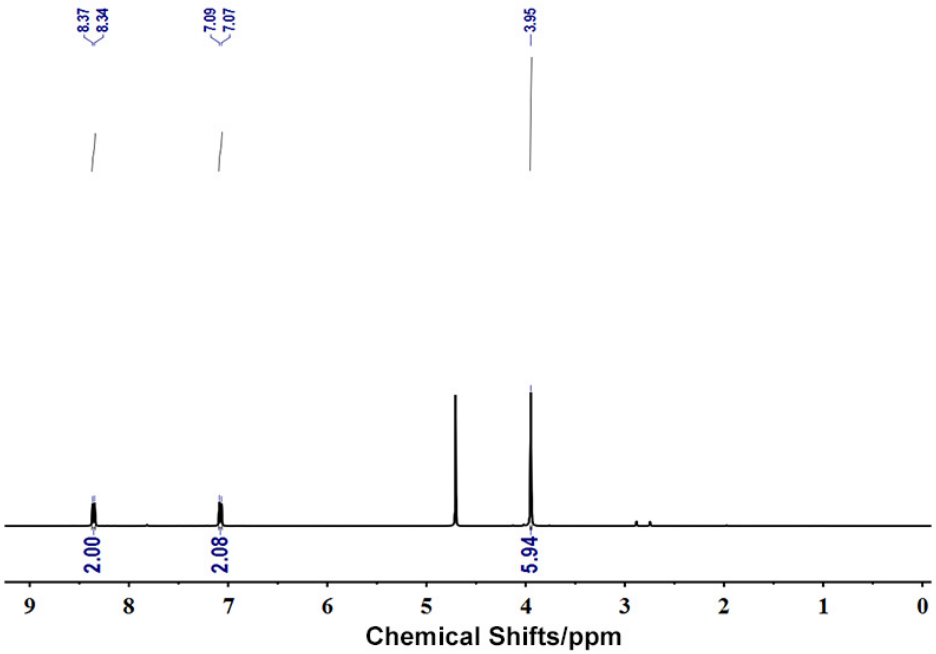


Fig. S1. ^{1}H NMR spectrum (400 MHz, D_2O, 25 °C) of DNDS.

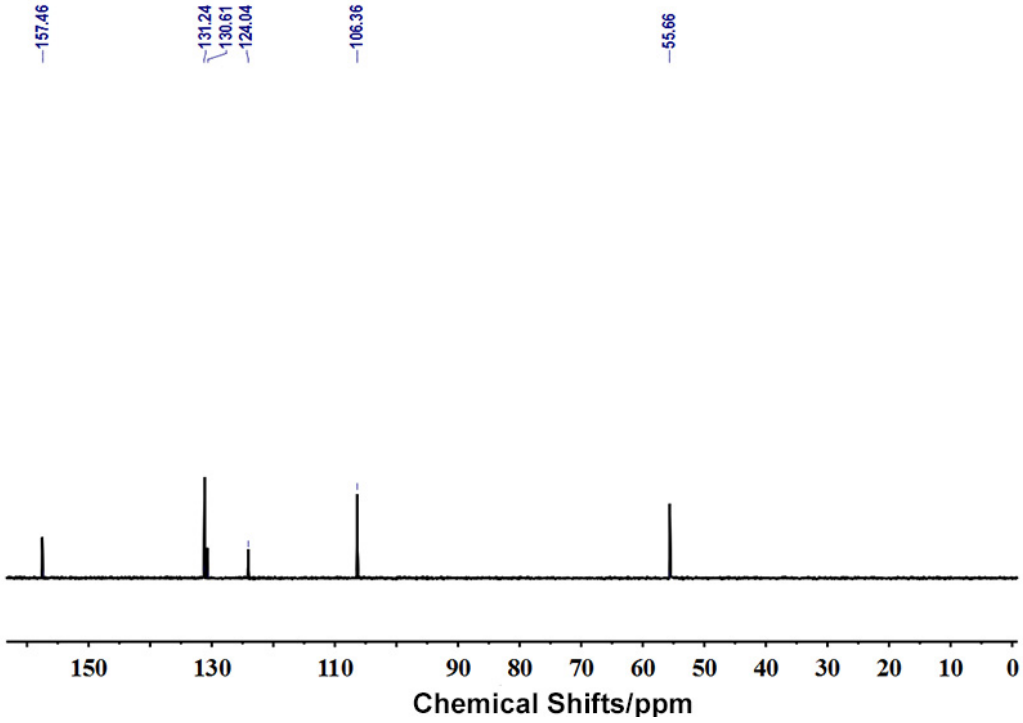


Fig. S2. ^{13}C NMR spectrum (100 MHz, D_2O, 25 °C) of DNDS.

