Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Photoprinting and expansion-induced erasure with supramolecular hydrogels crosslinked by pseudo-rotaxanation

Yanqin Rong,[a] Ran Liu,[a] Pengyue Jin,[a] Chunhong Liu,[a] Xiaoqian Wang,[a] Lizhi Fang,[a] Long Chen,[a] Wanhua Wu[a] and Cheng Yang*[a]

[a] Key Laboratory of Green Chemistry & Technology of Ministry of Education, College of Chemistry, Sichuan University, 29 Wangjiang Road, Chengdu 610064, China. E-mail: yangchengyc@scu.edu.cn

Table of contents

1. Experimental details

Materials and Instruments.

Cyclodextrins (α, β, γ-CD) and NaN_3 were respectively purchased from Tokyo Chemical Industry and Tianjin Meilin Industry and Trade Co., Ltd. Other used raw materials, including triphenylphosphine, p-toluene sulfonyl chloride and 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NDA), and related reagents (ethanol, acetone, pyridine and DMF) were provided from Tianjin Kermel Chemical Reagent Co., Ltd and Chengdu Kelon Chemical Reagent Factory. Several NH_2-CDs samples in the experiment were synthesized as described in previously reported literature.[1] Likewise, CB [6] was also obtained and purified in advance according to the procedures in the literature.[2] ^1H and ^{13}C NMR spectra at 400 and 101 MHz, respectively, were measured at the ambient temperature on Bruker AMX-400 and all chemical shifts were calibrated with TMS as the internal standard. HRMS data were performed on Waters-Q-TOF Premiers (ESI) and MALDI-TOF mass spectrometer, reported in the unit of mass to charge (m/z). UV-vis spectra were recorded using a JASCO V-650 spectrometer. Scanning electron microscopy (SEM) images were recorded on HITACHI SU-3500 instrument and Fourier transform infrared (FT-IR) spectroscopy measurements were performed on a IRTracer100 spectrophotometer. Circular dichroism spectra were measured on a JASCO J-1500 spectrometer. During the experiments, the photographs of hydrogels were taken with Digital Single Lens Reflex of Canon EOS 70D. The ultra-pure water was supplied with the Millipore system from USA.

Mechanical properties tests:

The mechanical properties of the pseudorotaxane gels were measured using an INSTRON 3366 universal tensile testing with a 1KN load cell to perform the standard stress/strain experiments. Samples were prepared into a rectangular specimen shape (length: ~30 mm: width: 8 mm; thickness: ~1.5 mm), and the tensile rate was 50 mm min^{-1}. Young's modulus was determined from the initial slope of the stress-strain curves. Toughness was calculated by integrating the area below the stress/strain curve.

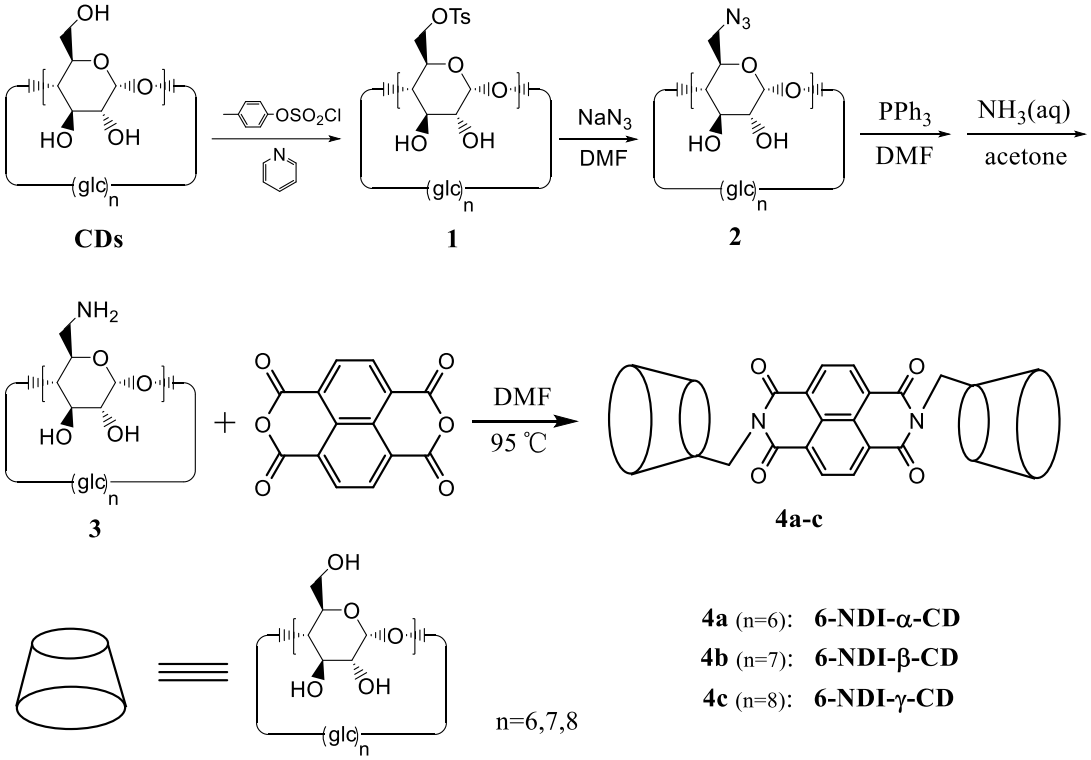
Self-healing experiments:

A sample was cut into two completely separate pieces. The cut faces were gently pressed together, and the sample was placed in a glass-surface vessel to heat at 50 °C for keeping several hours.

Shape memory studies:

The 40 × 8 × 1 mm^3 hydrogel sample was first immersed in deionized water for about 30 s. After stretching the sample, it was wrapped onto a glass rod and fixed with tapes to deform it into a spiral shape for 10 min. Finally, the spirally shaped sample was heated at 50 ℃ by immersing it in deionized water until the shape of the deformed hydrogel achieved recovery. And all the processes were recorded.

2. Synthesis of compound 1–4, DHNDI, axle molecules and Pseudorotaxane gel



Scheme S1. The chemical structure and synthesis route of compounds **1-4**.

Synthesis of compounds 1-4:

Compound **1-3** was prepared according to our previous report.[3]

1: Native β-CD (5.0 g, 4.4 mmol) was dissolved in pyridine (80 mL), and p-toluene sulfonyl chloride (4.0 g, 21.1 mmol) was added in batches under stirring. The reaction mixture was further stirred at room temperature for 5 h, and the solvent was removed under reduced pressure. The crude products were subjected to a C18 reversed-phase column (gradient elution: 10–40 % EtOH), and 6-OTs-β-CD was given as a white solid after freeze-drying (1.7 g, 30.2%).

2: A mixture of 6-OTs-β-CD (1.7 g, 1.3 mmol) and NaN_3 (0.34 g, 5.2 mmol) in 20 mL DMF was stirred and heated at 80 °C for 3 h. After completion of the reaction, DMF was removed under vacuum, and the residue obtained was purified by using a C18 reversed-phase column eluted with aqueous ethanol (gradient elution from 10–40 % EtOH of 1.0 L) to afford the pure product of 6-N_3-β-CD **2** (1.5 g, 80.1%).

3: In a flask, the mixture containing 6-N_3-β-CD (1.5 g, 1.3 mmol), phosphorus triphenyl (1.5 g, 5.7 mmol) in DMF (10 mL) was kept stirring at room temperature for 4 h. Then 5 mL aqueous ammonia solution was added to the reaction solution and stirred for additional 5 h to make the intermediate hydrolysis thoroughly. Then the reaction mixture was poured into acetone to yield a white precipitate, which was collected by filtering to give 6-NH_2-β-CD **3** (1.2 g, 82.0%).

4a-c:

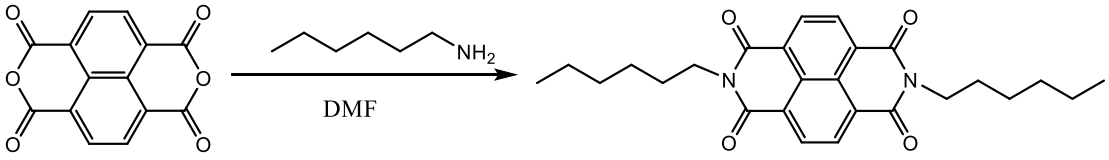
To a slurry of **3** (3.0 g, 2.6 mmol) and K_2CO_3 (200 mg) in dry DMF (100 mL) was added 1,4,5,8-naphthalene-tetracarboxylic dianhydride (400 mg, 1.5 mmol). Then the mixture was heated at 95 °C under magnetic stirring for 6 h. After the solvent was removed under reduced pressure, a small amount of water was added to dissolve the crude product, which was purified by a reversed-phase chromatographic column gradually eluted from 5% to 30% aqueous EtOH to afford solid 6-NDI-β-CD **4b** (yield: 70.8 %). According to the same experimental procedures as above, 6-NDI-α-CD (**4a**, yield: 65.6 %) and 6-NDI-γ-CD (**4c**, yield: 62.9%) were synthesized in good yields.

4a : (Pale yellow powder, 65.6 %). ^{1}H NMR (400 MHz, D_2O): δ 8.52 (s, 4H), 5.13 (dd, J = 34.3, 14.5 Hz, 6H), 4.97 (d, J = 3.2 Hz, 2H), 4.71 (s, 2H), 4.64 (s, 4H), 4.30 – 3.47 (m, 56H), 3.34 (d, J = 9.8 Hz, 6H), 3.22 (s, 4H), 2.80 (s, 2H), 2.13 (s, 2H). ^{13}C NMR (101 MHz, D_2O) δ 163.46, 131.87, 125.44, 125.42, 101.98, 101.53, 101.48, 101.24, 101.17, 101.08, 83.95, 81.20, 81.11, 80.77, 80.49, 73.41, 73.33, 73.15, 73.12, 73.06, 72.91, 72.06, 71.97, 71.88, 71.76, 71.64, 71.57, 71.46, 71.18, 68.99, 60.65, 60.47, 60.05, 59.73, 58.85, 41.50. MALDI-TOF MS m/z: $[M+Na]^+$ calculated for $[C_{86}H_{122}N_2NaO_{62}]^+$, 2197.6347; found, 2197.6344

4b : (Pale yellow powder, 2.3 g, Yield: 70.8 %). ^{1}H NMR (400 MHz, D_2O): δ 8.56 (s, 4H), 5.25 – 4.94 (m, 12H), 4.72 – 4.61 (m, 4H), 4.19 – 3.42 (m, 69H), 3.39 – 3.25 (m, 7H), 3.16 (t, *J* = 8.9 Hz, 2H), 2.78 (s, 2H), 2.35 (d, *J* = 10.8 Hz, 2H). ^{13}C NMR (101 MHz, D_2O) δ 163.75, 131.70, 125.72, 125.58, 102.46, 101.93, 101.87, 101.82, 101.66, 101.61, 101.36, 84.14, 81.11, 81.08, 81.07, 80.72, 80.71, 80.58, 73.07, 72.98, 72.94, 72.78, 72.56, 72.23, 72.12, 72.04, 71.92, 71.86, 71.81, 71.74, 71.64, 71.61, 71.09, 69.10, 60.42, 60.36, 60.03, 59.75, 59.73, 59.26, 41.49. MALDI-TOF MS m/z: $[M+Na]^+$ calcd for $[C_{98}H_{142}N_2NaO_{72}]^+$, 2522.7437; found, 2522.7438

