Electronic Supplementary Material (ESI) for Soft Matter

Supporting information

Dual Stimuli-Responsive Supramolecular Pseudo-polyrotaxane Hydrogels

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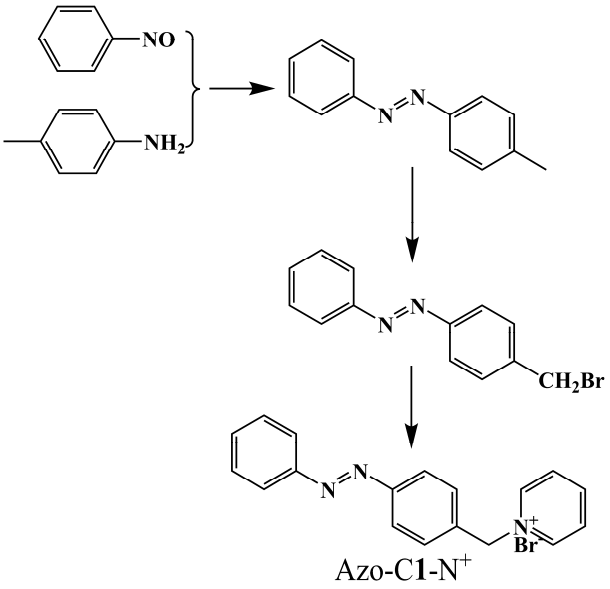
1. Synthesis and Characterization of Azo-C1-N^+

The compounds were synthesized according to the method reported by Jiang and coworkers as shown in **Scheme S1**.[1]



Scheme S1 Synthetic route of compound Azo-C**1**-N^+.

Nitrosobenzene (0.54g, 5 mmol), *p*-aminotoluene (0.54 g, 5 mmol) were dissolved in 5 mL acetic acid. The mixture was stirred for 24 h in sealed round-bottom flask. The acetic acid was evaporated under reduced pressure. The final crude product was purified by column chromatography to afford 4-methyl azobenzene.

A mixture of 4-methyl azobenzene (0.98g), NBS (0.90 g), BPO (49.3 mg) and CCl_4 (20 mL) were refluxed for 12 h. After removing the solvent, the product was purified by column chromatography.

A solution of 4-bromomethyl azobenzene (0.27 g) in 20 mL pyridine was refluxed for 12 h. After removing the solvent, the crude product was dissolved in methanol. The solution was added dropwise to plenty of ethyl ether during stirring, and the yellow precipitate was filtered and dried in vacuum. ^{1}H NMR spectrum of Azo-C**1**-N^+ was shown in **Fig. S1.**