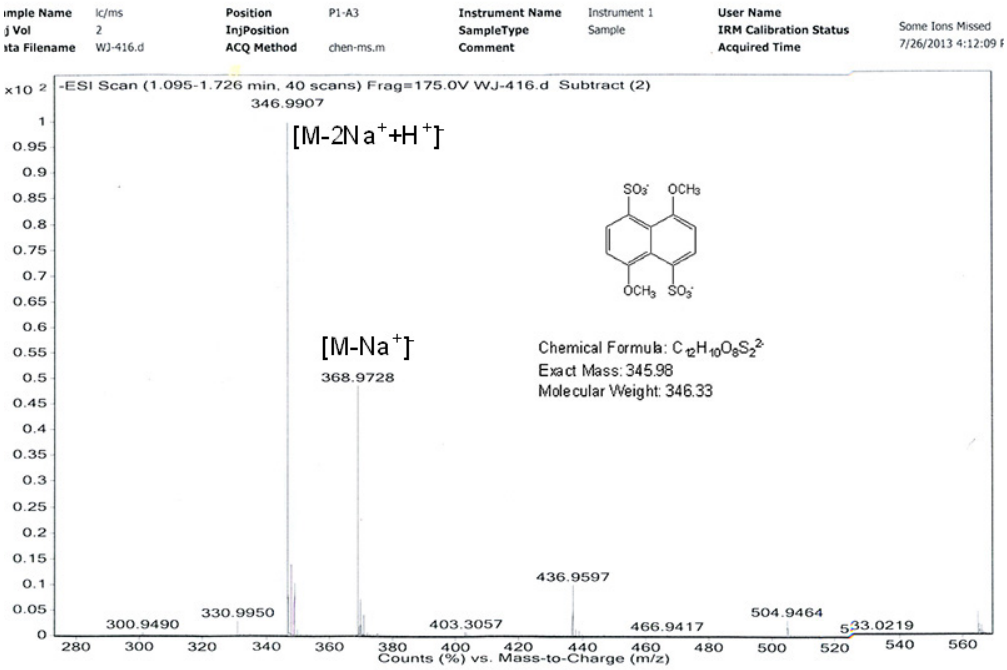


Fig. S3. ESI-HRMS spectrum of DNDS.

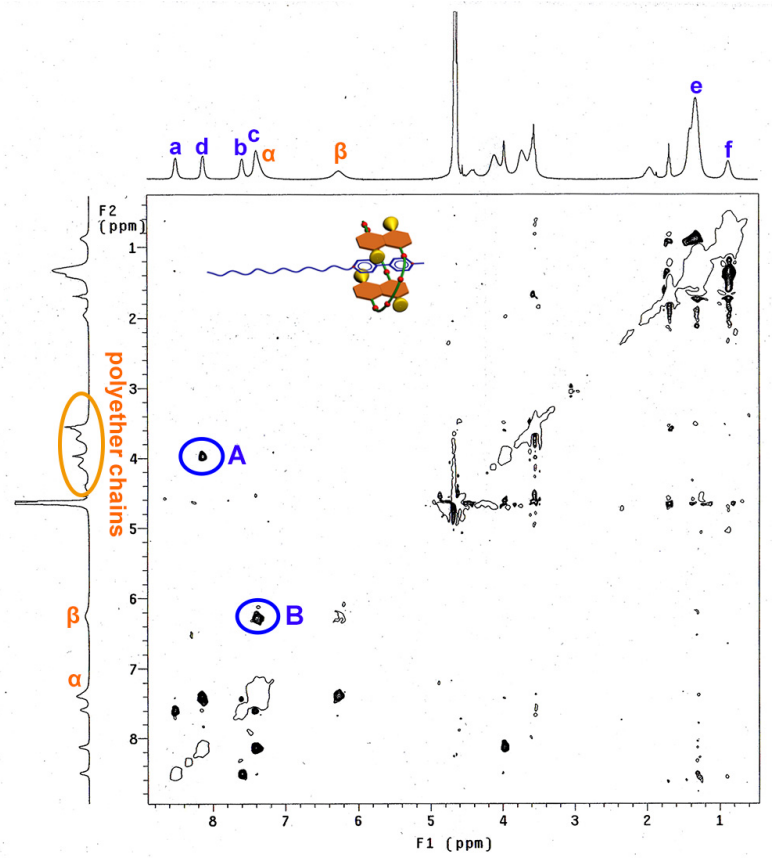


Fig. S4. ^{1}H ROESY spectrum of [2]pseudorotaxane **2**⊂**1** in D_2O at 25 °C.

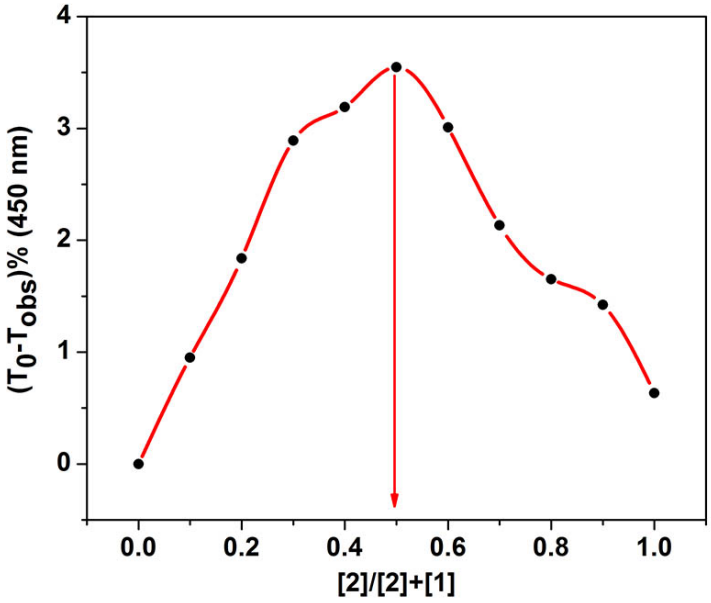


Fig. S5. Job's plot of [2]pseudorotaxane **2**⊂**1** at total concentration of 0.01 mM at 25 °C.