4c : (Light yellow powder, Yield: 62.9%).^{1}H NMR (400 MHz, D_2O): δ 8.56 (s, 4H), 5.30 – 4.93 (m, 16H), 4.62 (s, 3H), 4.22 – 3.41 (m, 79H), 3.39 – 3.21 (m, 8H), 3.13 (s, 2H), 2.72 (s, 2H), 2.44 (s, 2H).^{13}C NMR (101 MHz, D_2O) δ 163.68, 131.78, 125.52, 125.49, 101.66, 101.59, 101.57, 101.53, 101.40, 101.38, 101.28, 101.20, 83.60, 80.68, 80.46, 80.36, 80.21, 80.05, 79.78, 72.93, 72.78, 72.21, 71.79, 71.71, 69.00, 60.32, 60.26, 60.19, 59.96, 59.82, 59.48, 59.46, 41.38. MALDI-TOF MS *m/z*: $[M+Na]^+$ calcd for $[C_{110}H_{162}N_2NaO_{82}]^+$, 2846.8494; found, 2846.8491

Synthesis of compound DHNDI:

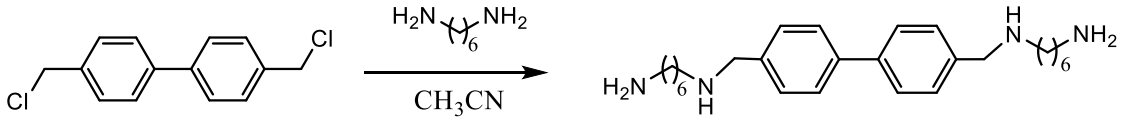


DHNDI

For comparison, **DHNDI** was synthesized from commercially available samples. Thus, 1,4,5,8-naphthalene-tetracarboxylic dianhydride (600 mg, 2.2 mmol) and n-hexylamine (3.0 mL, 22.4 mmol) were dissolved in anhydrous DMF (50 mL) in a round bottom flask. After the addition of K_2CO_3 (250 mg), the mixture was stirred for 6 h at 95 °C. DMF and hexylamine were then removed under reduced pressure, and the residue was dissolved in 30 mL DCM, which was purified by a chromatographic column to afford the pale brown solid **DHNDI** in 55 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 4H), 4.24 – 4.15 (m, 4H), 1.74 (dt, *J* = 15.3, 7.5 Hz, 4H), 1.48 – 1.40 (m, 4H), 1.39 – 1.29 (m, 8H), 0.90 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.00, 131.02, 126.91, 41.10, 31.65, 28.21, 26.89, 22.75, 14.19. HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{26}H_{31}N_2O_4]^+$, 435.2278; found, 435.2280.

Synthesis of axle molecules:

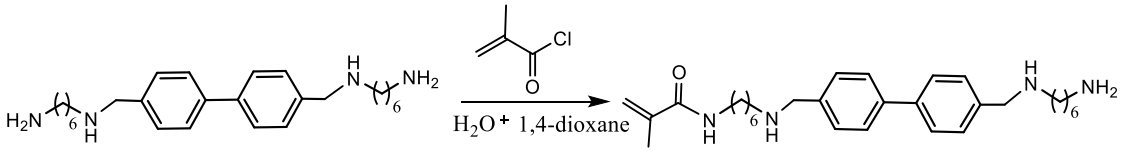
Axle-1:



Axle-1

4, 4’-bis(chloromethyl)biphenyl (500 mg, 2.0 mmol), and hexanediamine (2.3 g, 19.8 mmol) were dissolved in dry CH_3CN (40 mL), and the solution was heated at 70 °C for 24 h. After the solvent was removed under vacuum by rotary evaporators, the resultant precipitate was dissolved in an HCl aqueous solution, which was further collected and purified on a C18 reversed-phase chromatographic column to give a white solid **Axle-1** (492 mg, yield: 60.3%). ^{1}H NMR (400 MHz, D_2O) δ 7.68 (d, *J* = 8.3 Hz, 4H), 7.47 (d, *J* = 8.3 Hz, 4H), 4.18 (s, 4H), 3.03 – 2.95 (m, 4H), 2.87 (t, *J* = 7.6 Hz, 4H), 1.66 – 1.51 (m, 8H), 1.30 (m, 8H). ^{13}C NMR (101 MHz, D_2O) δ 140.79, 130.46, 130.35, 127.66, 50.50, 46.93, 39.29, 26.44, 25.24, 25.07. HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{26}H_{43}N_4]^+$, 411.3482; found, 411.3462

Axle-2:

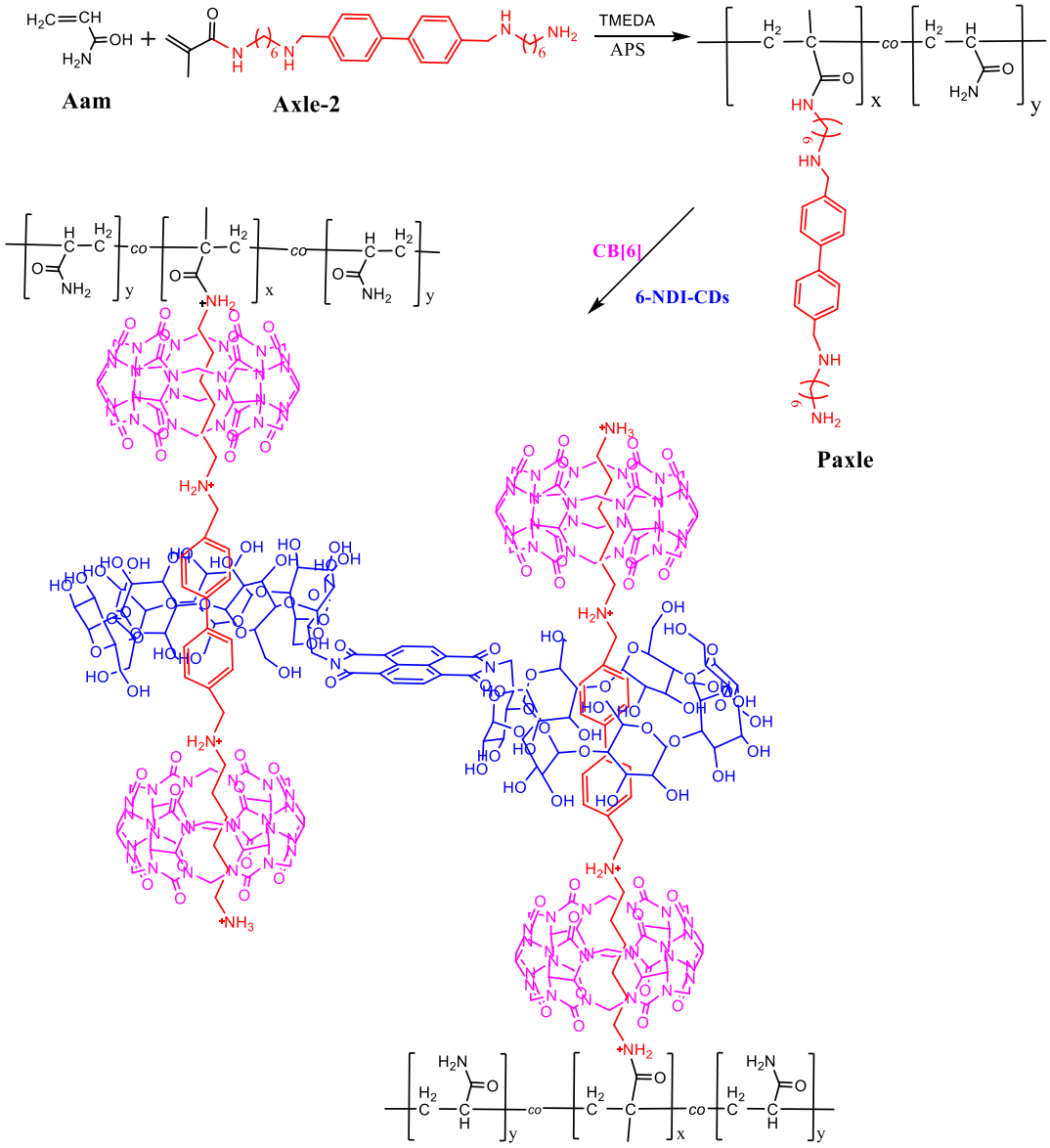


Axle-2

A solution of **Axle-1** (500 mg, 1.2 mmol) in H_2O (50 mL) containing a certain amount of $NaHCO_3$ (pH 8.5) was stirred at 0°C for 30 minutes. Methacryloyl chloride (130 μL, 1.3 mmol) and triethylamine (203 μL) in 1,4-dioxane (60 mL) were dropwise added to the above mixture in an ice bath. The mixture was then allowed to react for 1 h at 0°C and 20 h at the ambient temperature. When the organic solvent was evaporated under reduced pressure, the residue was purified by a C18 reversed-phase chromatographic column with ultra-pure water to give the **Axle-2** as a white solid in 17.1% yield. ^{1}H NMR (400 MHz, D_2O) δ 7.78 (d, *J* = 8.2 Hz, 4H), 7.57 (d, *J* = 8.2 Hz,

4H), 5.61 (s, 1H), 5.38 (s, 1H), 4.27 (s, 4H), 3.21 (t, *J* = 6.9 Hz, 2H), 3.07 (dd, *J* = 15.9, 9.9 Hz, 4H), 2.97 (t, *J* = 7.6 Hz, 2H), 1.88 (s, 3H), 1.76 – 1.60 (m, 6H), 1.56 – 1.47 (m, 2H), 1.44 – 1.29 (m, 8H). ^{13}C NMR (101 MHz, D_2O) δ 163.03, 162.67, 140.83, 139.21, 130.43, 127.66, 120.57, 117.69, 114.80, 50.44, 46.83, 39.24, 32.56, 27.96, 26.44, 25.20, 17.62. HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{29}H_{45}N_4O]^+$, 479.3744; found, 479.374

Synthesis of the SPH:



Scheme S2. The formation of the **SPH**

The hydrogel was prepared by co-polymerizing **Axle-2**/acrylamide mixtures and forming a pseudorotaxane composite structure by adding CB[6] and NDI-CD-dimer (6-NDI-CDs). Thus, acrylamide monomers and **Axle-2** were mixed in the deionized water and stirred to give a homogenous solution. Subsequently, as a redox initiation system,

ammonium peroxodisulphate/N, N, N, N'-tetramethylethylene-diamine (APS/TMEDA), was added in the **Axle-2**/acrylamide mixtures to form the co-polymer **Paxle** which made the solution viscous. After the addition of CB[6] and NDI-CD-dimer (6-NDI-CDs), the solid was gradually dissolved under the heated condition. The mixture was placed at 70 ℃ for 30 min, then transferred to different molds, and stood at room temperature until the viscous solution was coagulated to form a final hydrogel (**SPH**).

