Electronic Supplementary Information (ESI)

Light-controlled reversible self-assembly of nanorod suprastructures

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S1 Materials and instruments

Reagent grade β-cyclodextrin (β-CD) was purchased from Sigma and recrystallized twice from water followed by dehydration in vacuum at 95 °C. 4,4'-dipyridine (DPD) and zinc chloride ($ZnCl_2$) were commercially available and used without further purification. 2,3,3-trimethylindolenine, propane sultone, and 2-hydroxybenzaldehyde were commercially obtained and used without further purification. All other chemicals used in this study were of analytical grade.

The pH values were collected on a commercially available instrument. ^{1}H NMR spectra were recorded in deuterium oxide at 298 ± 0.1 K on a Bruker AV600 spectrometer. Fourier transform infrared spectra (FT-IR) were performed on a Bio-rad FTS6000 with samples prepared as KBr pellets. The UV-vis absorption spectral studies were carried out on a ThermoFisher EVO300 PC spectrophotometer. Transmission electron microscope (TEM) experiments were performed with a Tecnai G2 F20 to analyse the morphology of supramolecular assemblies. Dynamic light scattering (DLS) was conducted with Nanobrook 173plus (Brookhaven Co. USA) using a vertically polarized light at $\lambda = 488$ nm.

S2 Synthesis and characterization of compounds

Synthesis of MEH

The synthesis of MEH was carried out following a literature procedure.[1] Starting material 2,3,3-trimethyl-1-(3-sulfonatepropyl)-3H-indolium was synthesized by the reaction of 2,3,3-trimethylindolenine with propane sultone. To an anhydrous ethanol were added 2-hydroxybenzaldehyde and 2,3,3-trimethyl-1-(3-sulfonatepropyl)-3Hindolium. The reaction mixture was refluxed overnight, filtered at room temperature give orange solid MEH.

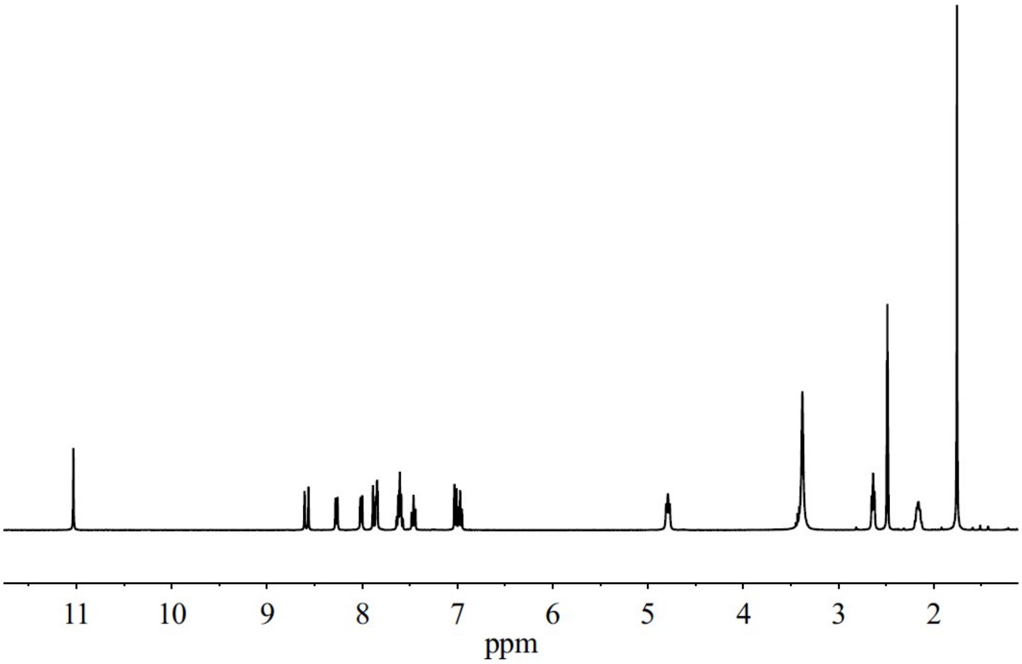

Figure S1. ^{1}H NMR spectrum of MEH (400 MHz, D_2O, 298 K).

Preparation of polypseudorotaxane 1

Complex β-CD/DPD was synthesized by the reaction of DPD with β-CD in aqueous solution. As for the synthesis of polypseudorotaxane **1**, an aqueous solution of $ZnCl_2$ was slowly added to an aqueous solution of β-CD/DPD. The reaction mixture was then stirred at 40 °C for 7 h. The resulting solution was concentrated under a reduced pressure. After filtration the solid was recrystallized from water and dried under vacuum.