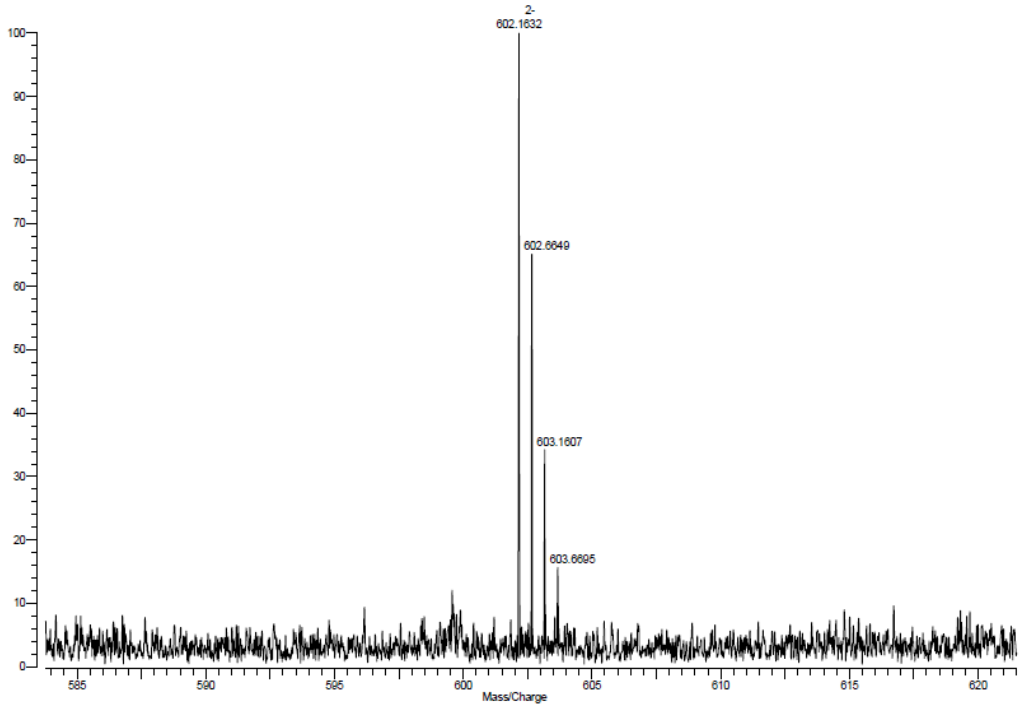


Fig. S6. ESI-MS spectrum of [2]pseudorotaxane **2**⊂**1**. The peak at *m*/*z* 602.1632 is assigned to $[\mathbf{1} + \mathbf{2}]^{2-}$, calcd.: 602.1624.

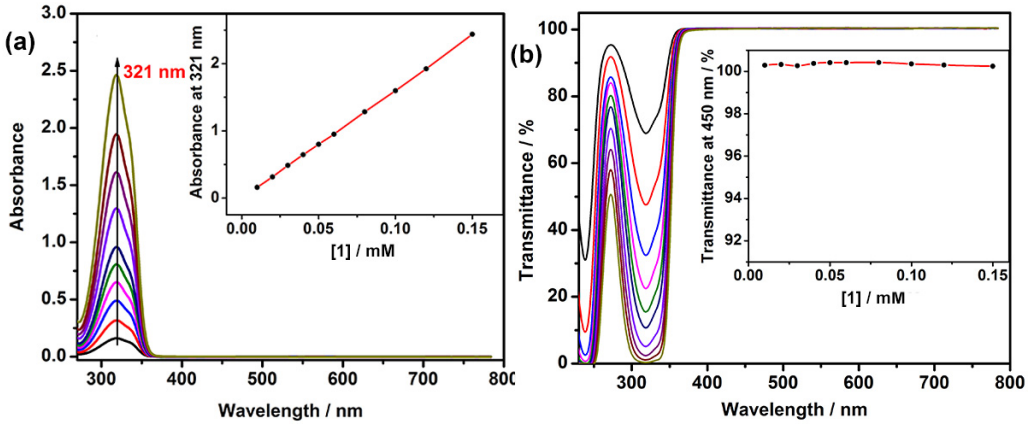


Fig. S7. UV-Vis absorption spectra (a) and optical transmittance (b) of host **1** at different concentrations (from 0.01 mM to 0.15 mM) at 25 °C in water. Inset: dependence of (a) the absorbance at 321 nm and (b) optical transmittance at 450 nm on **1** concentration, respectively.