3. NMR and HRMS spectra of compounds

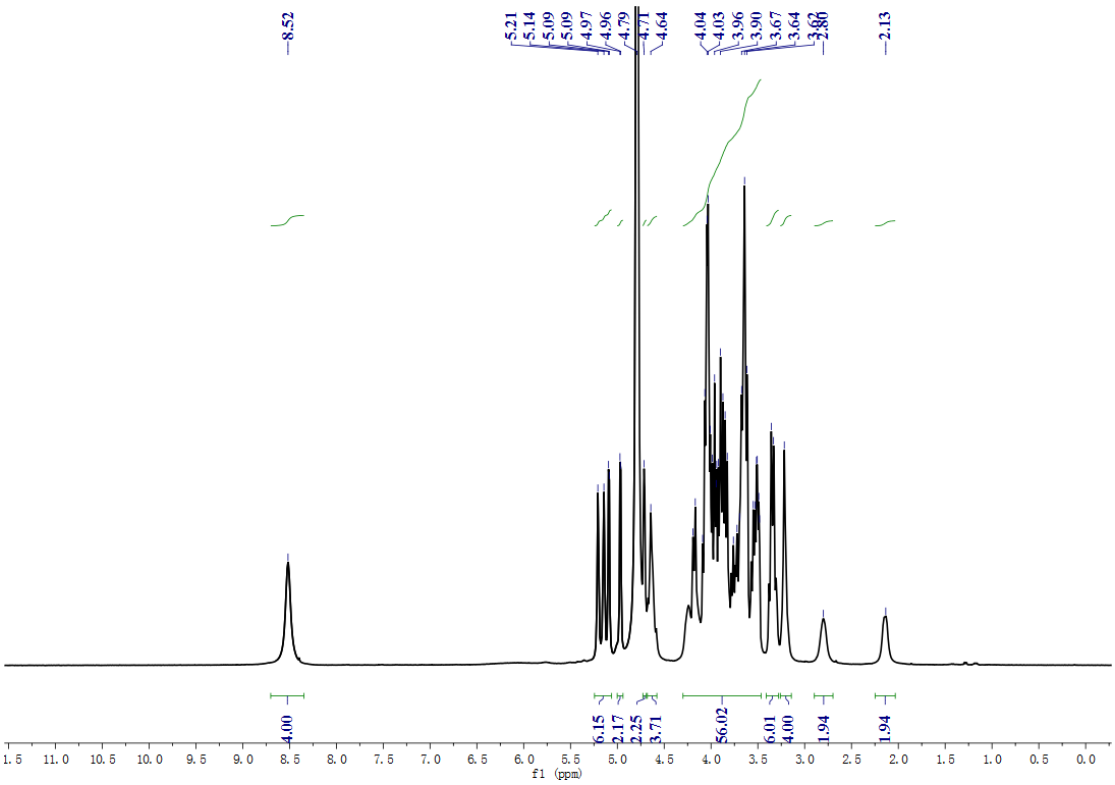


Fig. S1 ^{1}H NMR spectrum (400 MHz, D_2O) of **4a (6-NDI-α-CD)**

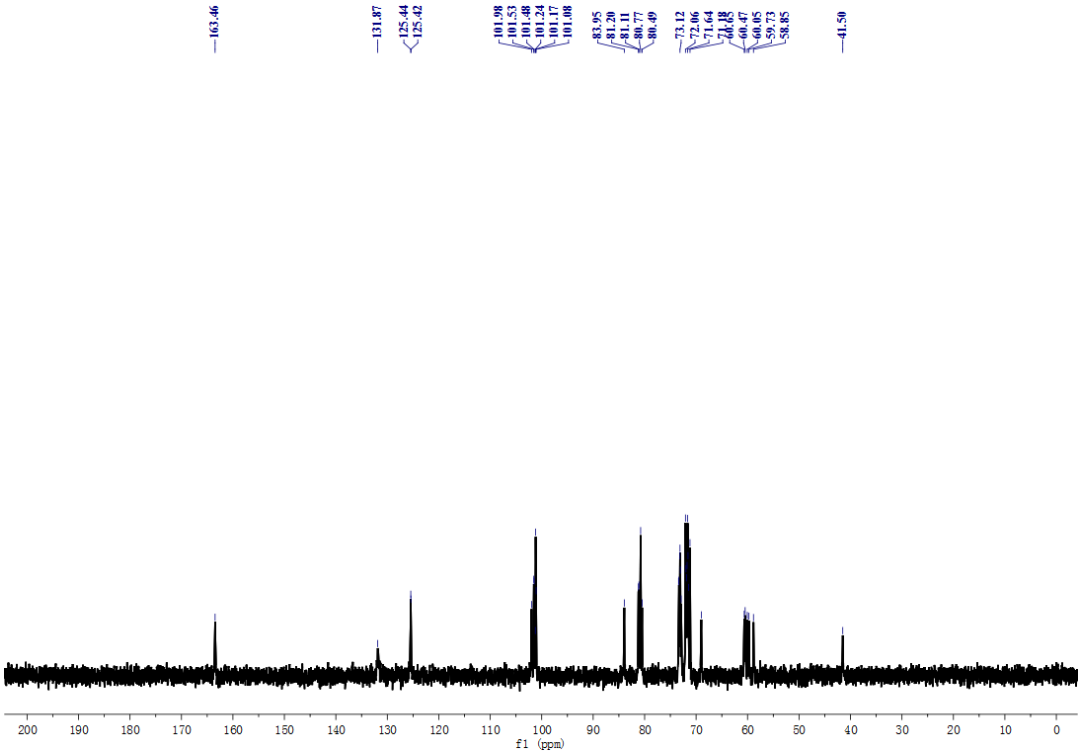


Fig. S2 ^{13}C NMR spectrum (101 MHz, D_2O) of **4a** (**6-NDI-α-CD)**

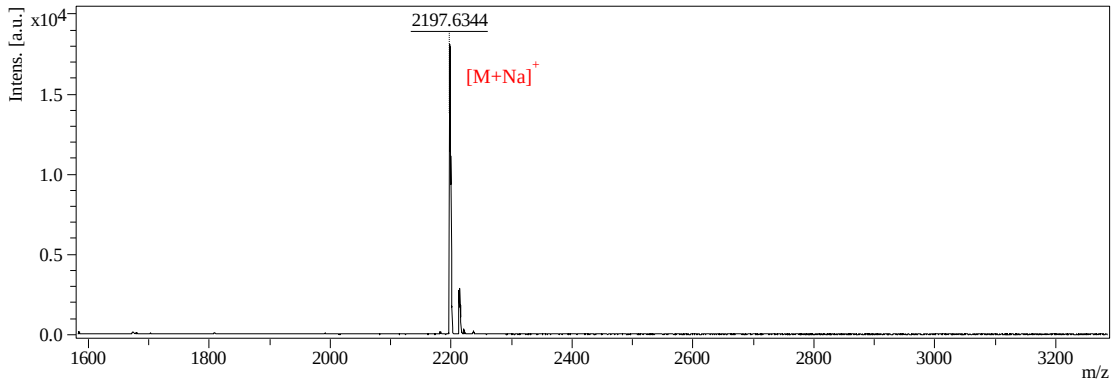


Fig. S3 MALDI-TOF mass spectrum of **4a** (**6-NDI-α-CD)**

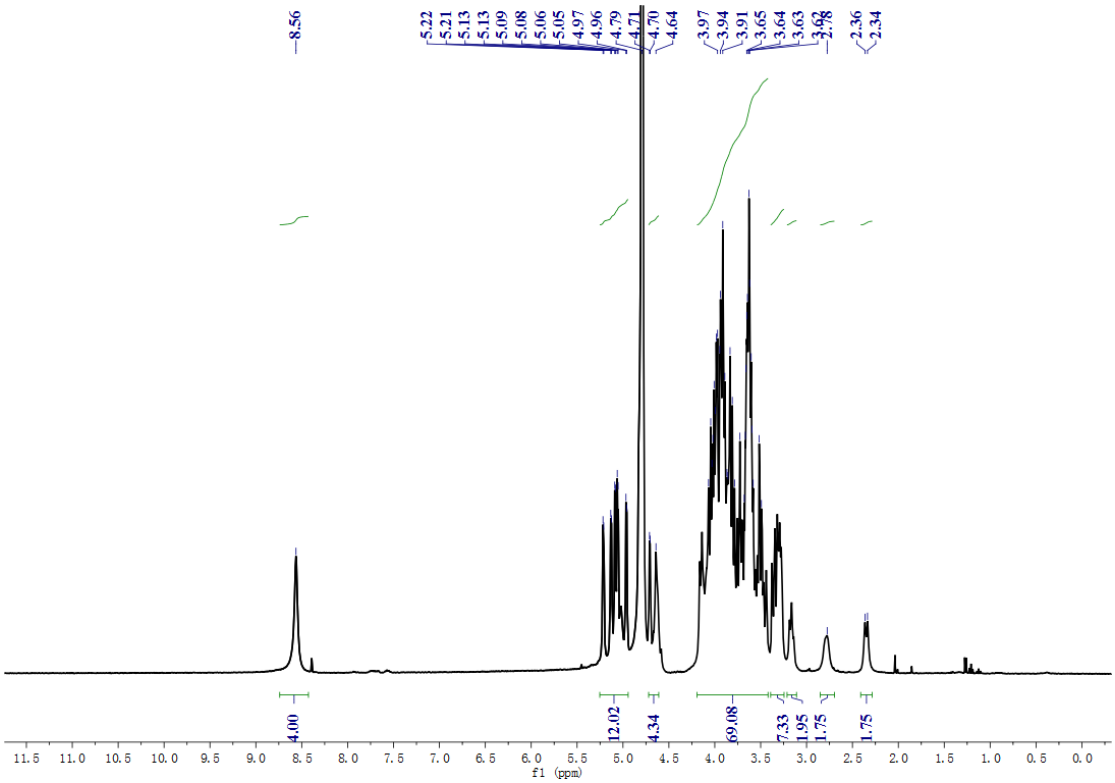


Fig. S4 ^{1}H NMR spectrum (400 MHz, D_2O) of **4b (6-NDI-β-CD)**

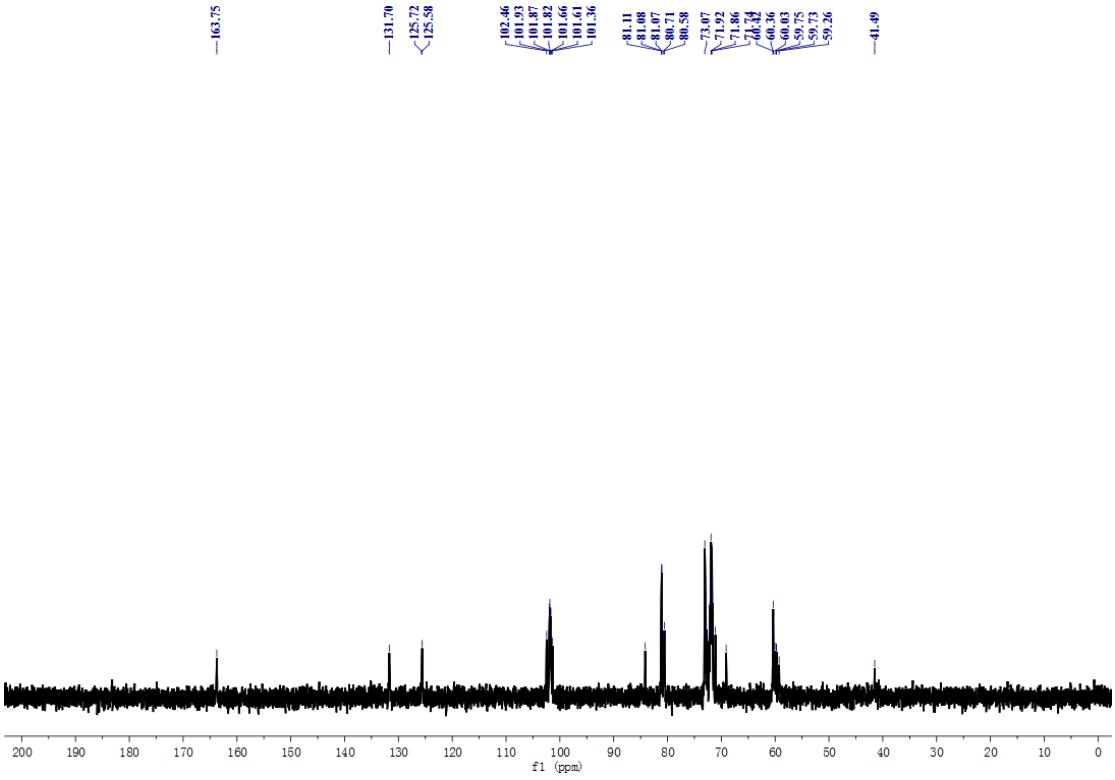


Fig. S5 ^{13}C NMR spectrum (101 MHz, D_2O) of **4b (6-NDI-β-CD)**