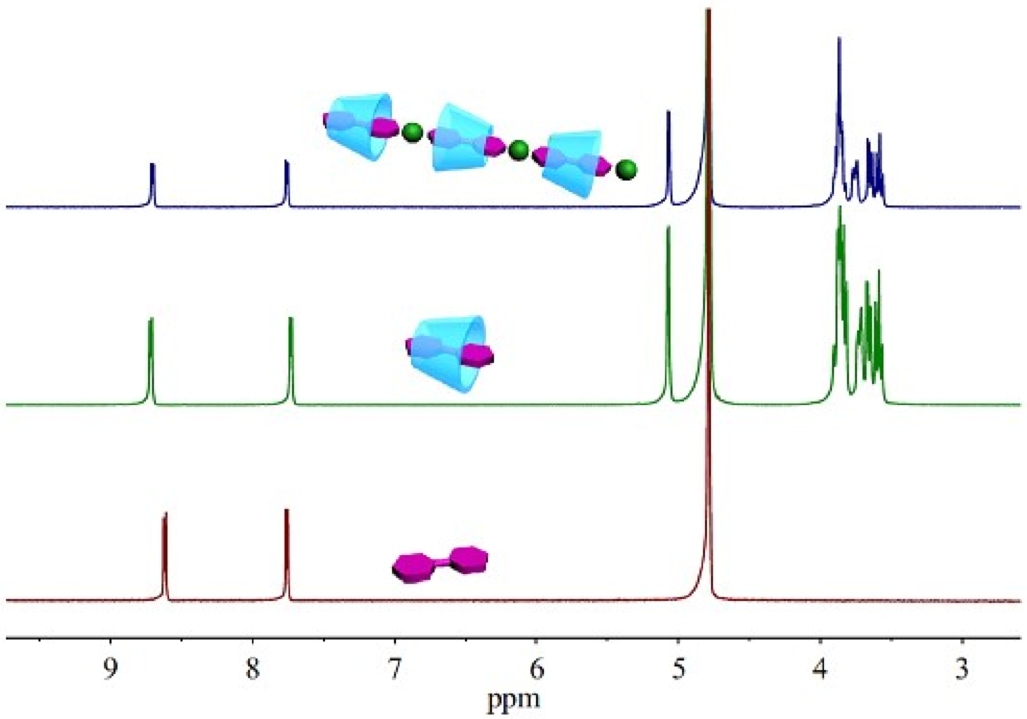

Figure S2. ^{1}H NMR spectra of polypseudorotaxane **1**，complex DPD⊂β-CD and DPD (400 MHz, D_2O, 298 K).

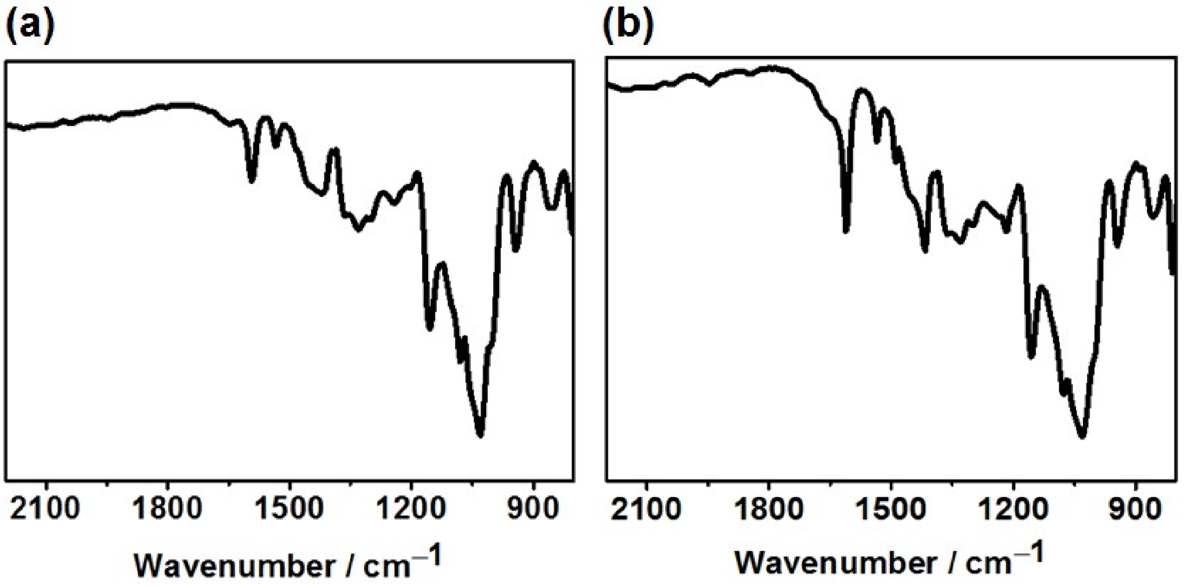

Figure S3. FT-IR of (a) complex DPD⊂β-CD and (b) polypseudorotaxane **1**.