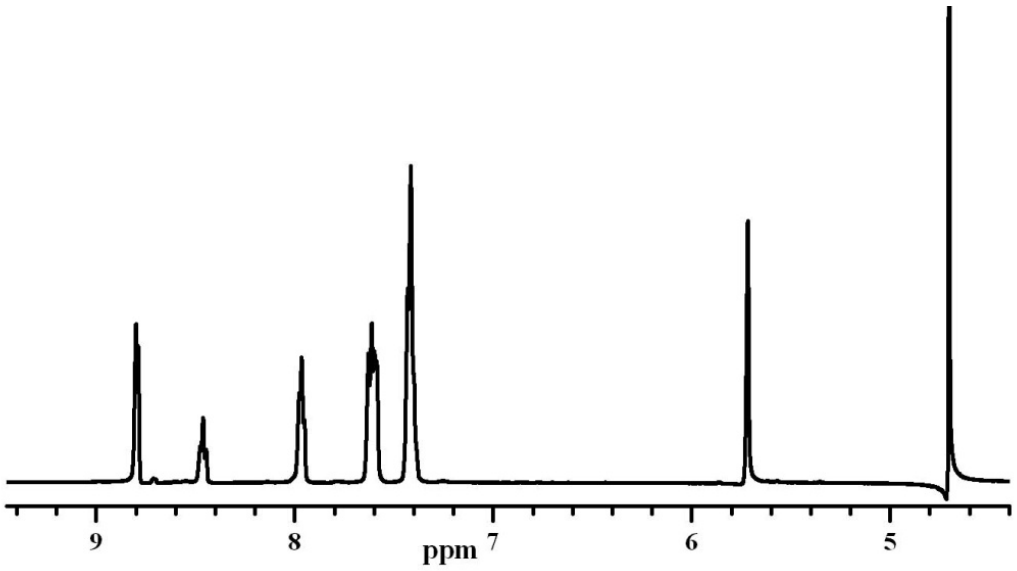
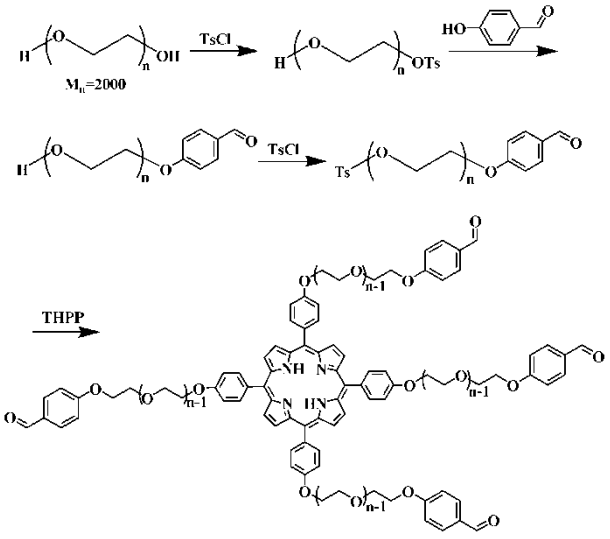


Fig. S1 ^{1}H NMR spectrum of Azo-C**1**-N^{+} in D_2O.

2. Synthesis and Characterization of THPP-(PEG$_{2000}$-BA)$_4$

THPP-(PEG$_{2000}$-BA)$_4$ was synthesized according to the method as shown in **Scheme S2.** High performance liquid chromatography (HPLC) experiment was performed on Agilent ZORBAX GF-250. Deionized water was used as the mobile phase at the rate of 0.5 mL·min^{-1}.



Scheme S2 Synthetic route of THPP-(PEG$_{2000}$-BA)$_4$.

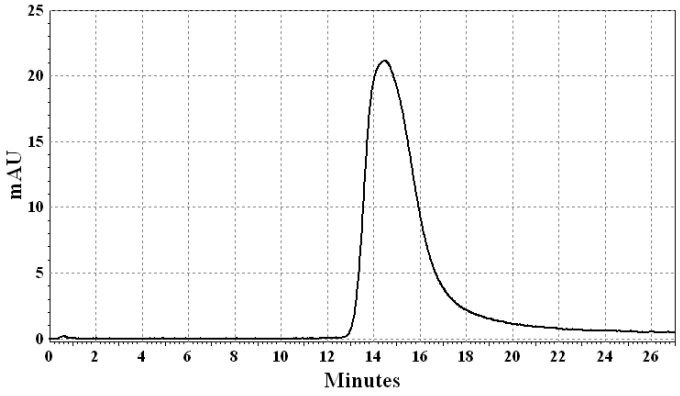


Fig. S2 HPLC spectrum of THPP-(PEG_{2000}-BA)$_4$.