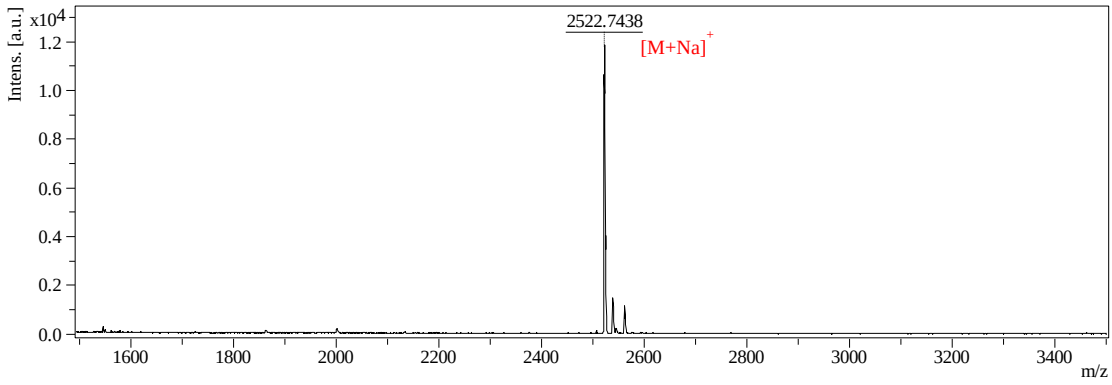


Fig. S6 MALDI-TOF mass spectrum of **4b (6-NDI-β-CD)**

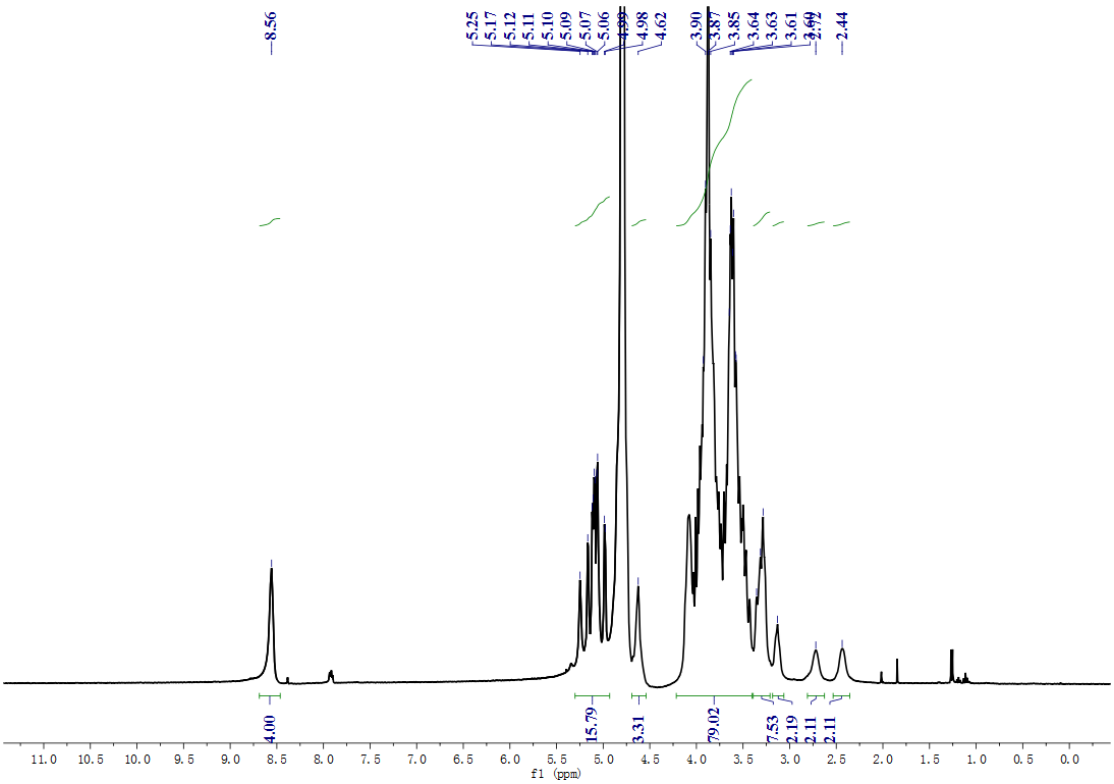


Fig. S7 ^{1}H NMR spectrum (400 MHz, D_2O) of **4c (6-NDI-γ-CD)**

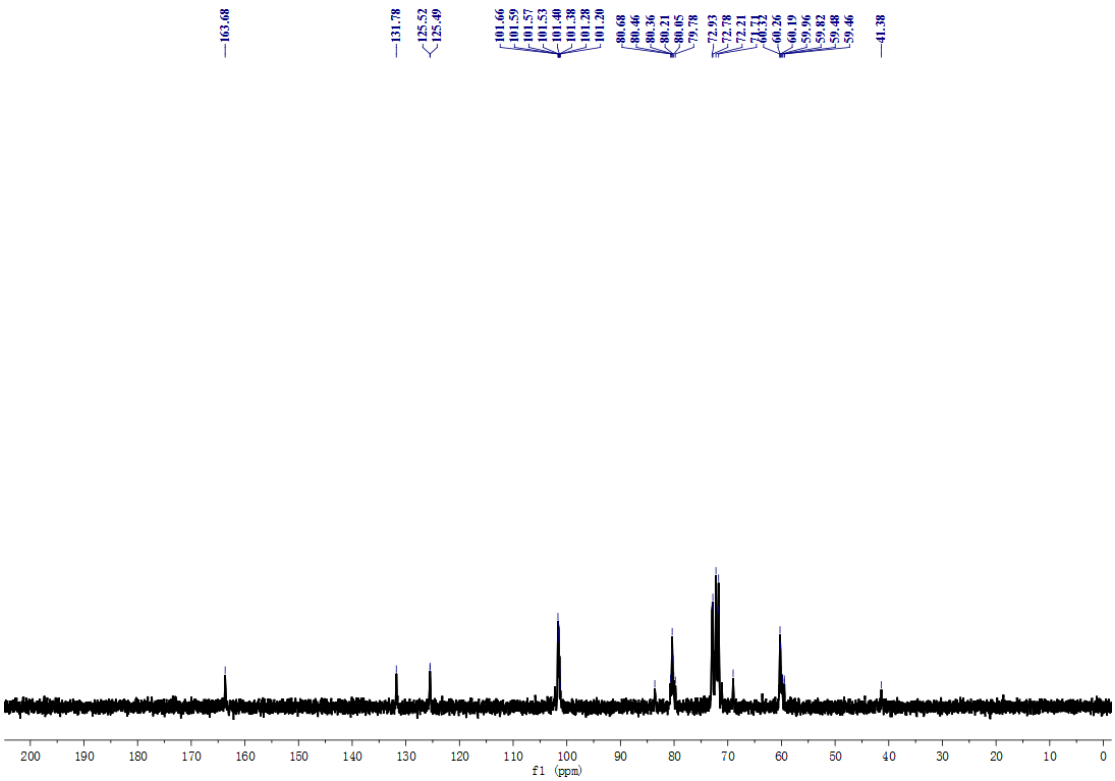


Fig. S8 ^{13}C NMR spectrum (101 MHz, D_2O) of **4c (6-NDI-γ-CD)**

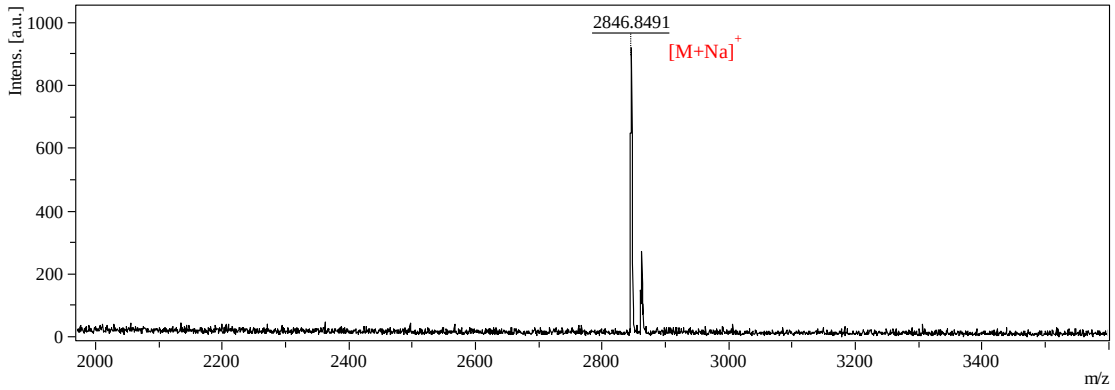


Fig. S9 MALDI-TOF mass spectrum of **4c (6-NDI-γ-CD)**

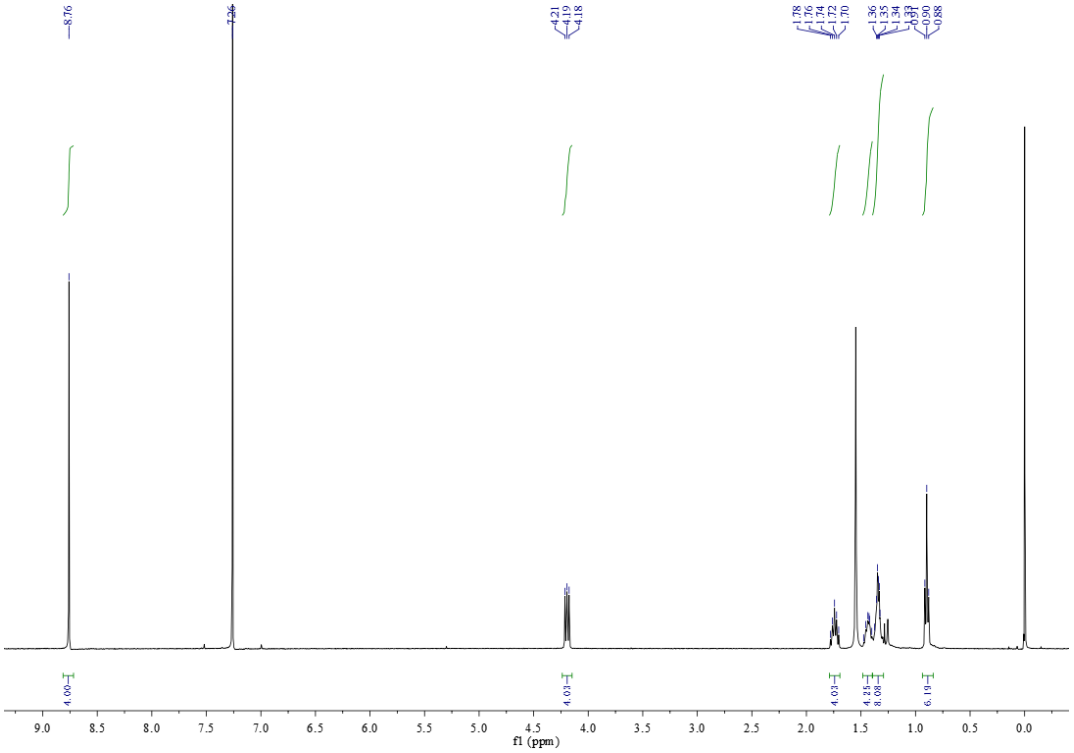


Fig. S10 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of sample **DHNDI**