S3 Protonation of DPD and DPD@polypseudorotaxane by Hydrochloric Acid (HCl)

Adding of DPD with HCl to adjust the pH to 3 was performed in D_2O. ^1H NMR changes were monitored during the adding process because of the protonation of DPD. In addition, the protonation of polypseudorotaxane **1** at different pH values was carried out by adding a series of DCl to a D_2O solution of **1** and detected by ^1H NMR.

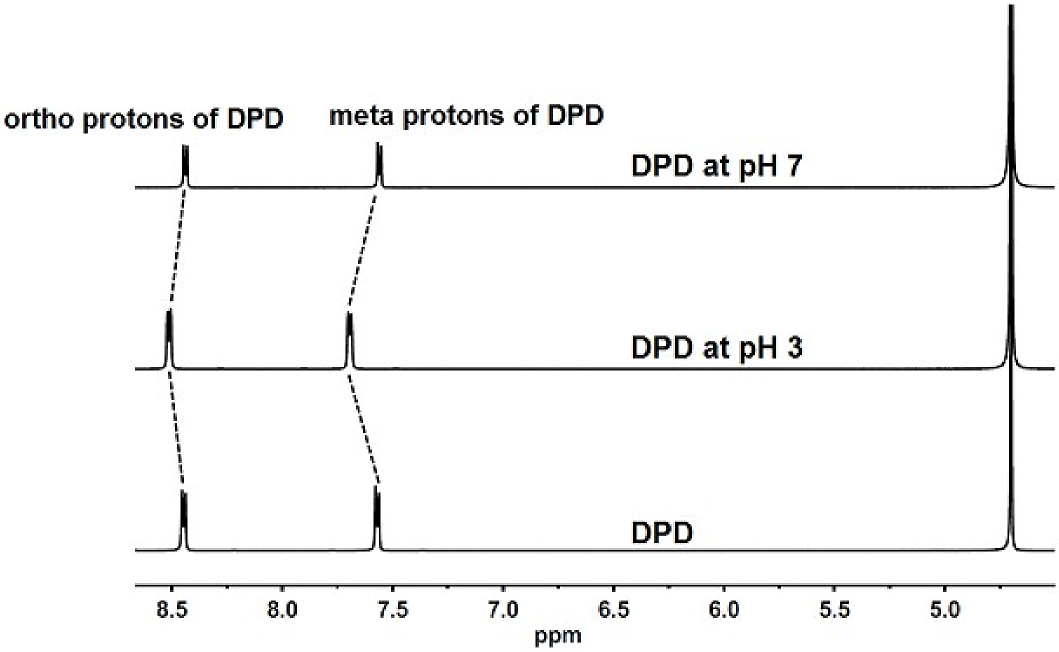

Figure S4. ^1H NMR of DPD upon the sequential addition of HCl and NaOH (400 MHz, D_2O, 298 K).