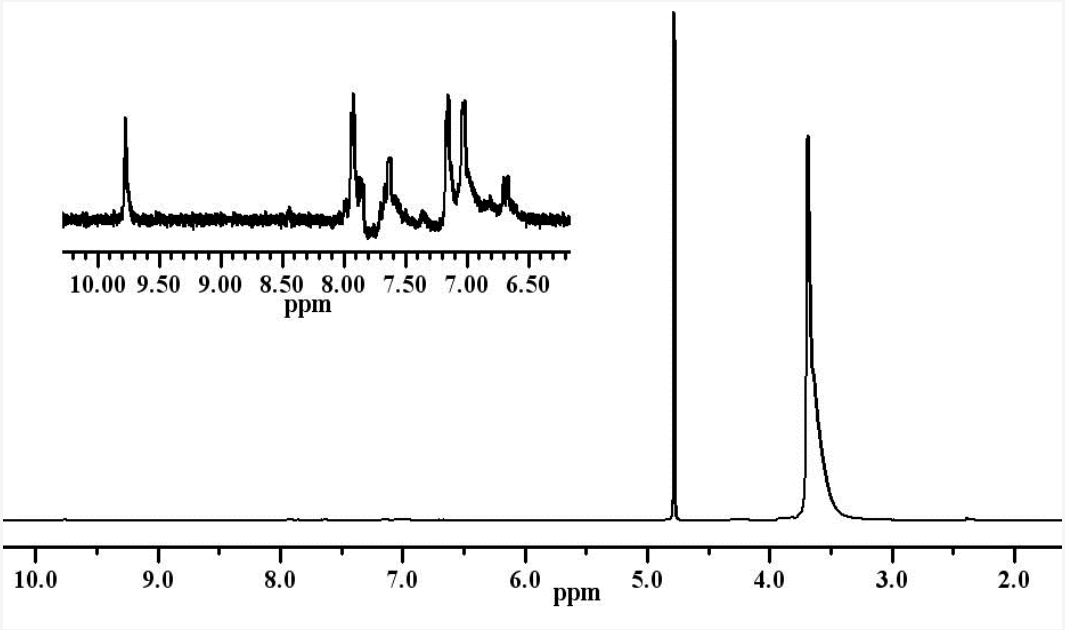


Fig. S3 ^{1}H NMR spectrum of THPP-(PEG_{2000}-BA)$_4$ in D_2O. The insert represented local intensity increasement.

3. The gelation ability of THPP-(PEG_{2000}-BA)$_4$

THPP-(PEG_{2000}-BA)$_4$/α-CD gels (as shown in **Fig. S4**) were prepared by mixing α-CD aqueous solution and THPP-(PEG_{2000}-BA)$_4$ aqueous solution at different concentrations followed by sonication and standing. The final concentrations of THPP-(PEG_{2000}-BA)$_4$ and α-CD were shown in **Table S1**. Considering the similar chain length between PEG_{8000} and THPP-(PEG_{2000}-BA)$_4$, we select PEG_{8000} as a reference compound. The concentration of α-CD was fixed to be 50 mg·mL^{-1}, and different amounts of PEG_{8000} were used to mix with α-CD (**Fig. S5**). The final concentration of α-CD was fixed at 50 mg·mL^{-1}. The ^{1}H NMR signals of benzaldehyde shifted downfield and all the proton signals of α-CD became broad after gelation (**Fig. S7**). Dynamic laser light scattering (DLS) performed in very dilute solutions was used to monitor the formation of linear PPR (**Fig. S6**). The

concentration of THPP- $(PEG_{2000}\text{-}BA)_4$ and α-CD was 0.01 $mg{\cdot}mL^{-1}$ and 0.025 $mg{\cdot}mL^{-1}$, much lower than that used to form the hydrogel, so the PPR could form but no precipitation and gelation took place.

Table S1 Preparation of the PPR hydrogel.

	[THPP- $(PEG_{2000}\text{-}BA)_4$]/ $mg{\cdot}mL^{-1}$	[α-CD]/ $mg{\cdot}mL^{-1}$	Gelation time/ h
A	10	50	10
B	20	100	2
C	30	150	1