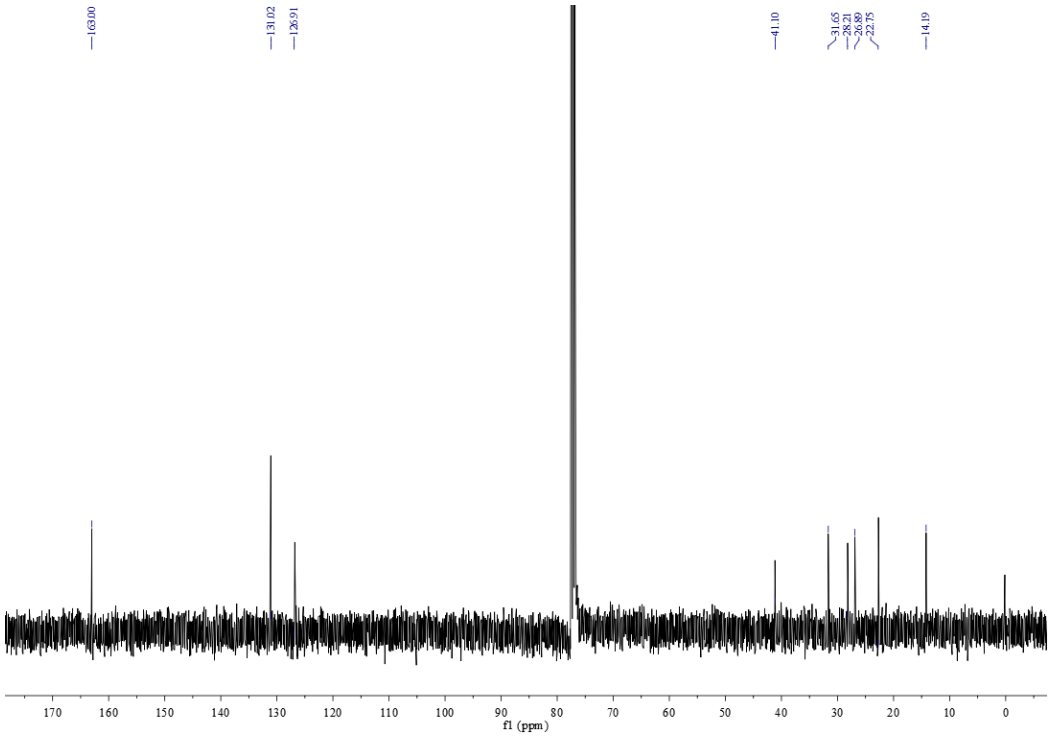


Fig. S11 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **DHNDI**

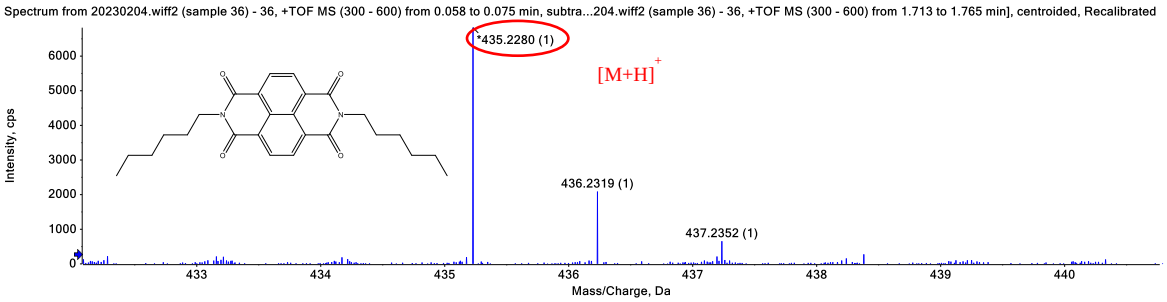


Fig. S12 HRMS spectrum of **DHNDI**

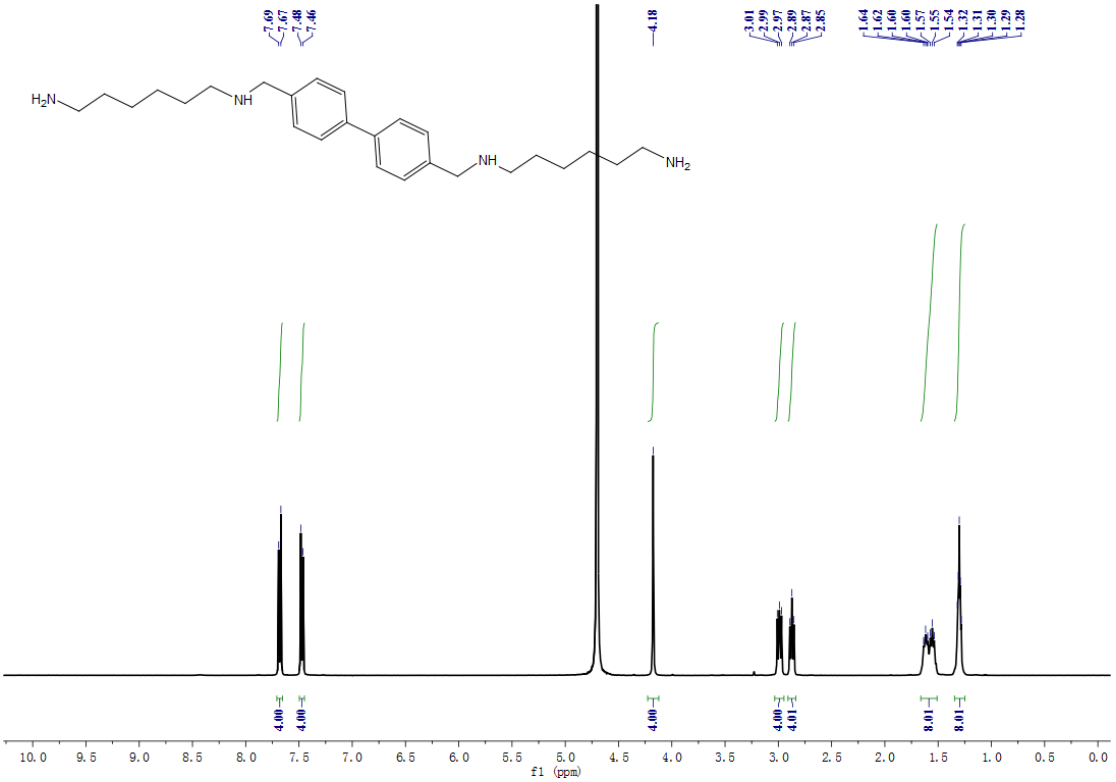


Fig. S13 ^{1}H NMR spectrum (400 MHz, D_2O) of **Axle-1**

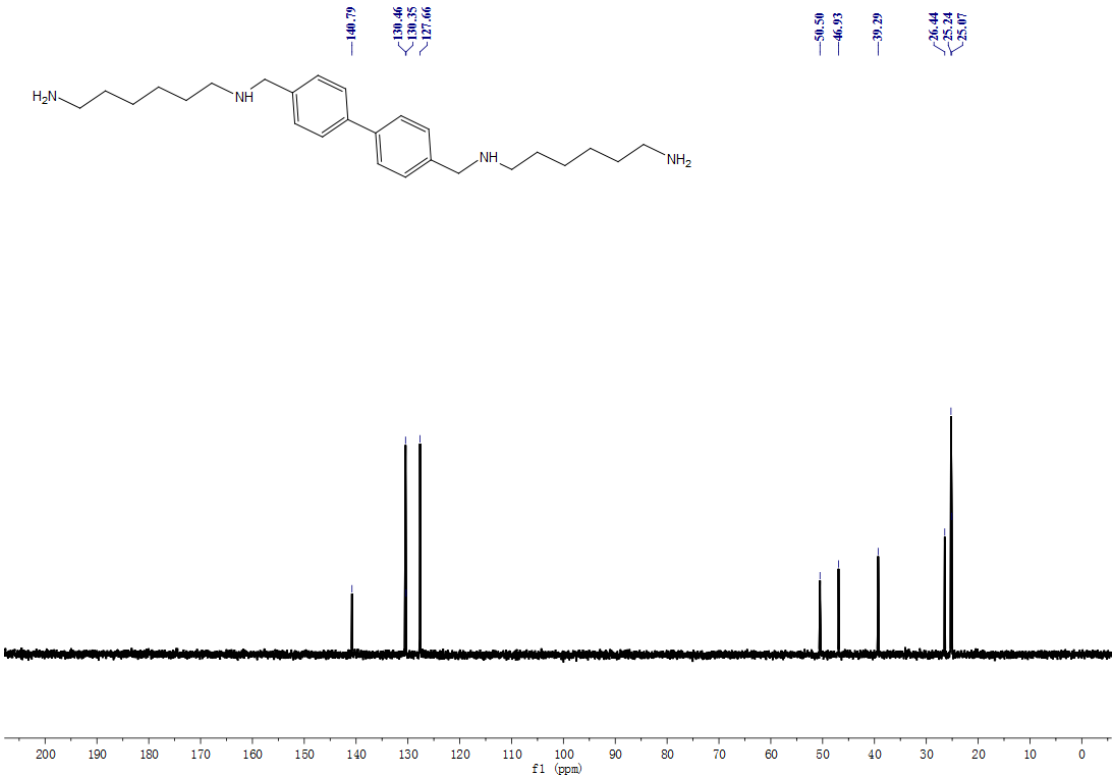


Fig. S14 ^{13}C NMR spectrum (101 MHz, D_2O) of **Axle-1**

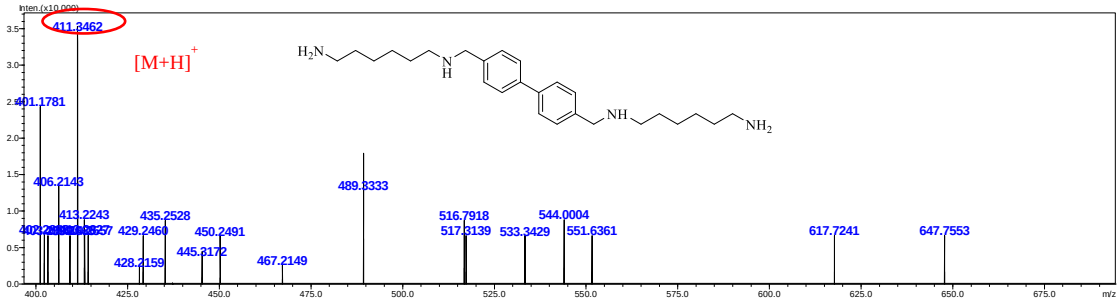


Fig. S15 HRMS spectrum of **Axle-1**

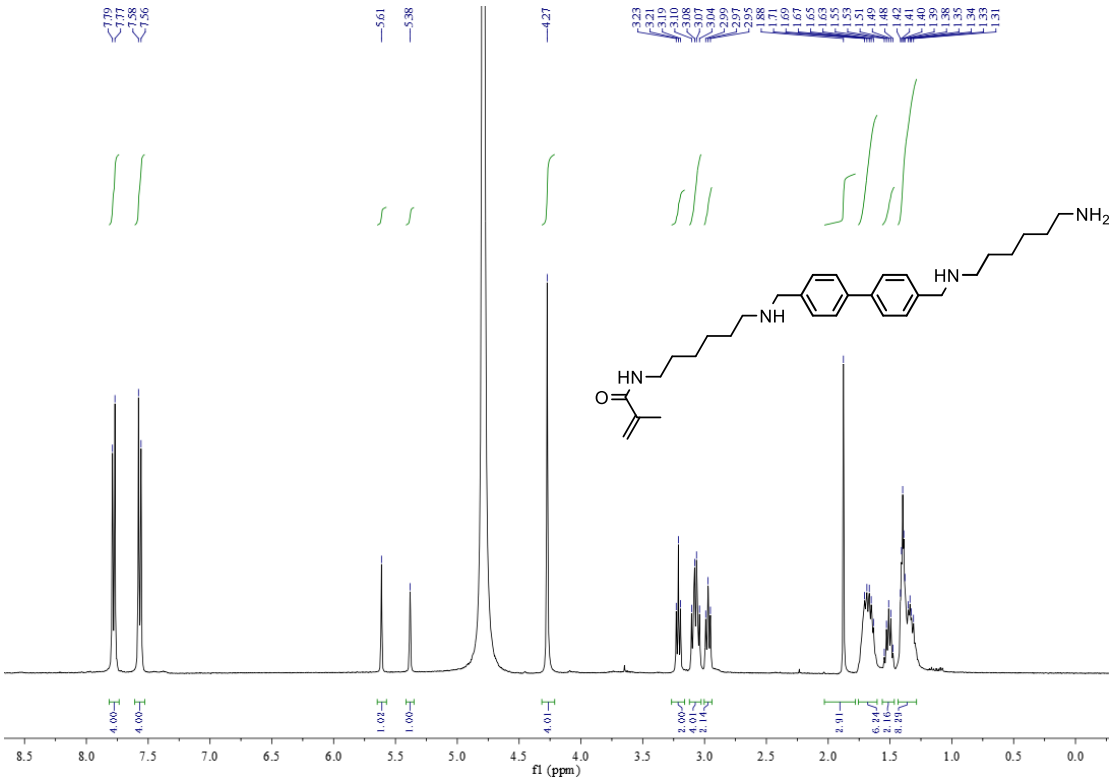


Fig. S16 ^{1}H NMR spectrum (400 MHz, D_2O, room temperature) of sample **Axle-2**