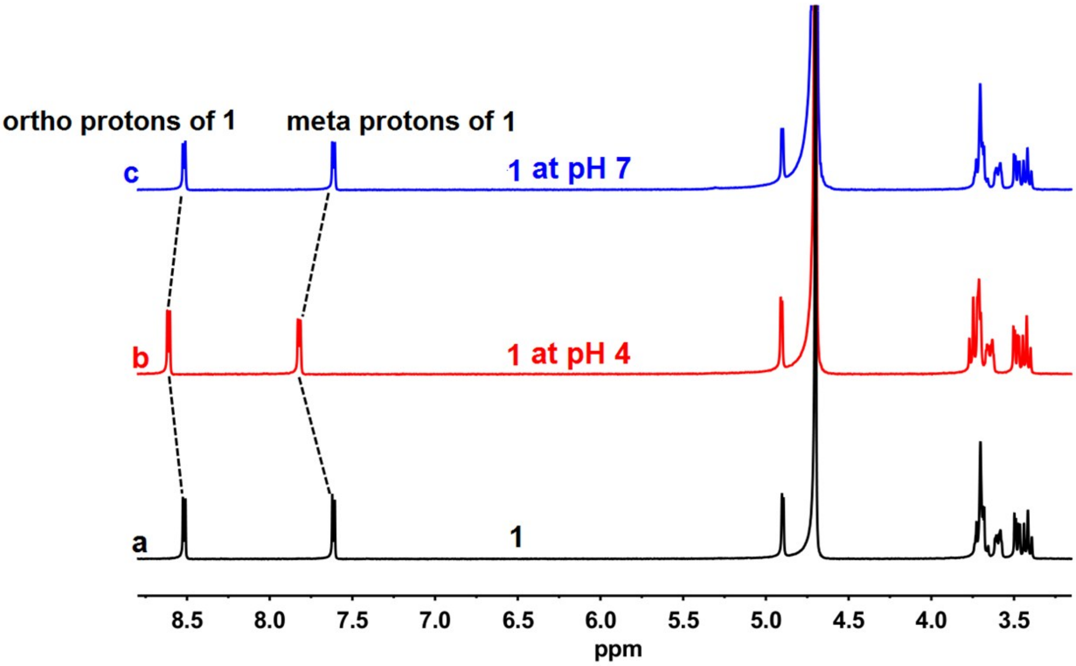

Figure S5. ^{1}H NMR of (a) **1** (2.0×10^{-4} M) (b) **1** (2.0×10^{-4} M) + HCl with pH 4 (c) **1** (2.0×10^{-4} M) + HCl + NaOH with pH 7 (400 MHz, D_2O, 298 K).

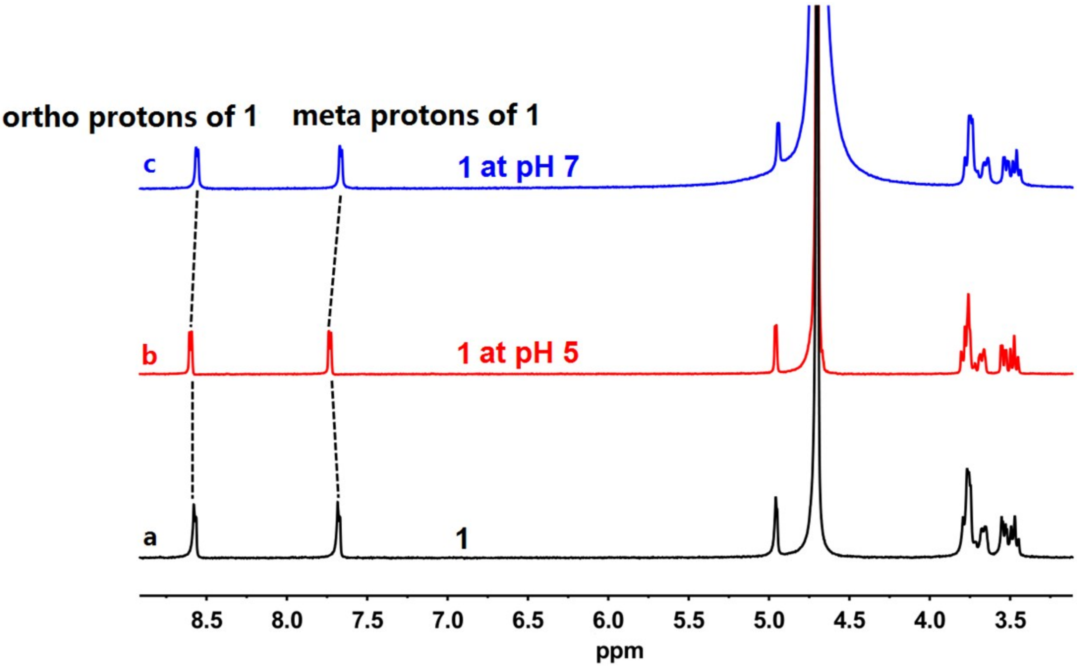

Figure S6. ^{1}H NMR of (a) **1** (2.0×10^{-4} M) (b) **1** (2.0×10^{-4} M) + HCl with pH 5 (c) **1** (2.0×10^{-4} M) + HCl + NaOH with pH 7 (400 MHz, D_2O, 298 K).