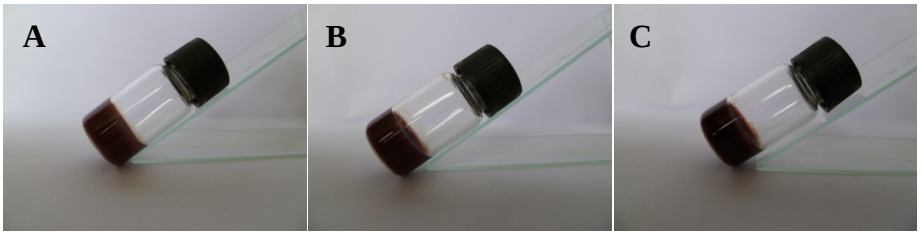


Fig. S4 THPP-$(PEG_{2000}\text{-}BA)_4$/α-CD gels at different concentrations: A) THPP-$(PEG_{2000}\text{-}BA)_4$ 10 $mg{\cdot}mL^{-1}$, α-CD 50 $mg{\cdot}mL^{-1}$; B) THPP-$(PEG_{2000}\text{-}BA)_4$ 20 $mg{\cdot}mL^{-1}$, α-CD 100 $mg{\cdot}mL^{-1}$; C) THPP- $(PEG_{2000}\text{-}BA)_4$ 30 $mg{\cdot}mL^{-1}$, α-CD 150 $mg{\cdot}mL^{-1}$.

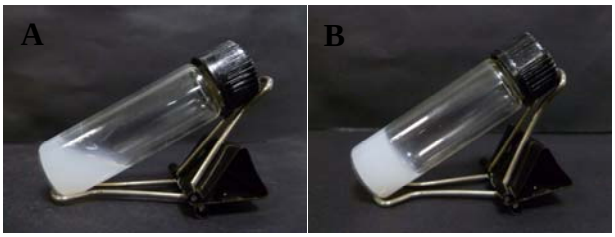


Fig. S5 The mixtures of PEG_{8000} of different concentrations with α-CD of 50 $mg{\cdot}mL^{-1}$: A) the turbid solution of PEG_{8000} of 10 $mg{\cdot}mL^{-1}$ and α-CD after standing for 24h; B) the gel of PEG_{8000} of 20 $mg{\cdot}mL^{-1}$ and α-CD after standing for 12h.

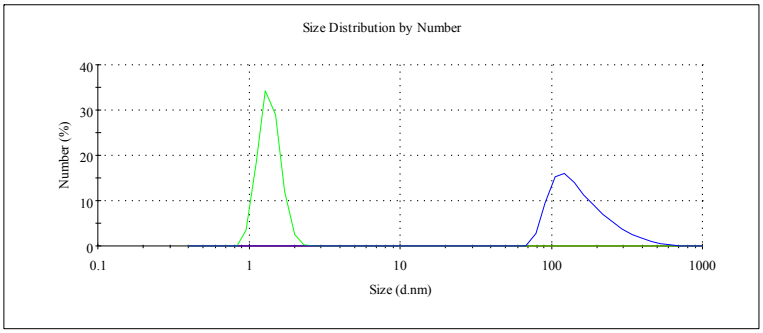


Fig. S6. DLS results for α-CD (green) and THPP-$(PEG_{2000}\text{-}BA)_4$/α-CD (blue).

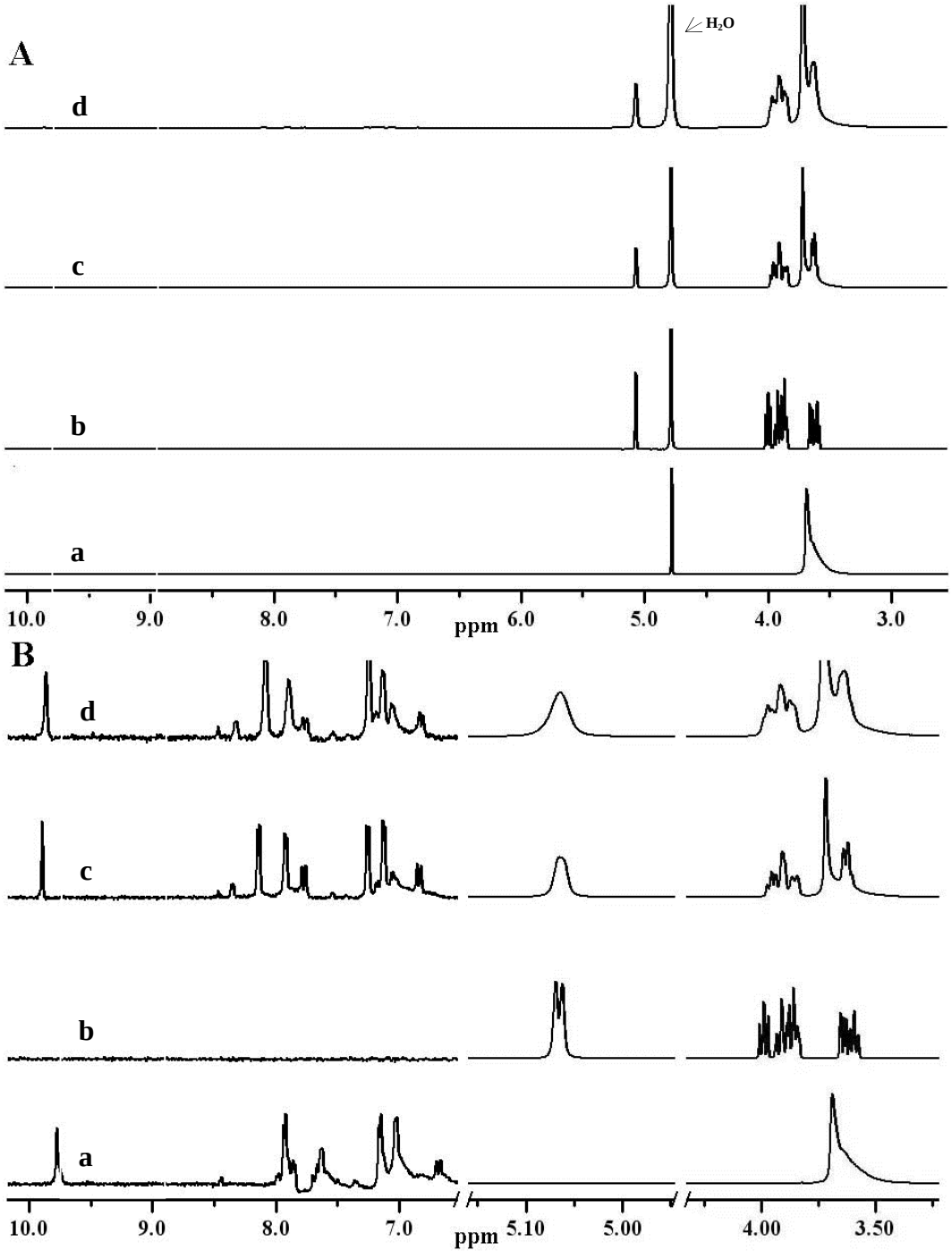


Fig. S7 ^{1}H NMR spectra of a) THPP-$(PEG_{2000}\text{-}BA)_4$, b) free α-CD, c) THPP-$(PEG_{2000}\text{-}BA)_4$/α-CD sol (20 min) and d) THPP-$(PEG_{2000}\text{-}BA)_4$/α-CD gel (2 h) in D_2O. The bottom graph B) represented local intensity increasement and local amplification of A).

4. Photoresponsive ability of hydrogel

Equivalent molar amount of Azo-C**1**-N^+ to α-CD was added to the THPP-$(PEG_{2000}\text{-}BA)_4$/α-CD gel and stood. UV-Vis and NMR spectra were utilized to monitor the *trans-cis* isomerization.

