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. 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$_2$O, 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. 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$_2$O, 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$_2$O, 25 °C) of DNDS.

Fig. S2. $^{13}$C NMR spectrum (100 MHz, D$_2$O, 25 °C) of DNDS.
Fig. S3. ESI-HRMS spectrum of DNDS.

Fig. S4. $^1$H ROESY spectrum of [2]pseudorotaxane $\mathbf{2c\cdot 1}$ in D$_2$O 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 $[1 + 2]^{2-}$, 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.
**Fig. S11.** Zeta Potential of [2]pseudorotaxane 2\(\subset\)1 nanorods, [1] = [2] = 0.1 mM.
Fig. S12. $^1$H ROESY spectrum of [3]pseudorotaxane $2\subset 1 \cdot \alpha$-CD in D$_2$O at 25 °C.

Fig. S13. ESI-MS spectrum of [3]pseudorotaxane $2\subset 1 \cdot \alpha$-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 $[1 + 2 + \alpha$-CD$]^2^-$, calcd.: 1088.32.
**Fig. S14.** TEM image of [2]pseudorotaxane $2\subset 1$ aggregates in the presence of excess $\alpha$-CD, $[1] = [2] = 0.1$ mM, $[\alpha$-CD$] = 0.5$ mM.

**Fig. S15.** (a) Absorption spectra of $3\subset \alpha$-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 $3\subset \alpha$-CD ($[3] = [\alpha$-CD$] = 0.05$ mM) by alternate irradiation with UV and visible light at 25 °C.
**Fig. S16.** Circular dichroism changes of mixture solution of $3 + \alpha$-CD upon alternate irradiation with UV and visible light. Inset: Cycling of the photo-mediated $trans$ and $cis$ isomerization of $3$ in the mixture ($[3] = [\alpha$-CD] = 0.1 mM, 25 °C, respectively).

**Fig. S17.** Circular dichroism spectra of different components of $1 + 2$, $2 + \alpha$-CD, $1 + \alpha$-CD, $1 + 2 + \alpha$-CD, $3 + \alpha$-CD and four-components mixture of $1 + 2 + \alpha$-CD + 3, ($[1] = [2] = [\alpha$-CD] = 0.1 mM, $[3] = 0.5$ mM, 25 °C, respectively).
Fig. S18. TEM images of (a) $\alpha$-CD + 3, (b) 1 + $\alpha$-CD + 3, (c) 1 + $\alpha$-CD. [1] = 0.1 mM, [$\alpha$-CD] = 0.2 mM, [3] = 0.3 mM, respectively).

Fig. S19. (a) Absorption spectra of a four-components mixture of [3]pseudorotaxane $2\subset1\cdot\alpha$-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] = [$\alpha$-CD] = 0.05 mM) by alternate irradiation with UV and visible light at 25 °C, ([1] = [2] = [$\alpha$-CD] = [3] = 0.05 mM, respectively).
Circular dichroism changes of the four-components mixture of [3]pseudorotaxane \(2\textcircled{1} \cdot \alpha\text{-CD} + 3\) 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] = [\(\alpha\text{-CD}\)] = 0.1 mM, [3] = 0.5 mM, 25 °C, respectively).

Generally, azobenzene isomerizes to predominantly trans and cis forms under visible (Vis) and ultraviolet (UV) light, respectively. According to previous reports, 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 \(\alpha\text{-CD}\). The \(^1\)H NMR of 1 + 2 + 3 + \(\alpha\text{-CD}\) 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 \(\alpha\text{-CD}\) from 3\(\subset\)\(\alpha\text{-CD}\) to amphiphilic [2]pseudorotaxane 2\(\subset\)1. As a result, owing to the formation and dissociation of inclusion complex 3\(\subset\)\(\alpha\text{-CD}\), a reversible conformational change in the transition from amphiphilic [2]pseudorotaxane 2\(\subset\)1 to water-soluble
pseudorotaxane $2\subset 1\cdot \alpha$-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: