Electronic Supplementary Information

Azobenzene Based Multistimuli Responsive Supramolecular Hydrogels

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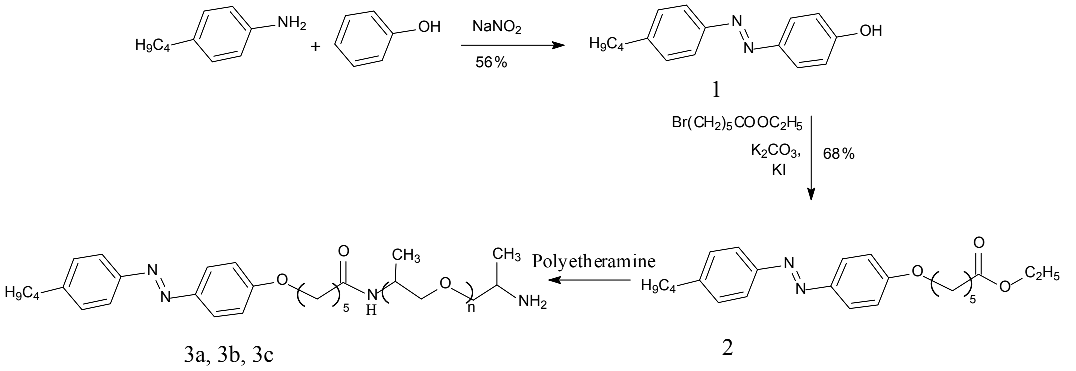
Experimental Section



Scheme S1. Synthesis of C$_4$-Azo-C$_5$-D$_{230}$ (n=2.5), C$_4$-Azo-C$_5$-D$_{400}$ (n=6.1), C$_4$-Azo-C$_5$-ED$_{900}$ (n=18.5).

Compound 1. A solution of sodium nitrite (2.27 g, 32.04 mmol in 15.7 mL of water) is added drop wise to a suspension of 4.5 g (26.70 mmol) of 4-butylaniline in a mixture of 10 mL HCl and 30 mL of water, keeping the temperature below 5 ºC. After 30 min. for stirring, the diazonium salt is formed. Then, 3.05 g of phenol (32.04 mmol) is added. The reaction was stirred for 1 hour. The solution was made basic with 100 mL of a saturated solution of NaHCO$_3$. A brown solid precipitated, which was filtered off and washed with distilled water. The product was isolated by recrystallization with ethanol. Mp: 68-69^{o}C, Yield: 56%.

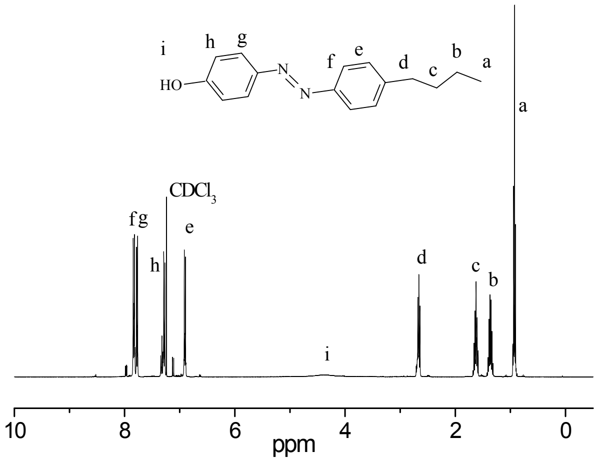


Fig. S1 ^{1}H NMR spectrum of compound 1 in CDCl$_3$.

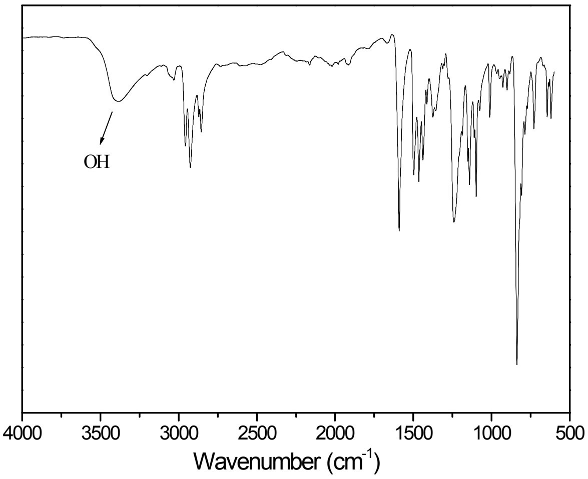


Fig. S2 FTIR spectrum of compound 1.