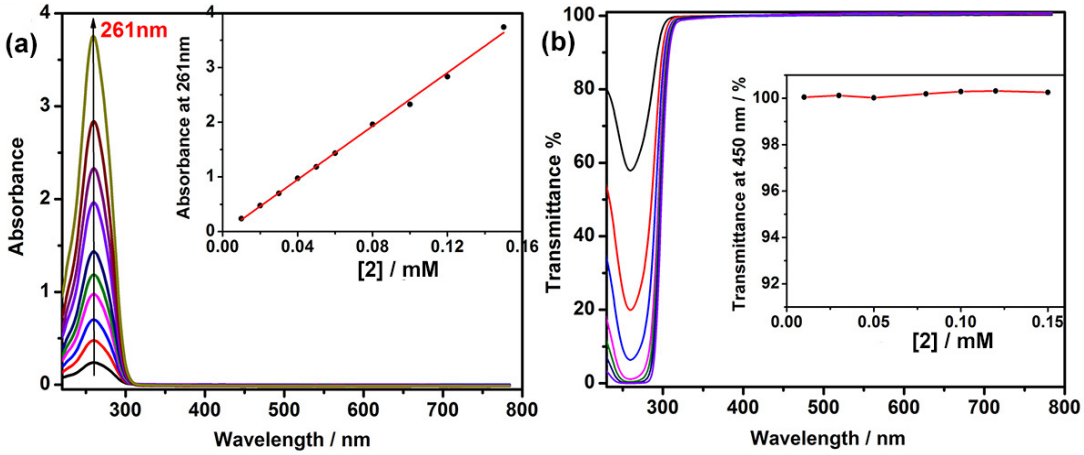


Fig. S8. UV-Vis absorption spectra (a) and optical transmittance (b) of guest **2** at different concentrations from 0.01 mM to 0.15 mM at 25 °C. Inset: dependence of the absorption at 261 nm (a) and optical transmittance at 450 nm on **2** concentration, respectively.

It should be noted that there was no obvious changes at longer wavelength region, and good linear relationship between absorbance or optical transmittance and the **1**/**2** concentration from 0.01 to 0.15 mM, indicating that free **1**/**2** was without any self-

aggregation behaviors under the concentration conditions.

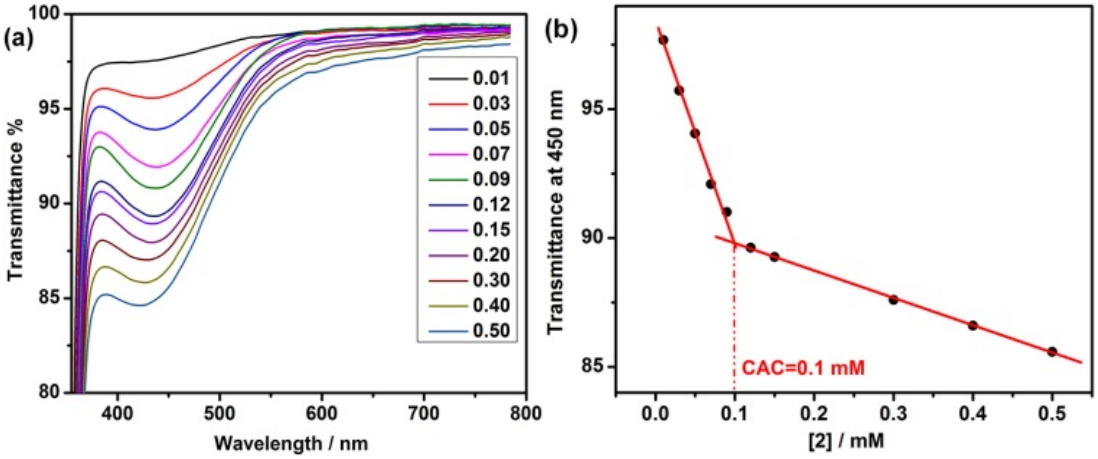


Fig. S9. (a) Dependence of the optical transmittance at 25 °C on **2** concentration in the presence of 0.1 mM **1**; (b) The corresponding CAC was determined to be 0.1 mM.

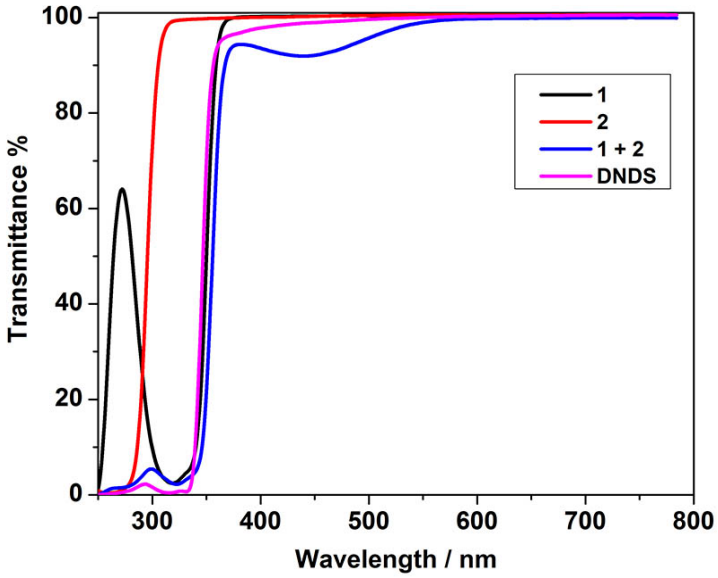
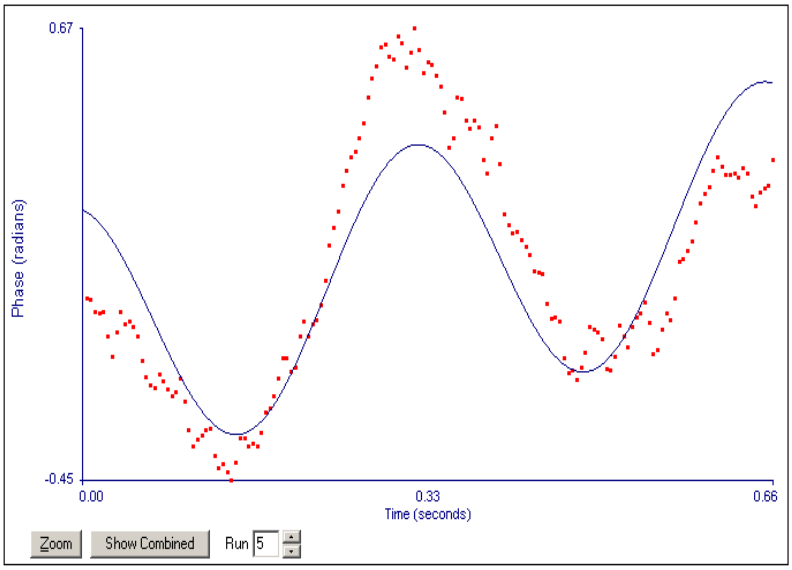