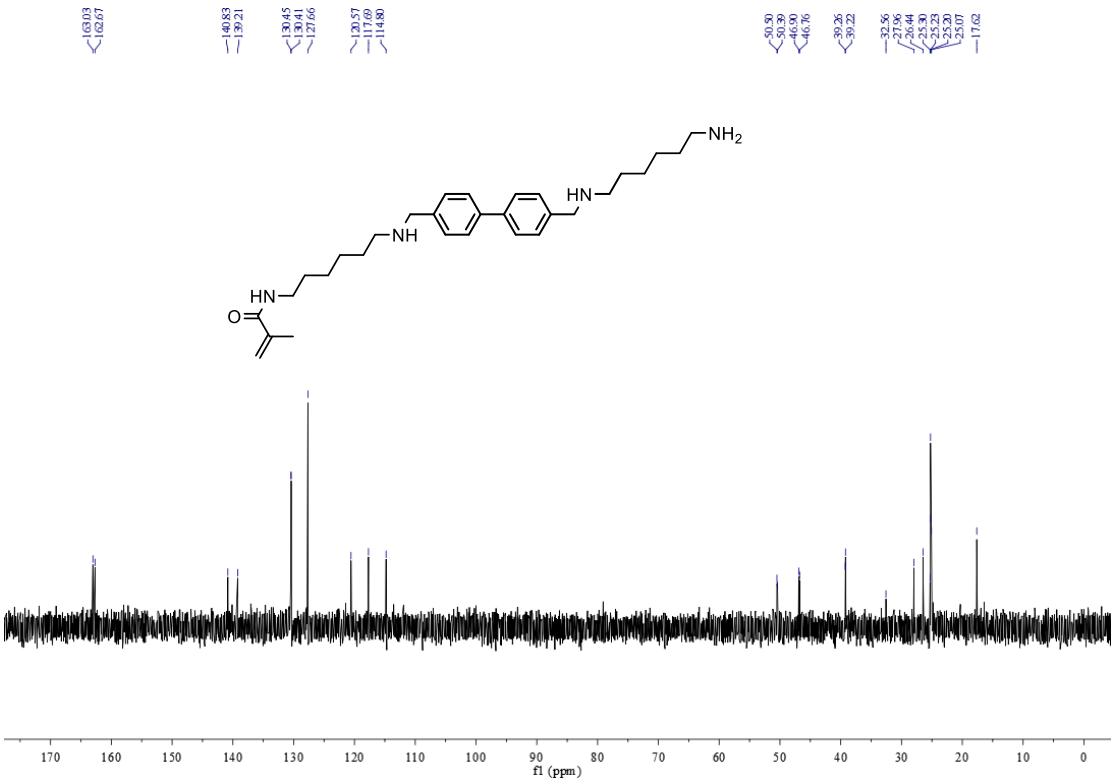


Fig. S17 ^{13}C NMR spectrum (101 MHz, D_2O) of **Axle-2**

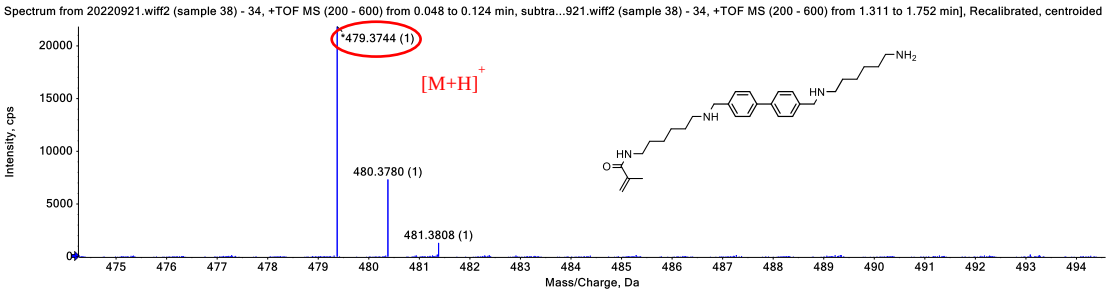
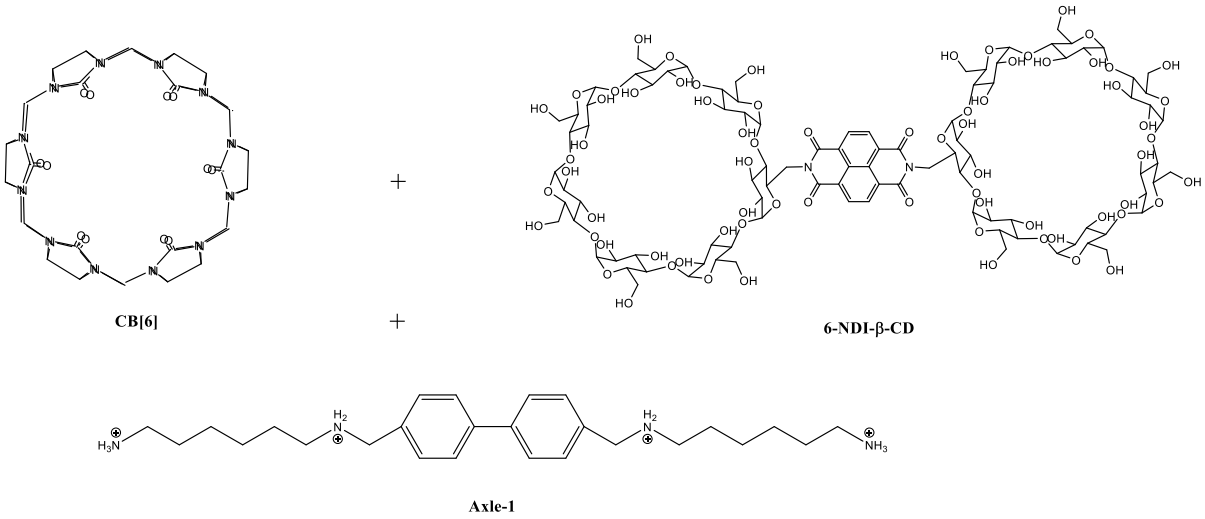
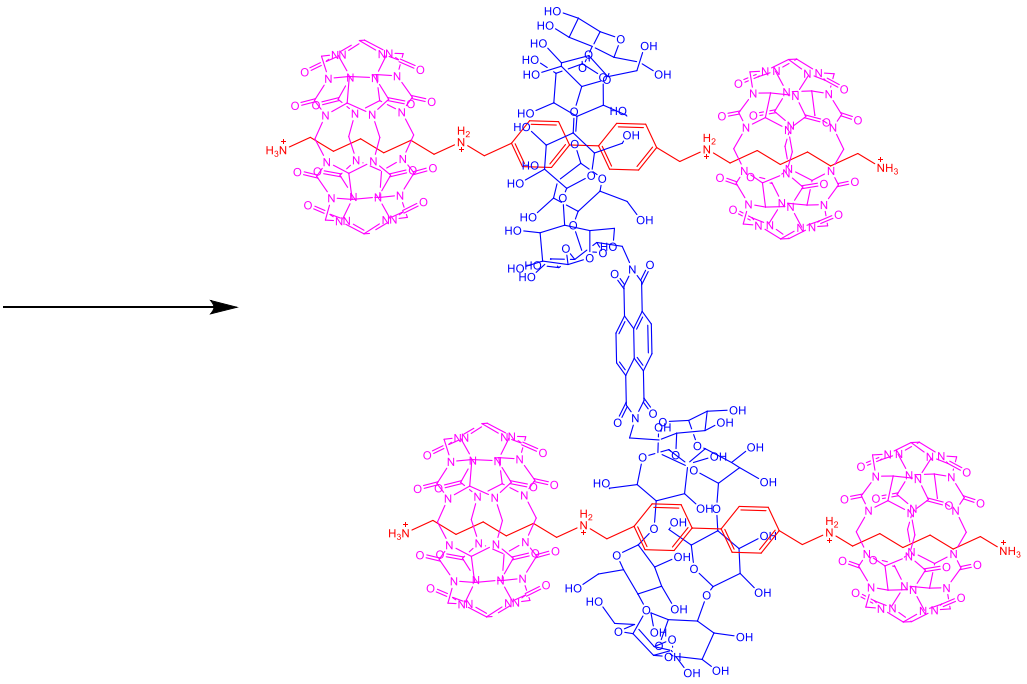


Fig. S18 HRMS spectrum of **Axle-2**

4. Synthesis and Characterization of the other Pseudorotaxane structure formed by CB[6], 6-NDI-β-CD and Axle-1





Scheme S3. The obtained pseudorotaxane structure mixed by CB[6], 6-NDI-β-CD and **Axle-1**

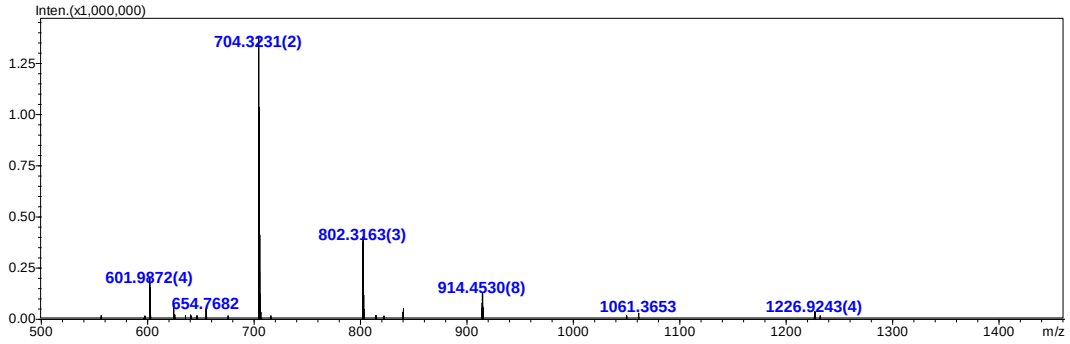


Fig. S19 HRMS spectrum measured for the mixture containing CB[6], **Axle-1** and 6-NDI-β-CD.