Compound 2. 18.5 mmol of compound **1**, anhydrous K_2CO_3 (5.11 g, 37.0 mmol) and KI (0.100 g) were dissolved in 100 mL of acetone, under nitrogen atmosphere. After 10 minutes stirring, 22.2 mmol of ethyl 6-bromohexanoate were added drop wise via syringe while the solution was refluxing. The mixture was stirred overnight under reflux. After cooling down to room temperature, salt solid was filtered off and acetone was evaporated. The product was recrystallized with ethanol. Mp: 60-62 °C, Yield: 68%.

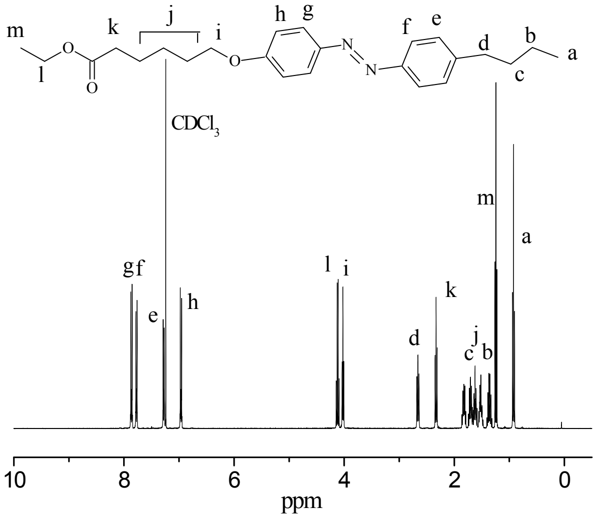


Fig. S3 ^{1}H NMR spectrum of compound 2 in $CDCl_3$.

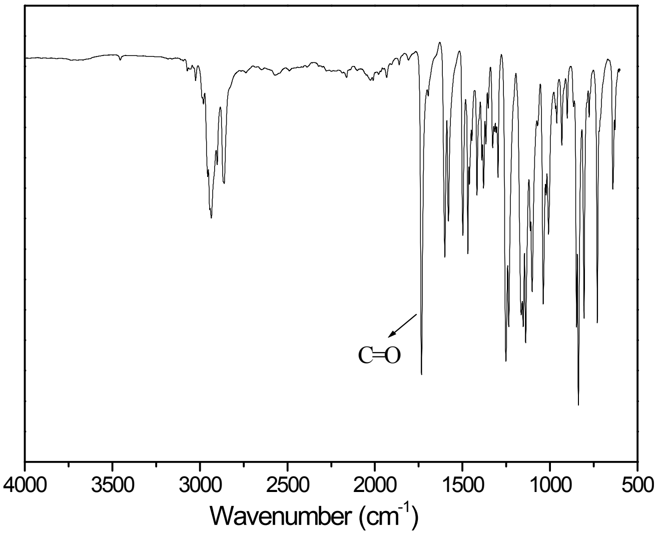


Fig. S4 FTIR spectrum of compound 2.

Compound 3b. 3.0g D_{400} (dissolved in 10 mL dichloromethane) and 0.05 g (dispersed in 1 mL ethanol) of sodium ethylate were added in flask. Then 1.0 g of the corresponding compound **2** was dissolved in dichloromethane (15 mL) was added in between 10 mins. The reaction mixture was heated to 30 °C, and stirred overnight. Then, the mixture was cooled to room temperature. The solid was filtered off and then it was washed with dichloromethane. Finally, the product was dried in the vacuum oven at 30 °C overnight. Yield: 48%.

Compound 3a was synthesized according to the similar method with compound

3b using D_{230} instead of D_{400} in same molar rate. Yield: 50%.

Compound 3c was synthesized according to the similar method with compound 3b using ED_{900} instead of D_{400} in same molar rate. Yield: 47%.

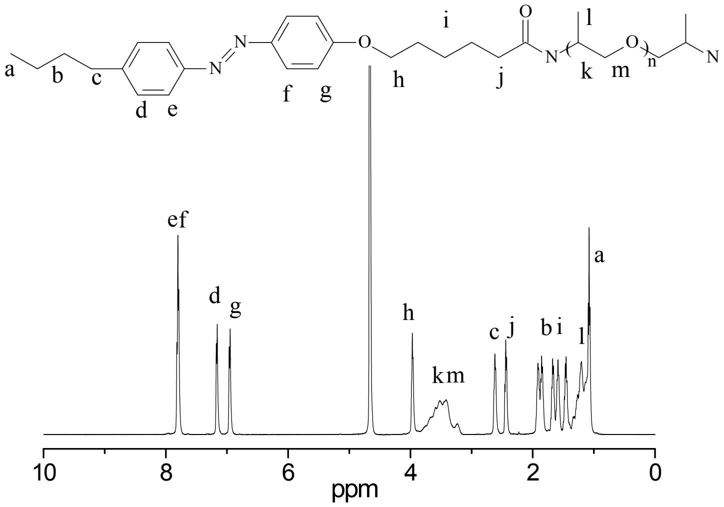


Fig. S5 ^{1}H NMR spectrum of compound 3b in D_2O.

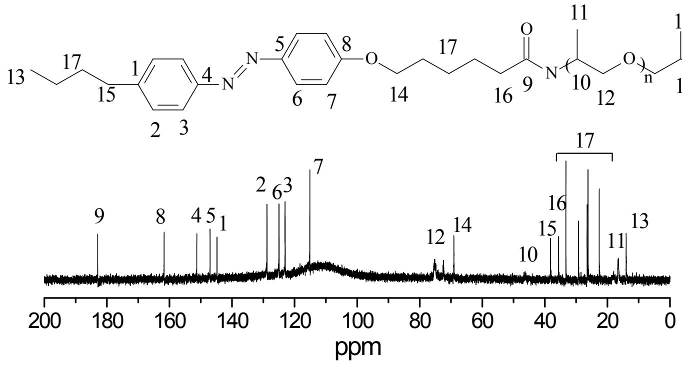


Fig. S6 ^{13}C NMR spectrum of compound 3b in D_2O.

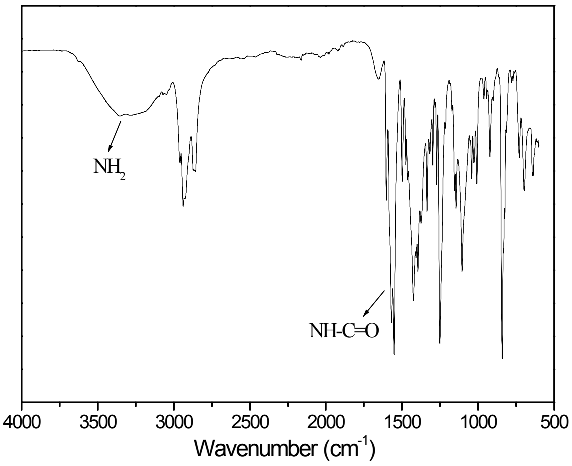
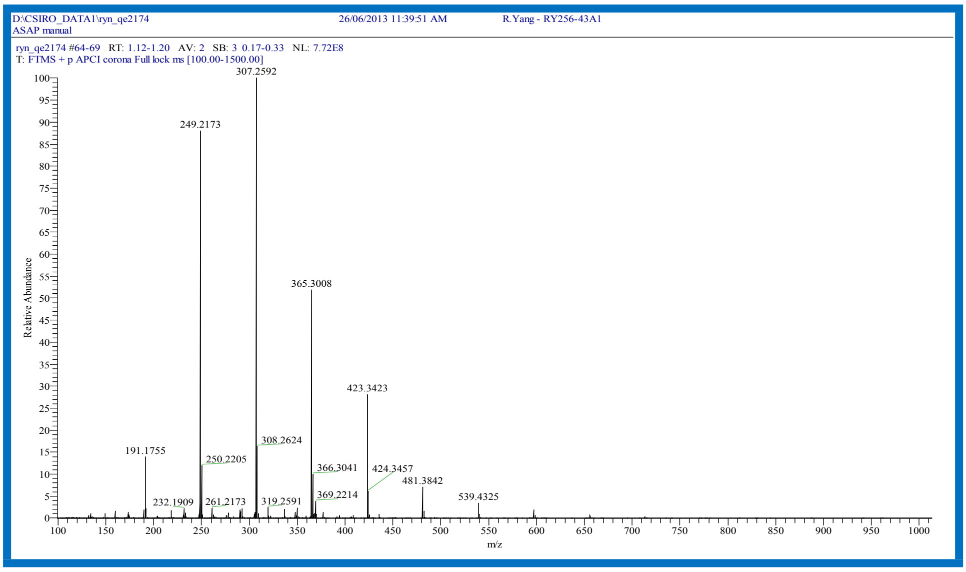


Fig. S7 FTIR spectrum of compound 3b.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ASAP manual

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Fig. S8 HRMS spectrum of compound 3b.

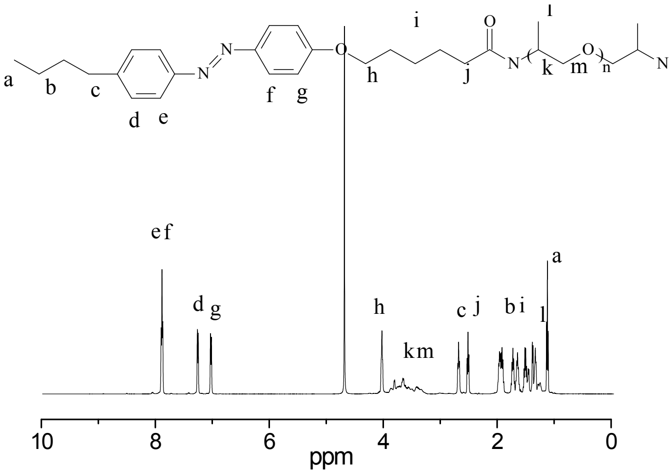

Fig. S9 ^{1}H NMR spectrum of compound 3a in D_2O.

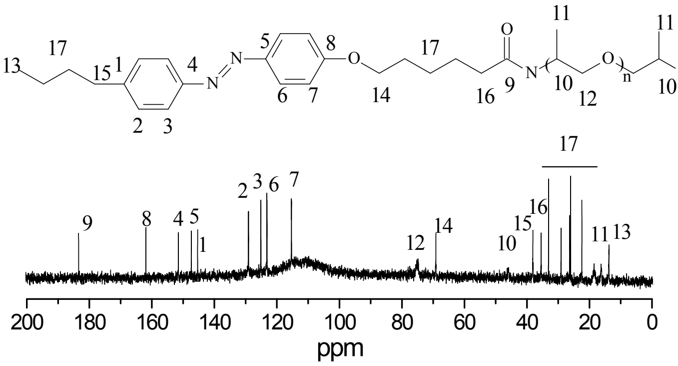

Fig. S10 ^{13}C NMR spectrum of compound 3a in D_2O.

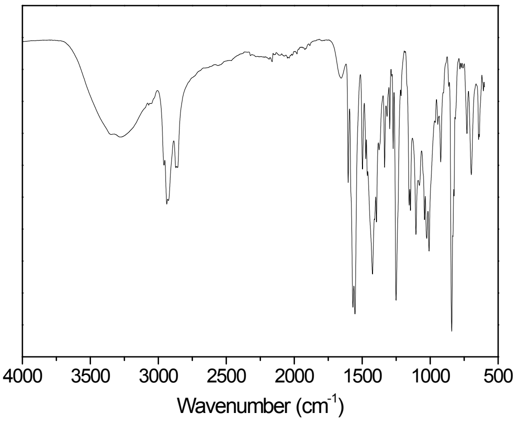

Fig. S11 FTIR spectrum of compound 3a.

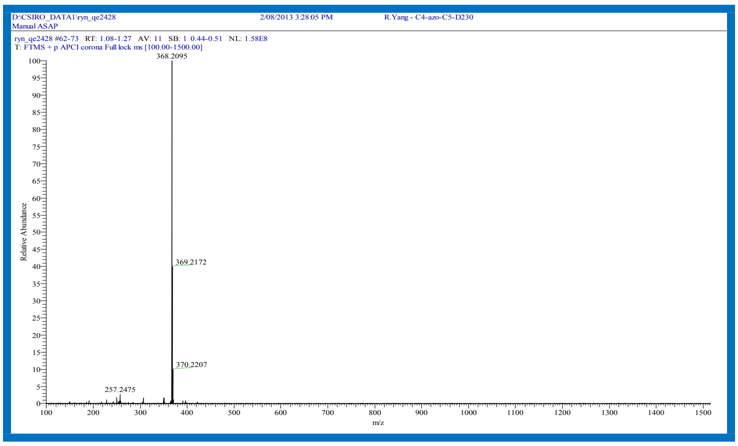

Fig. S12 HRMS spectrum of compound 3a.

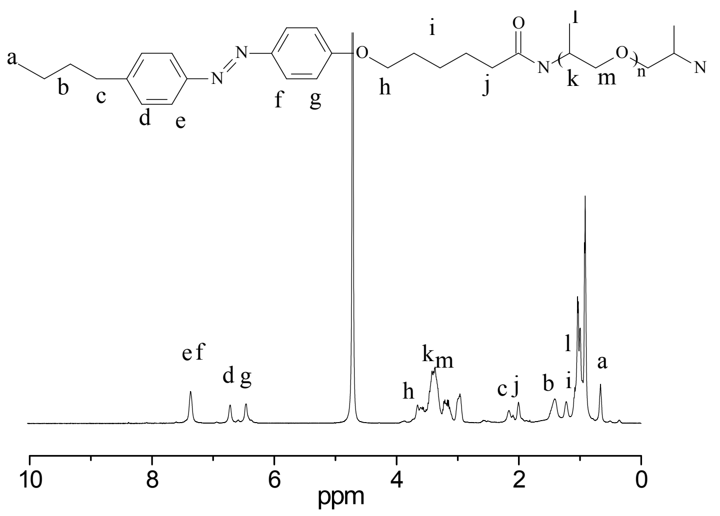

Fig. S13 ^{1}H NMR spectrum of compound 3c in D_2O.

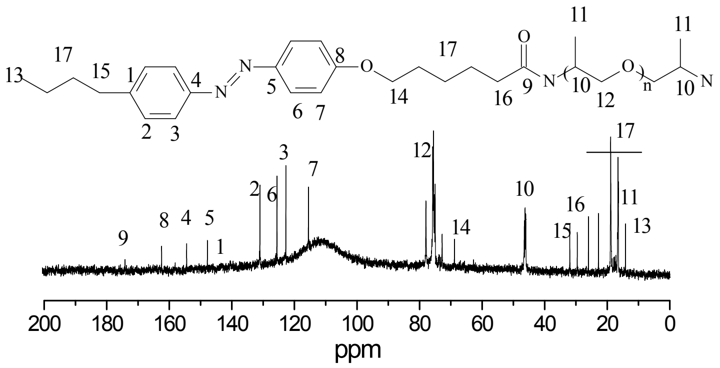

Fig. S14 ^{13}C NMR spectrum of compound 3c in D_2O.

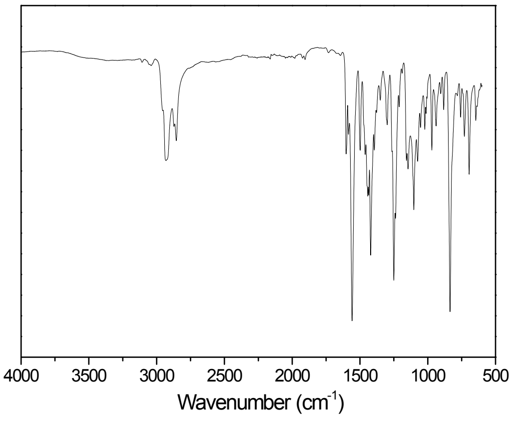

Fig. S15 FTIR spectrum of compound 3c.