Fig. S10. Optical transmittance of **1**, **2**, **1** + **2** and **2** + DNDS at 25 °C in water; [**1**] = 0.1 mM, [**2**] = 0.1 mM, [DNDS] = 0.20 mM, respectively.



Run	Mobility	Zeta Potential (mV)	Rel. Residual
1	-0.73	-9.33	0.0087
2	-0.76	-9.75	0.0141
3	-0.66	-8.42	0.0077
4	-0.75	-9.56	0.0065
5	-0.55	-7.00	0.0122
Mean	-0.69	-8.81	0.0098
Std. Error	0.04	0.51	0.0014
Combined	-0.68	-8.69	0.0057

Measurement Parameters:	
Conductance	= 133 µS
Current	= 0.28 mA
Electric Field	= 5.24 V/cm
Sample Count Rate	= 965 kcps
Ref. Count Rate	= 1933 kcps
Uncorrected Temp.	= 25.5 °C

Fig. S11. Zeta Potential of [2]pseudorotaxane **2**⊂**1** nanorods, [**1**] = [**2**] = 0.1 mM.

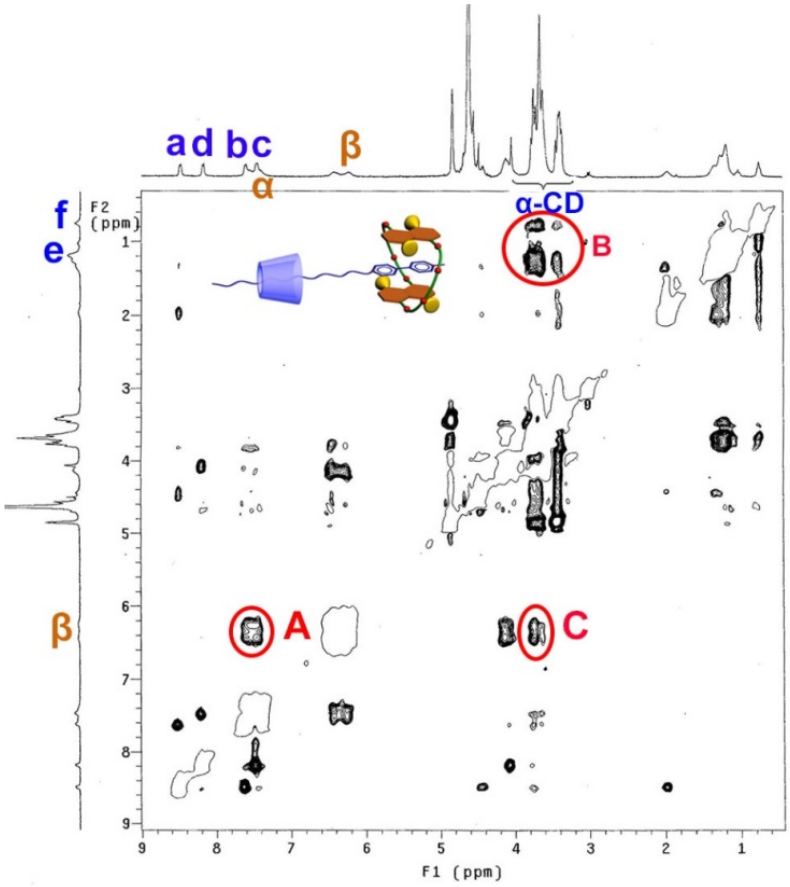


Fig. S12. ^{1}H ROESY spectrum of [3]pseudorotaxane **2**⊂**1**·α-CD in D_2O at 25 °C.