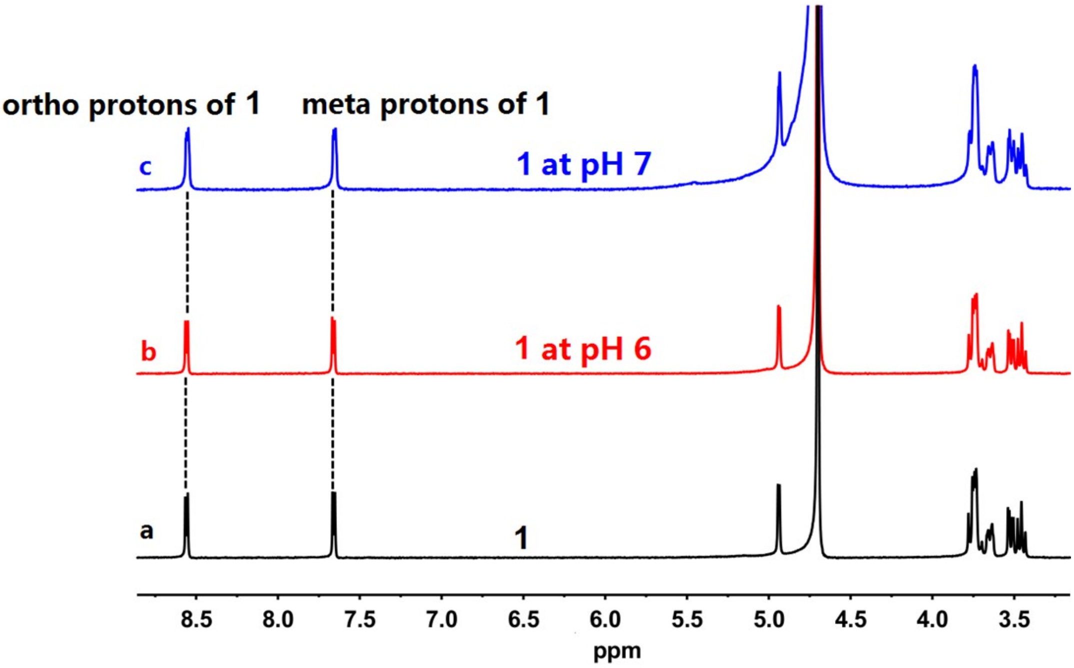

Figure S7. ^{1}H NMR of (a) **1** (2.0×10^{-4} M) (b) **1** (2.0×10^{-4} M) + HCl with pH 6 (c) **1** (2.0×10^{-4} M) + HCl + NaOH with pH 7 (400 MHz, D_2O, 298 K).

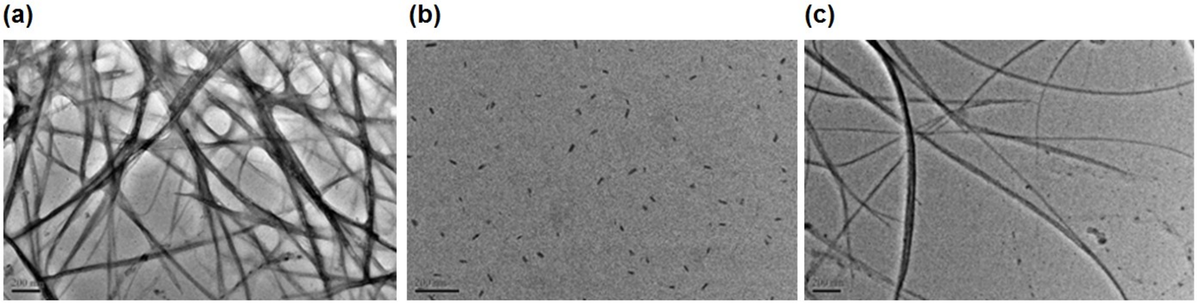

Figure S8. TEM of (a) **1,** (a) **1** (2.0×10^{-4} M) + HCl with pH 3, (b) **1** (2.0×10^{-4} M) + HCl + NaOH with pH 7.

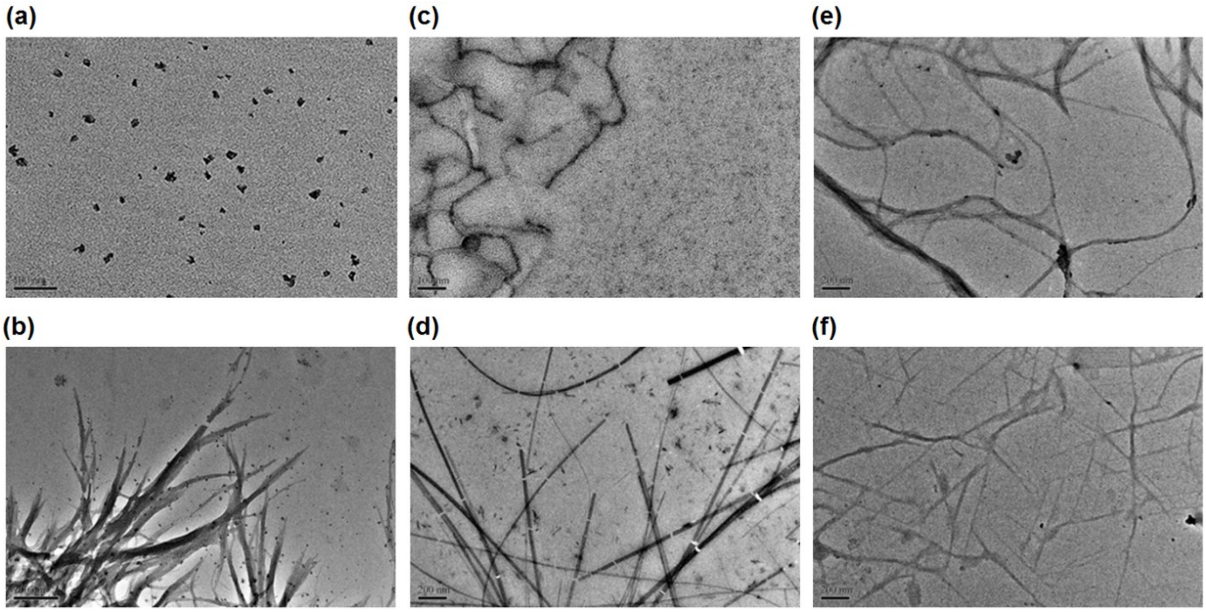

Figure S9. TEM of (a) **1** (2.0×10^{-4} M) + HCl with pH 4, (b) **1** (2.0×10^{-4} M) + HCl + NaOH with pH 7, (c) **1** (2.0×10^{-4} M) + HCl with pH 5, (d) **1** (2.0×10^{-4} M) + HCl + NaOH with pH 7, (e) **1** (2.0×10^{-4} M) + HCl with pH 6, (f) **1** (2.0×10^{-4} M) + HCl + NaOH with pH 7.

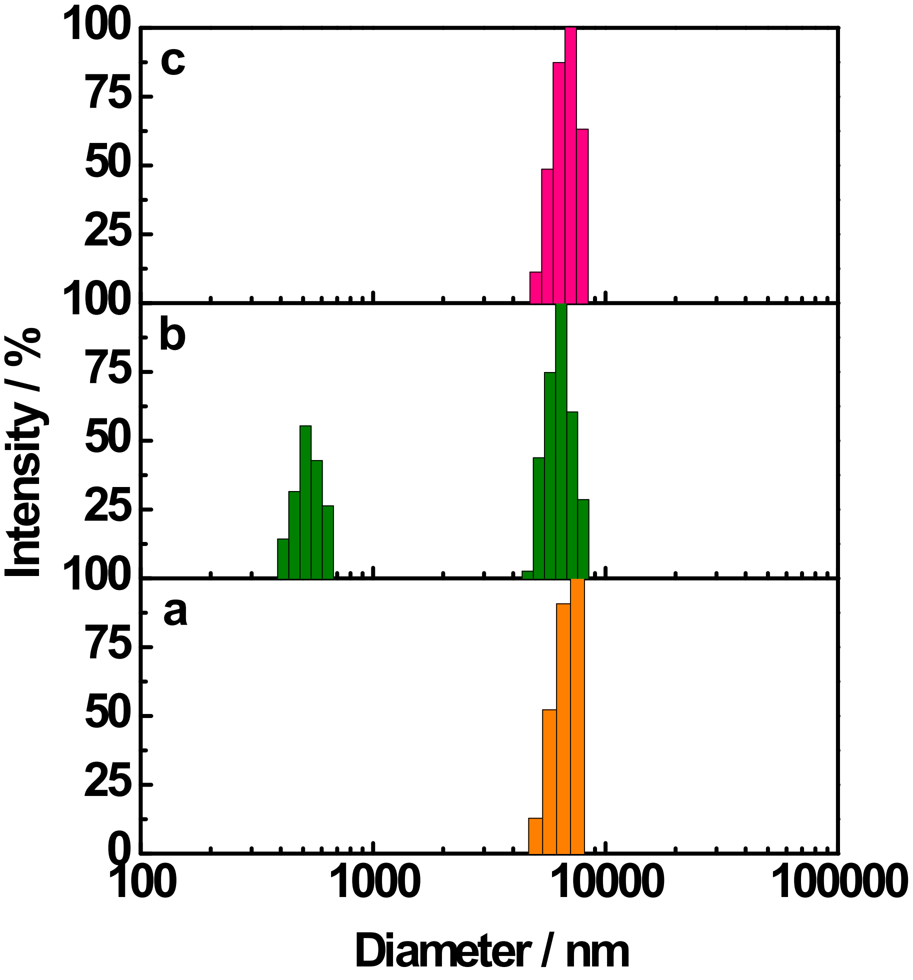

Figure S10. DLS of (a) **1** (2.0×10^{-4} M), (b) **1** (2.0×10^{-4} M) + HCl with pH 3, (c) **1** (2.0×10^{-4} M) + HCl + NaOH with pH 7.

S4 Protonation of DPD@1 by light

In a typical experiment, an aqueous solution of polypseudorotaxane **1** with MEH was exposed to visible light for 5 min to realize proton transfer from photoacid to DPD@**1**. Keeping the solution in the dark resulted in the rethreading of polypseudorotaxane **1**. pH measurements, UV-vis spectra, TEM images and DLS studies were recorded to monitor the threading-dethreading process.

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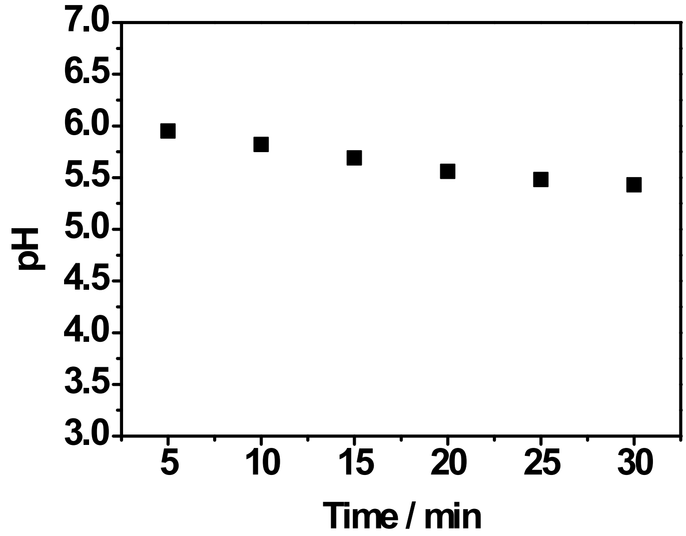

Figure S11. pH of **1** (2.0×10^{-4} M) + MEH (6.0×10^{-4} M) with different irridaition time.

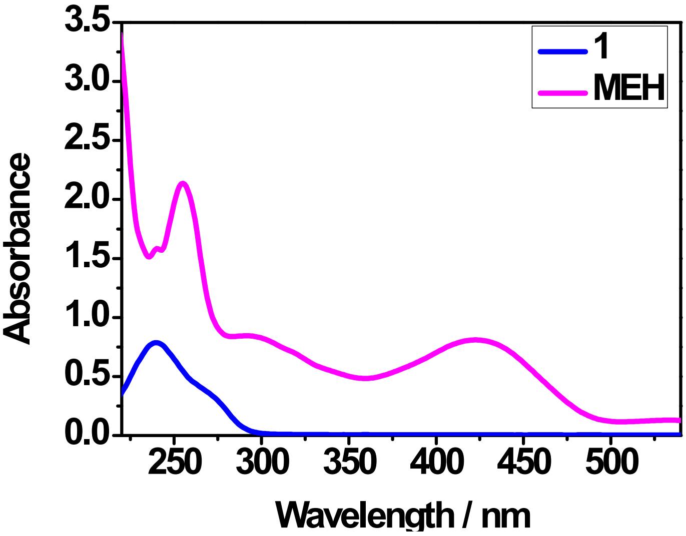

Figure S12. UV−vis absorption of MEH (2×10^{-4} M) and **1** (2×10^{-6} M), respectively