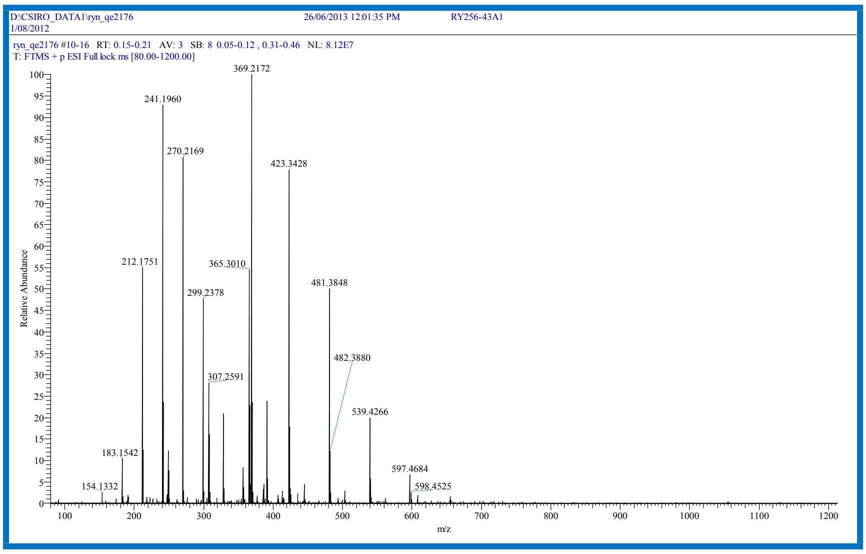

Fig. S16 HRMS spectrum of compound 3c.

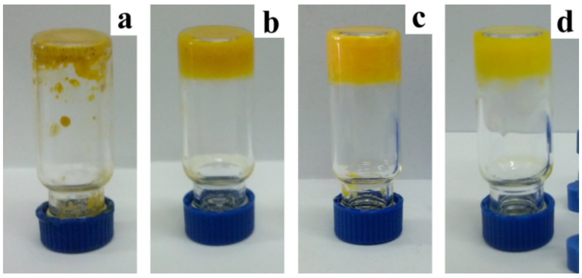

Fig. S17 Photographs of the C_4-Azo-C_5-D_{400} hydrosol at (a) 30.0 wt% (b) 10.0 wt% (c) 3.0 wt% (d) 1.0 wt%.

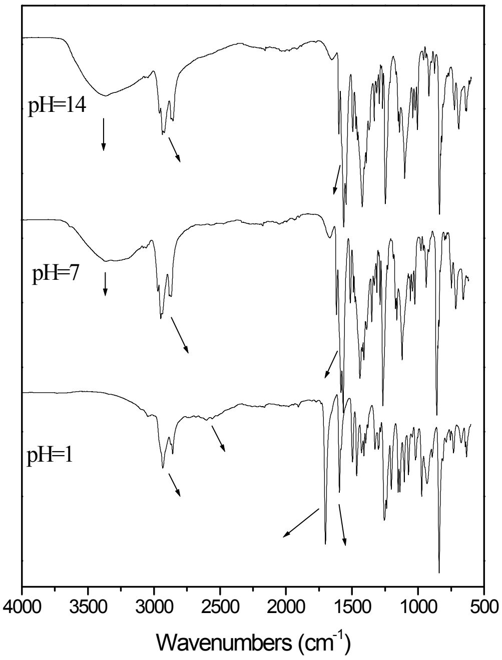

Fig. S18 FT-IR study of the C_4-Azo-C_5-D_{400} obtained from different pH.

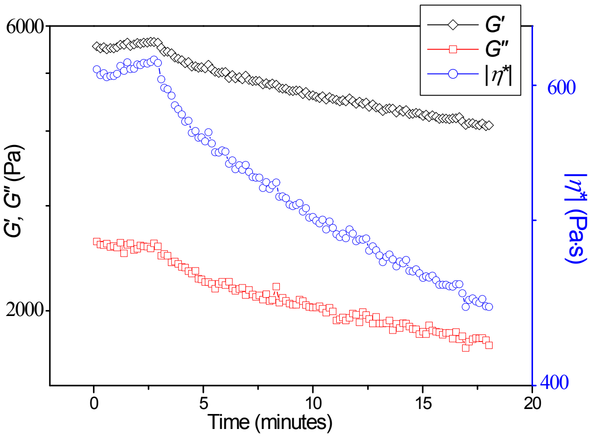

Fig. S19 Real-time photo-rheology measurements. C_4-Azo-C_5-D_{400} in water at 20 °C (10.0 wt %). The data were obtained at a constant frequency of 5 rad/s and a strain of 1.0 %. UV turned on at 3 min.