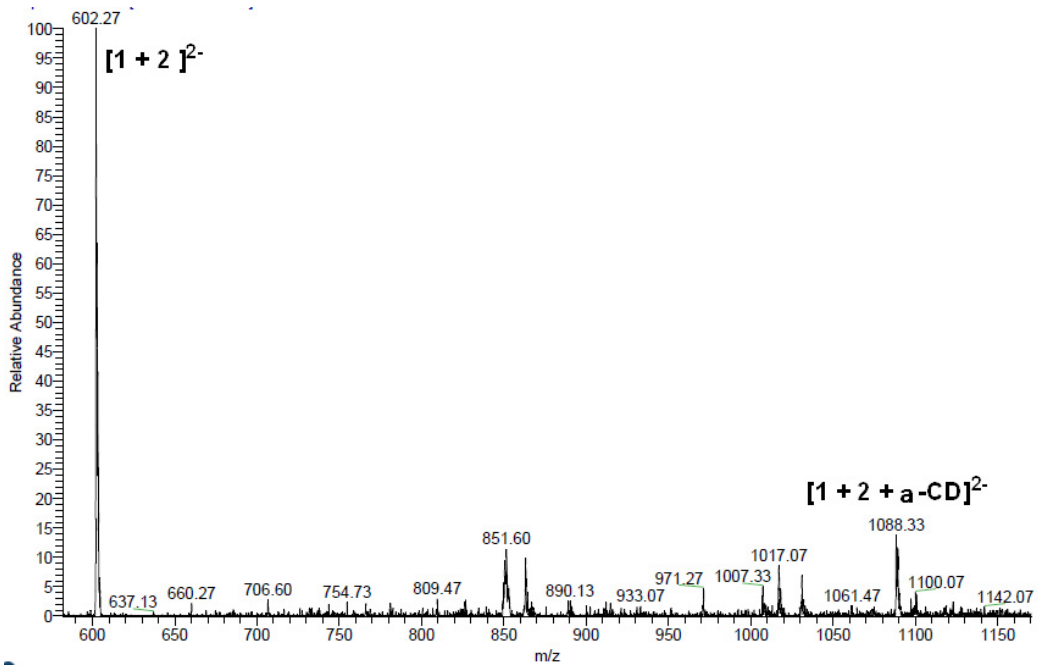


Fig. S13. ESI-MS spectrum of [3]pseudorotaxane **2**⊂**1**·α-CD. The peak at *m*/*z* 602.27 is assigned to [**1** + **2**]$^{2-}$, calcd.: 602.16; the peak at *m*/*z* 1088.33 is assigned to [**1** + **2** + α-CD]$^{2-}$, calcd.: 1088.32.

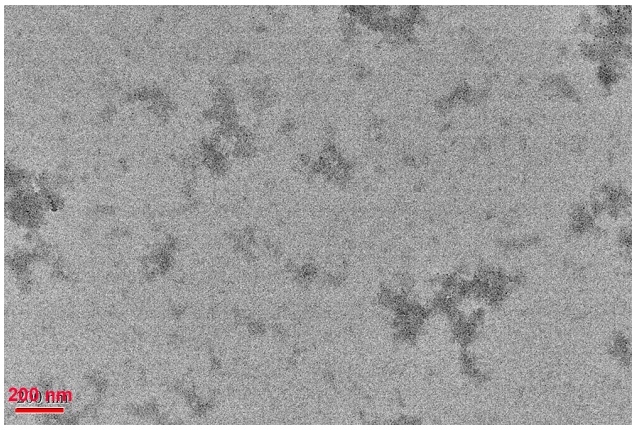


Fig. S14. TEM image of [2]pseudorotaxane **2⊂1** aggregates in the presence of excess α-CD, [**1**] = [**2**] = 0.1 mM, [α-CD] = 0.5 mM.

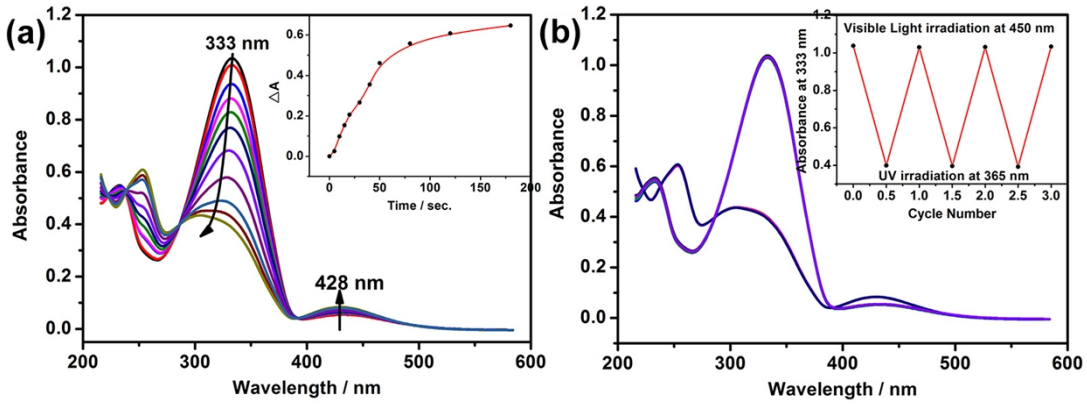


Fig. S15. (a) Absorption spectra of **3**⊂*α*-CD in water after UV irradiation at 365 nm, Inset: Absorbance changes at 333 nm versus irradiation time. (b) Cycling of the photo-mediated *trans* and *cis* isomerization of **3**⊂α-CD ([**3**] = [*α*-CD] = 0.05 mM) by alternate irradiation with UV and visible light at 25 ºC.