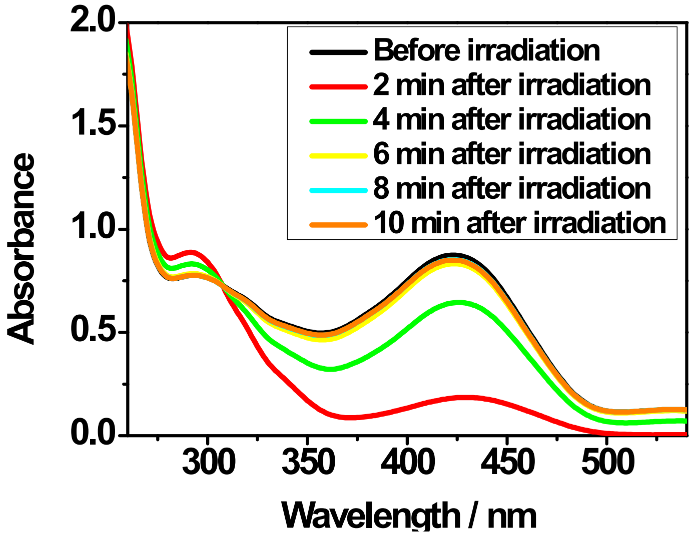

Figure S13. UV−vis absorption of MEH (2 × 10^{-4} M) before and after irradiation. (irradiation at 420 nm for 5 min, and spectra were collected every 2 min after irradiation)

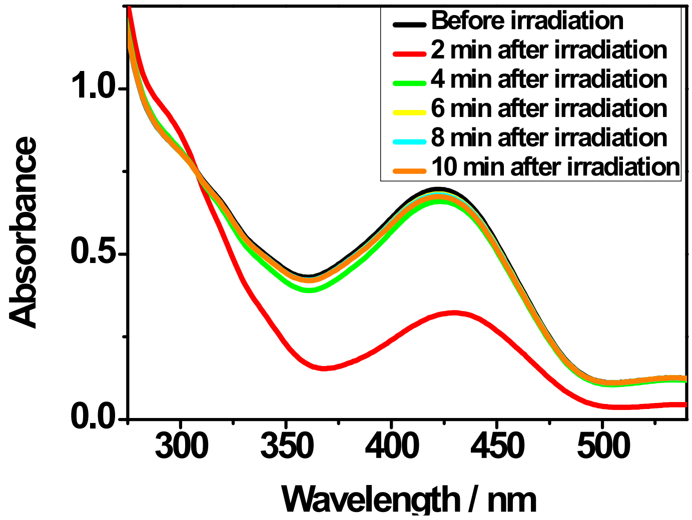

Figure S14. UV−vis absorption of MEH (2 × 10^{-4} M) + **1** (2 × 10^{-6} M) before and after irradiation. (irradiation at 420 nm for 5 min, and spectra were collected every 2 min after irradiation)

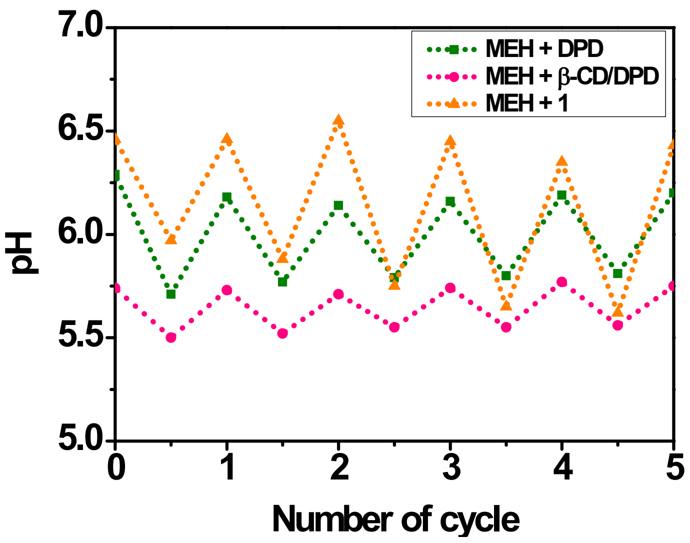

Figure S15. Cycles of pH change under irradiation and in the dark. For each cycle, the solution of DPD (2.95×10^{-3} M) + MEH (6.0×10^{-4} M) (red), and β-CD/DPD (2.95×10^{-3} M) + MEH (6.0×10^{-4} M) (blue) and **1** (2.0×10^{-4} M) + MEH (6.0×10^{-4} M) (red) were irradiated with 420 nm for 5 min and kept in the dark for 15 min.

References:

1. Pires, M. M.; Przybyla, D. E.; Rubert Pérez, C. M.; Chmielewski, J. *J. Am. Chem. Soc.* 2011, **133**, 14699–14703.