[CB[6]+**Axle-1**]$^{2+}$ calcd for: m/z = 704.3250, found: m/z = 704.3231
[2CB[6]+ **Axle-1**]$^{3+}$ calcd for: m/z = 802.3183, found: m/z = 802.3163
[2CB[6]+ **Axle-1**]$^{4+}$ calcd for: m/z = 601.9906, found: m/z = 601.9872
[2CB[6]+ **Axle-1**+6-NDI-β-CD]$^{4+}$ calcd for: m/z = 1226.9292, found: m/z = 1226.9243
[4CB[6]+2 **Axle-1**+6-NDI-β-CD]$^{8+}$ calcd for: m/z = 914.3345, found: m/z = 914.4530

5. UV-vis spectra of 6-NDI-CDs

The photo-induced reduction of 6-NDI-CDs in solution

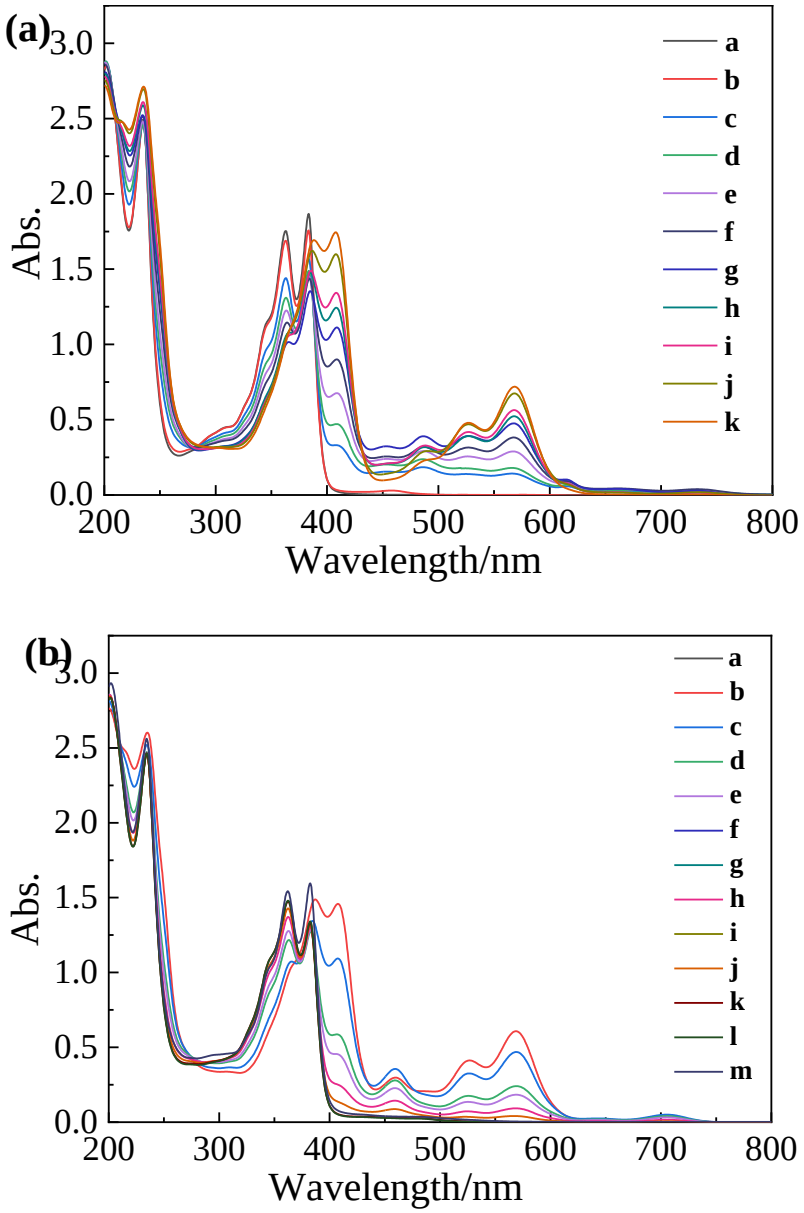


Fig. S20 (a) UV-Vis spectral change of 0.1 mM 6-NDI-α-CD in aqueous solution upon photoirradiation at 20 °C. **a** is the unirradiated sample, **b**~**k** represents the spectral change upon photoirradiation with a 365 nm LED lamp. (b) UV-Vis spectral changes after exposing the photoirradiated 6-NDI-α-CD to the air at 20 °C. From **a** to **m** is the UV-Vis spectral change within two hours after the sample was exposed to air.

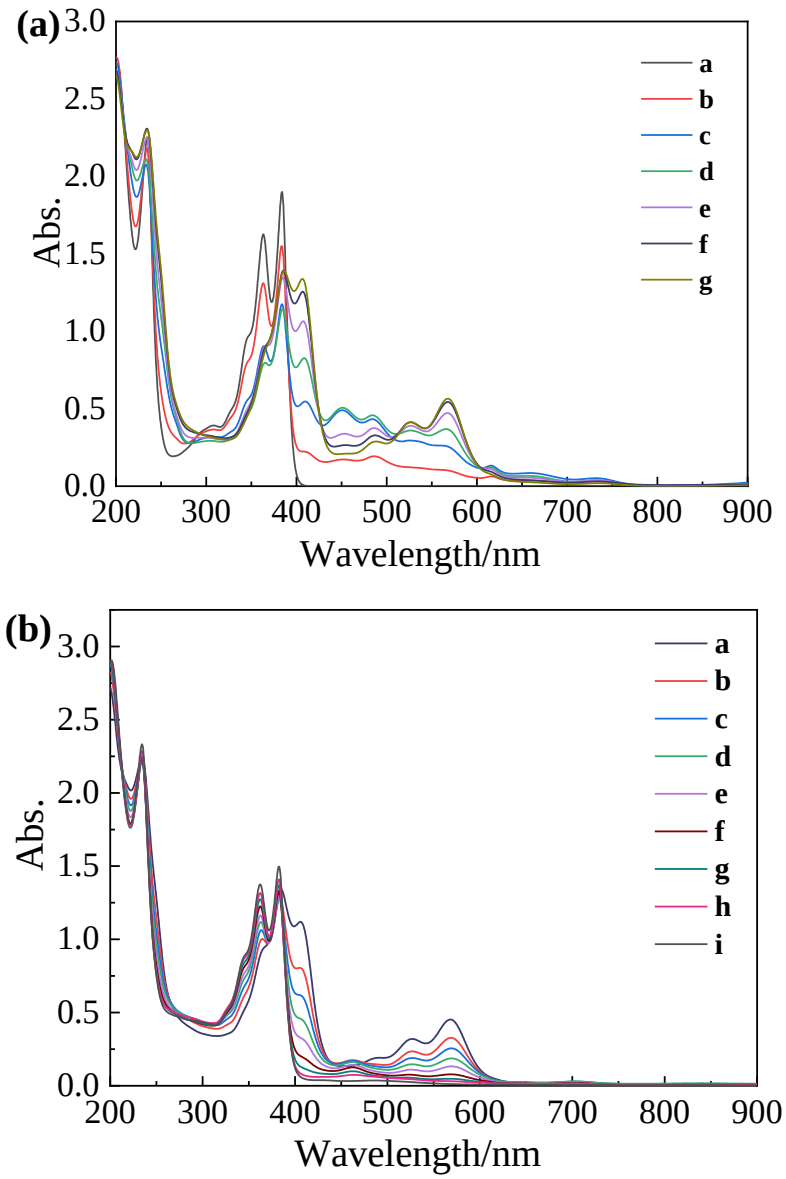


Fig. S21 (a) UV-Vis spectral changes of 0.1 mM 6-NDI-γ-CD in aqueous solution upon photoirradiation at 20 °C. **a** is the unirradiated sample, **b**~**g** represents the spectral change upon photoirradiation with a 365 nm LED lamp. (b) UV-Vis spectral changes after exposing the photoirradiated 6-NDI-γ-CD to the air at 20 °C. From **a** to **i** is the UV-Vis spectral change within two hours after the sample was exposed to air.

Photochromism of 6-NDI-CDs

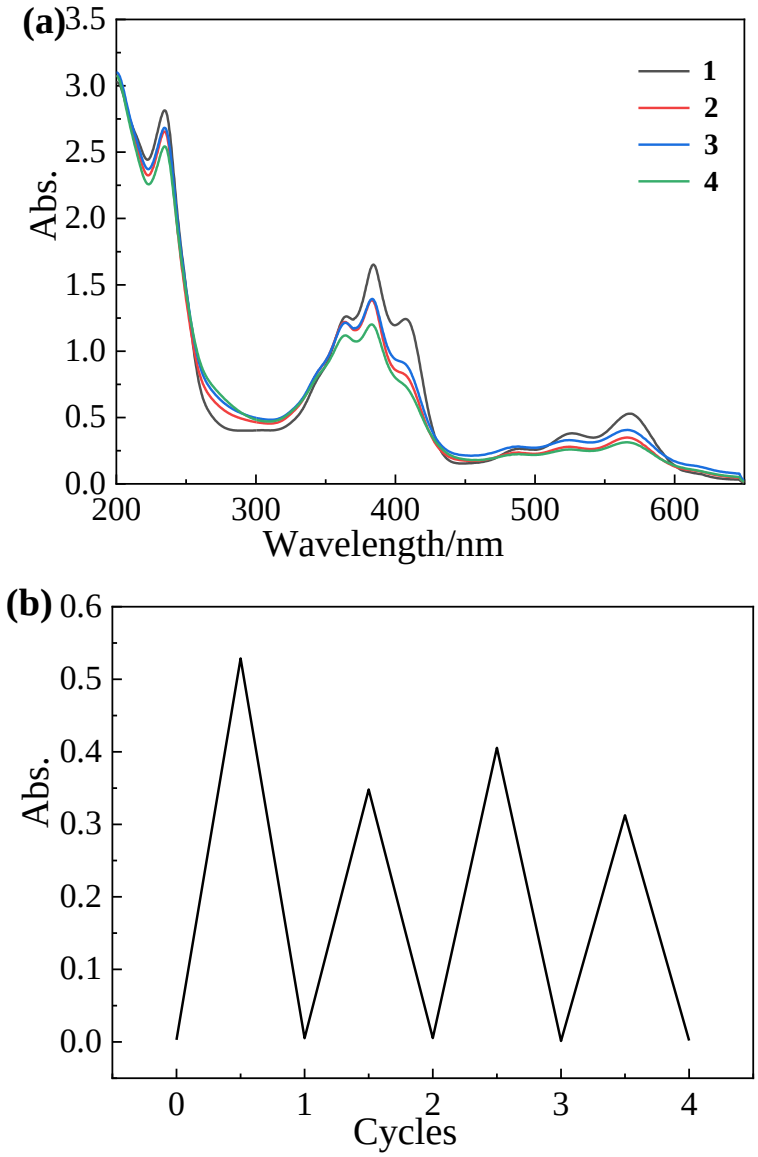


Fig. S22 (a) UV-Vis absorption spectra of photoirradiated samples of 6-NDI-β-CD; (b) The plot of the absorption value at 567.5 nm versus the number of cycles for writing/erasing (n=1, 2, 3, 4)