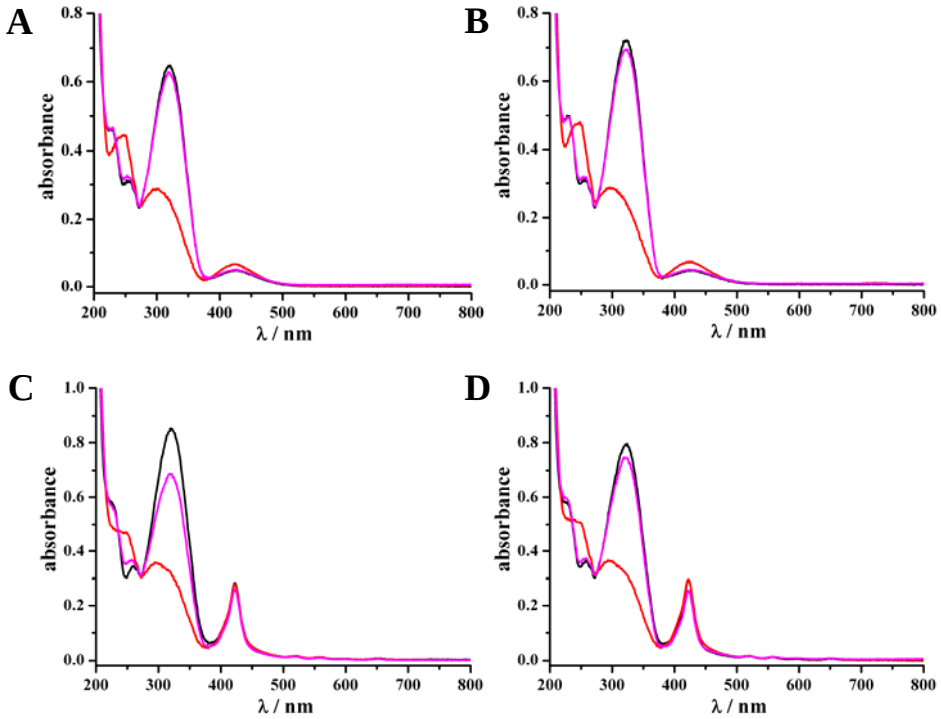


Fig. S8 UV-Vis absorption spectra of the aqueous solution of A) Azo-C**1**-N^+; B) Azo-C**1**-N^+/α-CD; C) THPP-$(PEG_{2000}\text{-}BA)_4$/Azo-C**1**-N^+; D) THPP-$(PEG_{2000}\text{-}BA)_4$/Azo-C**1**-N^+/α-CD before UV irradiation (black), after UV irradiation (red) and later after Vis irradiation (magenta).

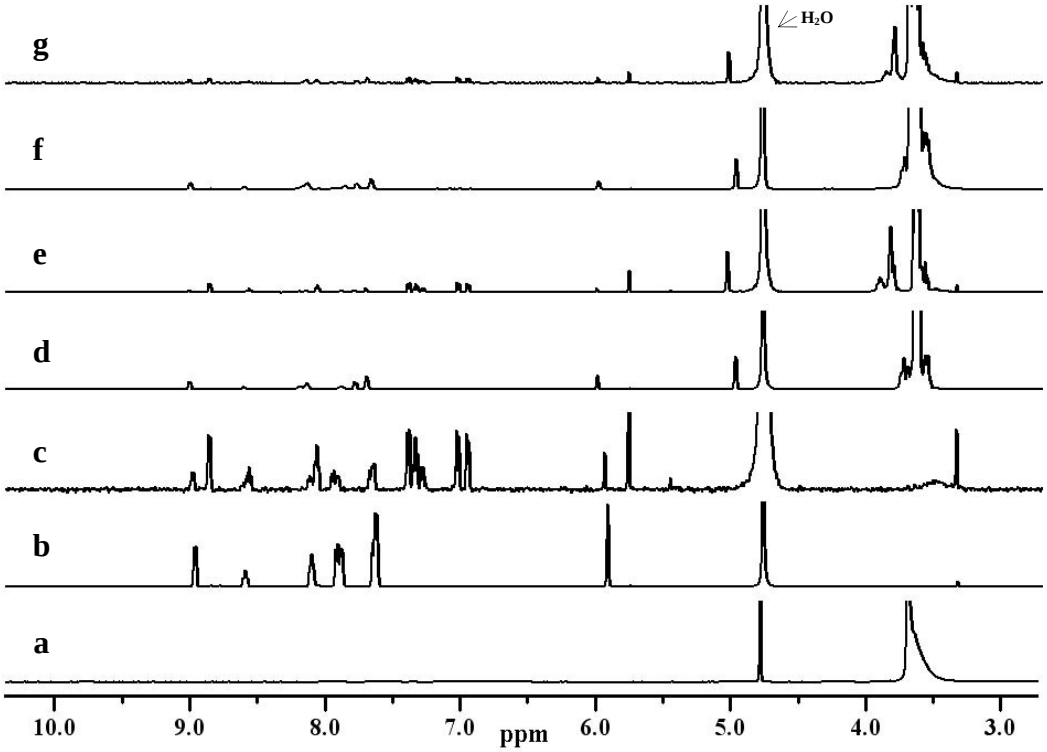


Fig. S9 ^{1}H NMR spectra of a) THPP-$(PEG_{2000}\text{-}BA)_4$; b) and c) Azo-C**1**-N^+; d) and e) Azo-C**1**-N^+/α-CD; f) and g) THPP-$(PEG_{2000}\text{-}BA)_4$/Azo-C**1**-N^+/α-CD in D_2O. Thereinto, b), d) and f) represented that before UV irradiation and c), e) and g) represented that after UV irradiation.