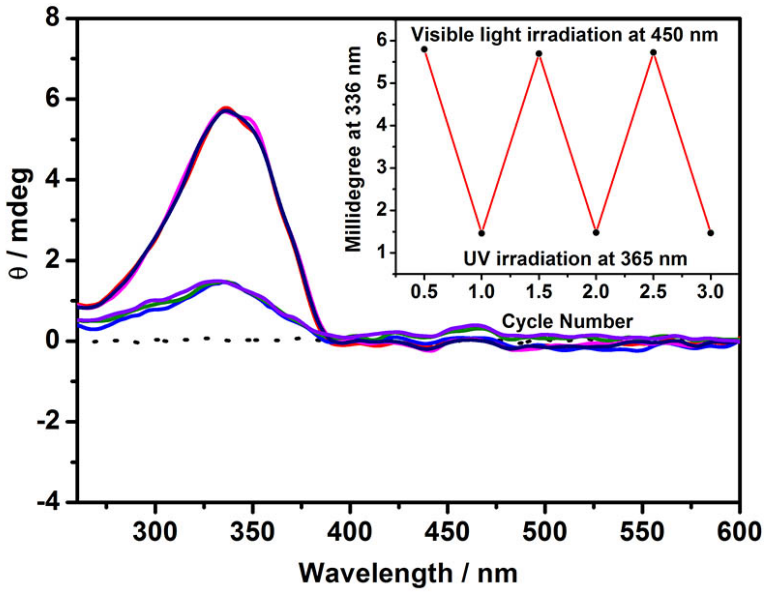


Fig. S16. Circular dichroism changes of mixture solution of **3** + α-CD upon alternate irradiation with UV and visible light. Inset: Cycling of the photo-mediated *trans* and *cis* isomerization of **3** in the mixture ([**3**] = [*α*-CD] = 0.1 mM, 25 ºC, respectively).

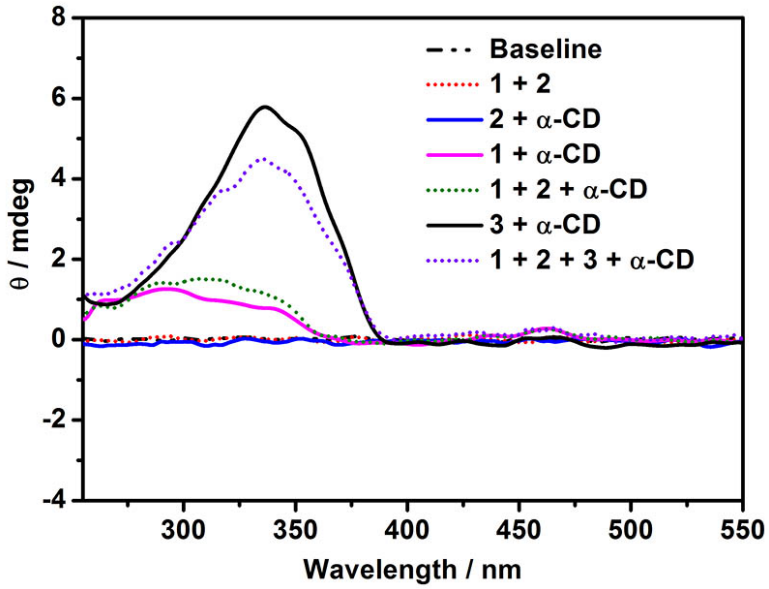


Fig. S17. Circular dichroism spectra of different components of **1** + **2**, **2** + α-CD, **1** + α-CD, **1** + **2** + α-CD, **3** + α-CD and four-components mixture of **1** + **2** + α-CD + **3**, ([**1**] = [**2**] = [*α*-CD] = 0.1 mM, [**3**] = 0.5 mM, 25 ºC, respectively).

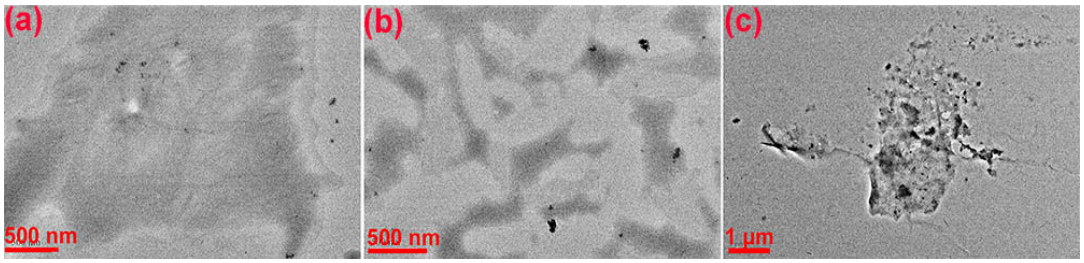


Fig. S18. TEM images of (a) α-CD + **3**, (b) **1** + α-CD + **3**, (c) **1** + α-CD. [1] = 0.1 mM, [α-CD] = 0.2 mM, [**3**] = 0.3 mM, respectively).