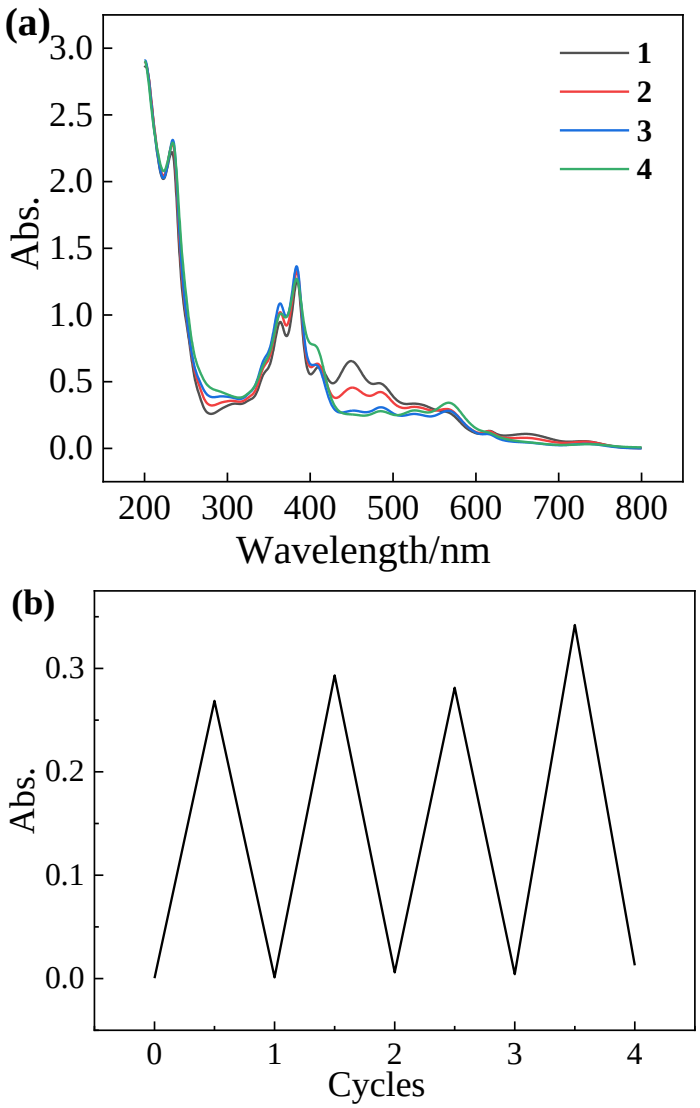
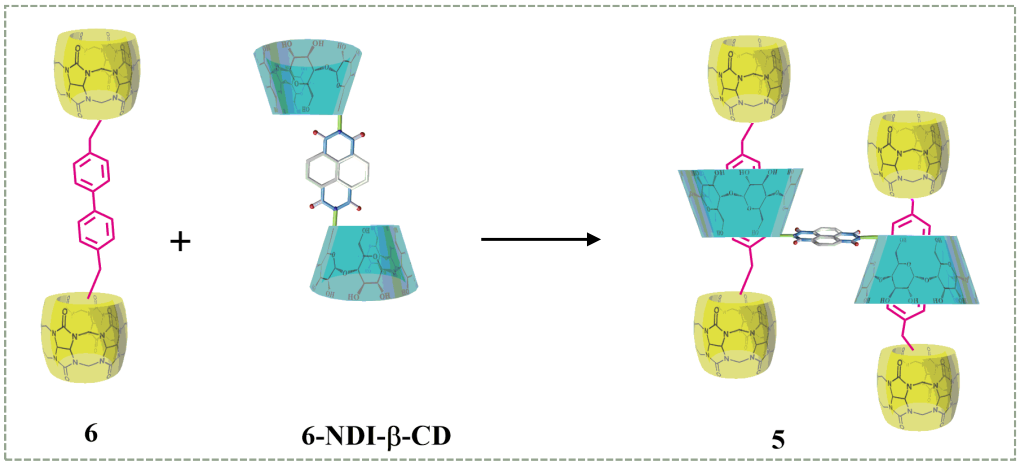


Fig. S23 (a) UV-Vis absorption spectra of photoirradiated samples of 6-NDI-γ-CD; (b) The plot of the absorption value at 567 nm versus the number of cycles for writing/erasing (n=1, 2, 3, 4)

6. Time-dependent CD spectral changes



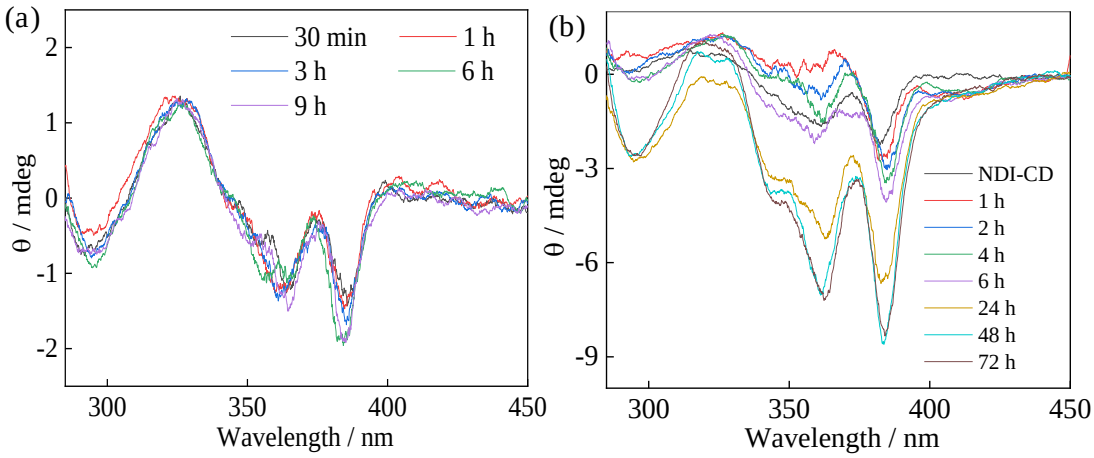


Fig. S24 Time-dependent CD spectral changes upon addition of 6-NDI-β-CD (0.1 mM) to the aqueous solution of (a) **Axle-1** (0.2 mM) and (b) the dumbbell-shaped complex **6** (0.2 mM) at 20 °C.

7. Properties investigations of the SPHs:

Swelling Properties:

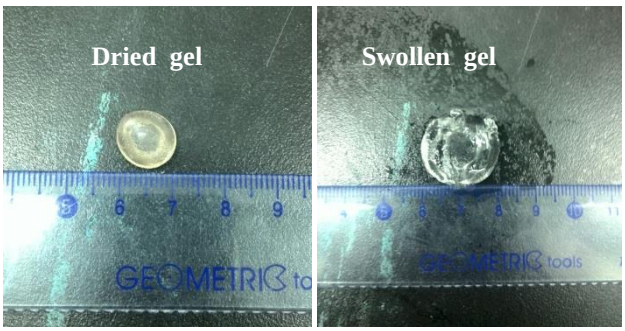


Fig. S25 Photographs of the swelling experiment of gel before and after being soaked for two hour in water. Left: the dried gel; right: the water-swollen gel.

A swelling experiment for **SPH** was conducted at ambient temperature by soaking the dry gel to give swollen gel (**Fig. S25**), which presented a distinct swelling behavior in water. As shown in Table S1, after being soaked in water for 2 hr, the diameter of the gel increased from 10 mm to 20 mm, and the weight raised to 1.2417 g from 0.2287 g of the dry gel. The swelling property was calculated by swelling degree or swelling ratio (Q) using the following equation:

$$Q = \frac{W_t - W_0}{W_0}$$

where W_t is the weight of the sample after swelling solution, and W_0 is the weight of the dry sample. The swelling ratio value of **SPH** was determined to be 4.4.

Table S1. The weight and size of the dried gel before and after immersion for 2 hr in water

	Weight (g)	Diameter (mm)	Swelling degree
The dried gel	0.2287	10	
The water-swollen gel	1.2417	20	4.4

Transparency experiment:

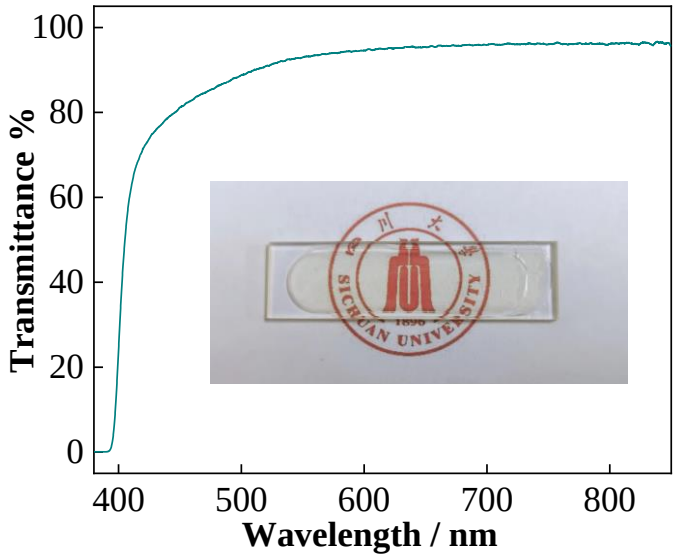


Fig. S26 Optical transmittance of **SPH** in the wavelength range of 380 to 850 nm; inset: light transmission photographs of **SPH** (water content: 62 wt%; thickness: 1.5 mm)

Stretching Properties:

Table S2. The parameters before and after stretching of **SPH** as well as at different time

	Gel length (cm)	Stretching ratio (%)
before stretching	2.5	—
stretching	30	1100%
3 min after stretching	4	—
6 hr after stretching	2.7	—

Anti-shear ability：

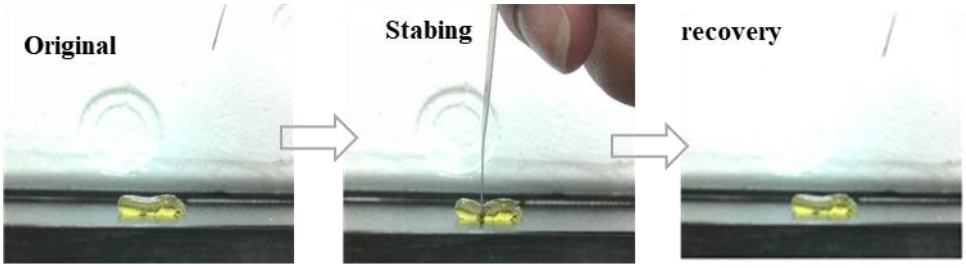


Fig. S27 Images of **SPH** punctured by using a sharp needle and then rapid recovery without piercing.

Mechanical properties:

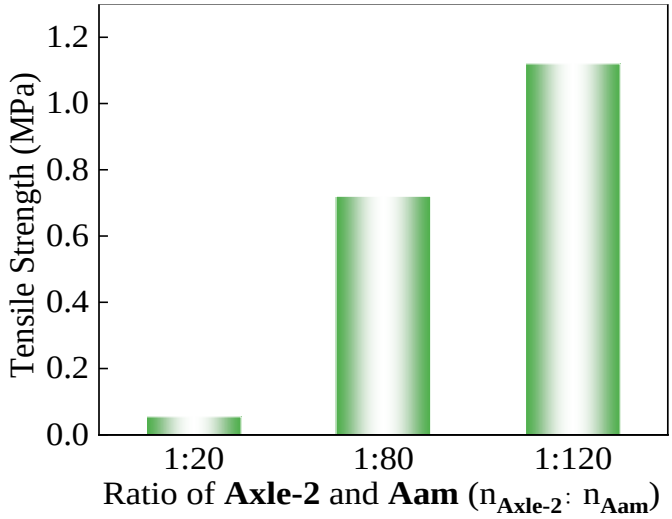


Fig. S28 Tensile strength of **SPH** with different ratios of **Axle-2** and **Aam**.

Table S3 Mechanical properties of **SPH**

Gel samples with different ratios of **Axle-2** and **Aam**	Fracture stress [MPa]	Fracture strain [%]	Young's modulus [MPa]	Toughness [MJ/m^3]
1:20	0.054	1966	0.065	0.09
1:80	0.72	903	0.18	3.80
1:120	1.12	243	1.01	1.93

Reference

1 A. R. Khan, P. Forgo, K. J. Stine and V. T. Souza, *Chem. Rev.*, 1998, **98**, 1977−1996.

2 S. Y. Jon, N. Selvapalam, D. H. Oh, J. K. Kang, S. Y. Kim, Y. J. Jeon, J. W. Lee and K. Kim, *J. Am. Chem. Soc.,* 2003, **125**, 10186.

3 C. Tu, W. H. Wu, W. T. Liang, D. J. Zhang, W. Xu, S. G. Wan, W. Lu and C. Yang., *Angew. Chem. Int. Ed.*, 2022, **61**, e202203541.