5. pH-controlled Preparation of hydrogel

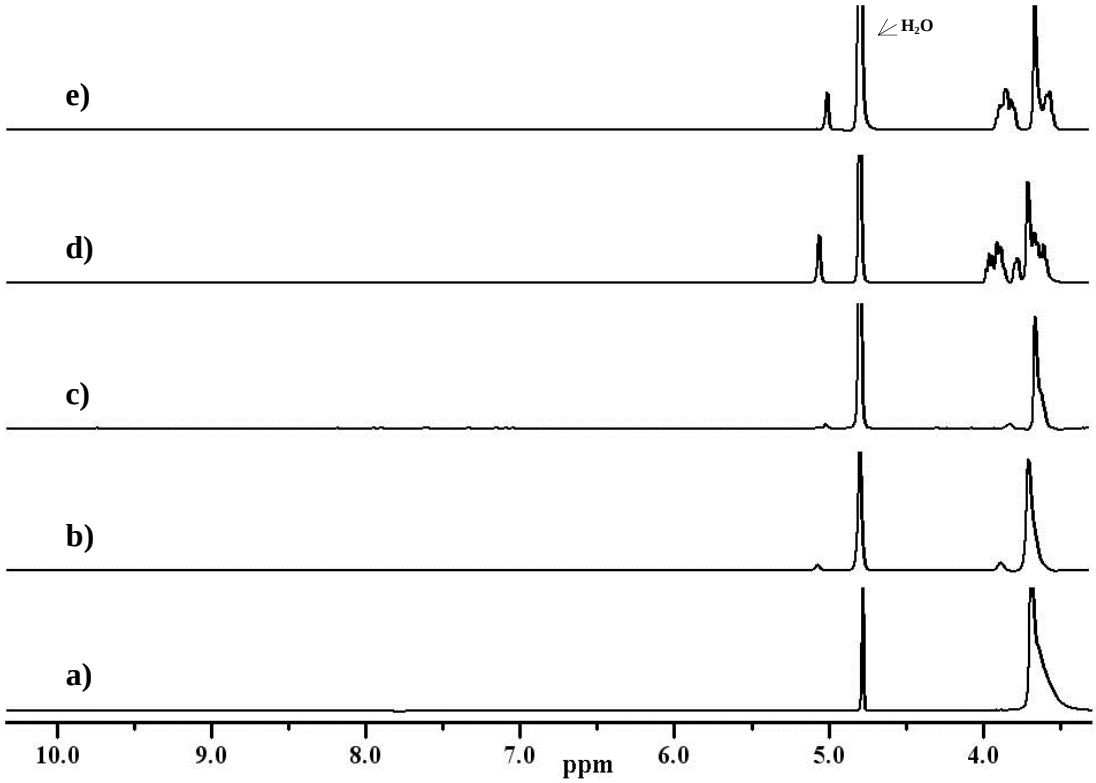


Fig. S10 ^{1}H NMR spectra of a) THPP-$(PEG_{2000}\text{-}BA)_4$; b) THPP-$(PEG_{2000}\text{-}BA)_4$/EDA-β-CD/ TEA; c) acidification of b); d) THPP-$(PEG_{2000}\text{-}BA)_4$/EDA-β-CD/α-CD/ TEA; and e) acidification of d) in D_2O.

Reference

1. X.J. Liao, G.S. Chen, X.X. Liu, W.X. Chen, F.E. Chen and M. Jiang, *Angew. Chem., Int. Ed.*, 2010, **49**, 4409-4413.