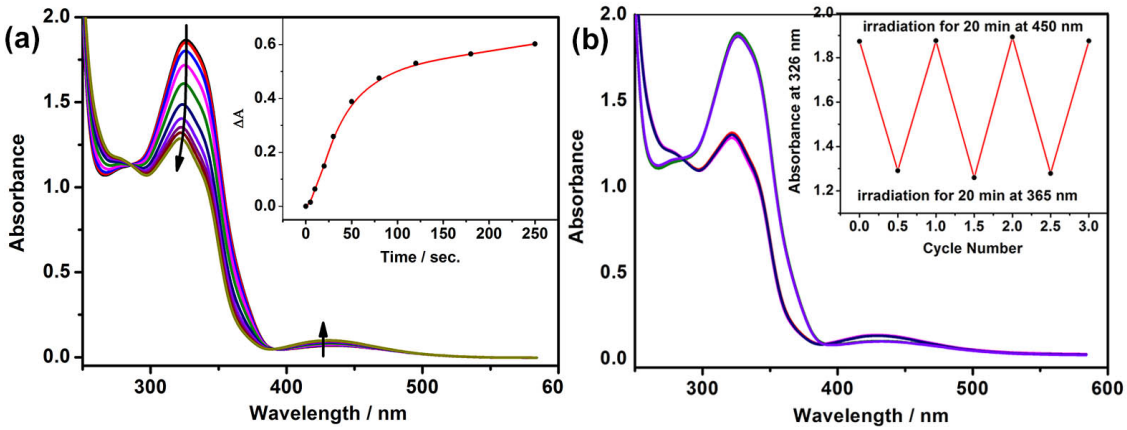


Fig. S19. (a) Absorption spectra of a four-components mixture of [3]pseudorotaxane **2**⊂**1**·α-CD + **3** after UV irradiation at 365 nm, Inset: Absorbance changes at 326 nm versus irradiation time. (b) Cycling of the photo-mediated *trans* and *cis* isomerization of the quaternary mixture ([**1**] = [*α*-CD] = 0.05 mM) by alternate irradiation with UV and visible light at 25 ºC, ([**1**] = [**2**] = [α-CD] = [**3**] = 0.05 mM, respectively).

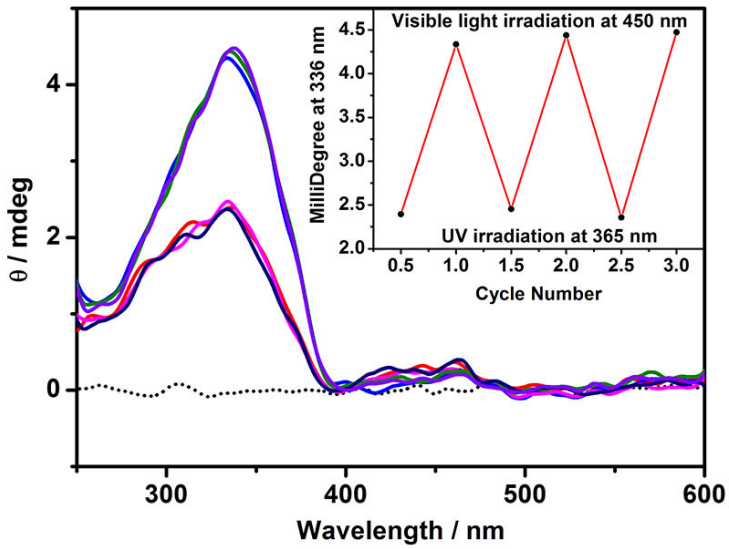


Fig. S20. Circular dichroism changes of the four-components mixture of [3]pseudorotaxane **2**⊂**1**·α-CD + **3** upon alternate irradiation with UV and visible light. Inset: Cycling of the photo-mediated *trans* and *cis* isomerization of **3** in the quaternary mixture ([**1**] = [**2**] = [α-CD] = 0.1 mM, [**3**] = 0.5 mM, 25 ºC, respectively).

Generally, azobenzene isomerizes to predominantly trans and cis forms under visible (Vis) and ultraviolet (UV) light, respectively.[4] According to previous reports,[5] we can conclude that the photoisomerization of azophenyl unit is a crucial factor to govern the formation and dissociation of inclusion complex between azobenzene and α-CD. The ^{1}H NMR of **1** + **2** + **3** + α-CD after UV irradiation in Fig. 3f (in the text), the Fig. S17, Fig. S19 & S20 jointly indicate the reversibility of the azobenzene photoisomerization in four-components solution, along with the transfer of α-CD from **3**⊂α-CD to amphiphilic [2]pseudorotaxane **2**⊂**1**. As a result, owing to the formation and dissociation of inclusion complex **3**⊂α-CD, a reversible conformational change in the transition from amphiphilic [2]pseudorotaxane **2**⊂**1** to water-soluble

[3]pseudorotaxane **2**⊂**1**·α-CD can be operated by the azobenzene photoisomerization. Combining these spectroscopic, NMR (Fig. 3f) of four-components system after UV irradiation and microscopic investigation results, we can speculate the reversibility of the assembly and disassembly processes was driven by the azobenzene photoisomerization in four-components solution.

References:

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[2] Y. Lei, *J. Phys. Chem.,* 1991, **95**, 7918.

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