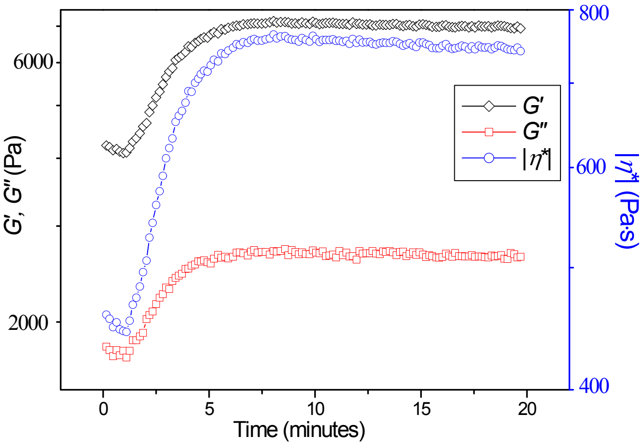

Fig. S20 Real-time photo-rheology measurements. C_4-Azo-C_5-D_{400} in water at 20 °C (10.0 wt %). The data were obtained at a constant frequency of 5 rad/s and a strain of 1.0 %. Visible light turned on at 1.0 min.

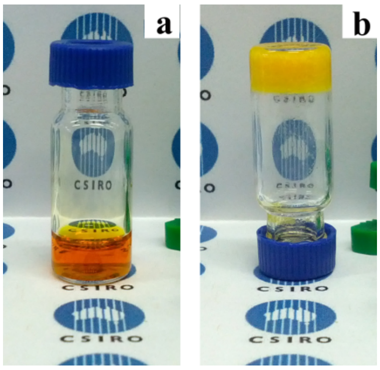

Fig. S21 Hydrogel formed from a solution of C_4-Azo-C_5-D_{400} in water (10 wt%) (a) solution,70 °C and (b) gel, 20 °C.

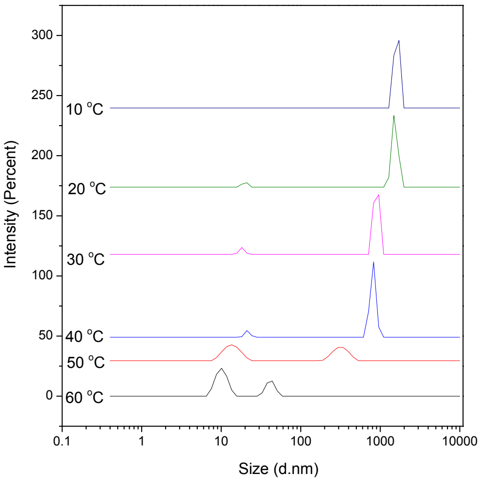

Fig. S22 DLS study of the C_4-Azo-C_5-D_{400} obtained from different temperature, (0.2 wt%).

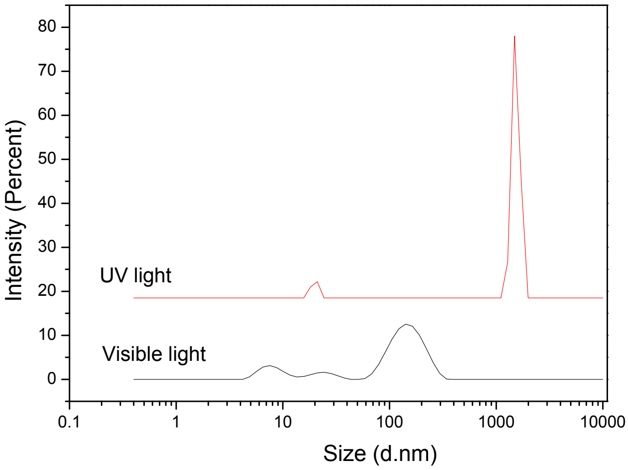

Fig. S23 DLS study of the C_4-Azo-C_5-D_{400} obtained before (red line) and after (black line) upon UV light (365 nm, 20 mW/cm²) exposure at 20 ºC, 0.2 wt%.

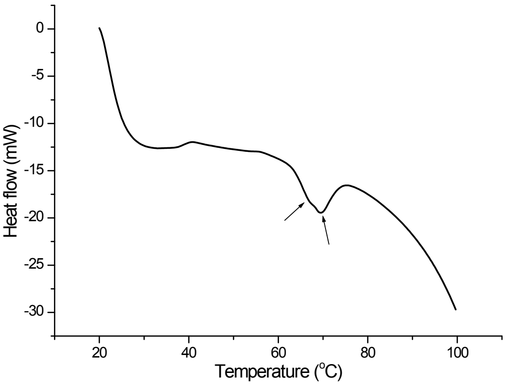

Fig. S24 DSC curves of the C_4-Azo-C_5-D_{400} in water (10 wt%)