Supporting Information

Photoswitchable thermogelling system based on host-guest approach

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1. Materials and Methods.

1.1. Materials

Acrylamide (AM, J&K, 99%), acrylonitrile(AN, J&K, 99%), ammonium persulfate (APS, Sigma, 99%), acetic anhydride (Adamas, 98%),1-tetradecene (Adamas, 98%), 1-hexadecene (Adamas,98%), α-cyclodextrin (α-CD, Sigma, 99%), pyrene (J&K, 99%), 4-(phenylazo)benzoic acid (PBA, Sigma, 99%) , benzophenone (J&K, 99%) were used as received . Water used in this study was deionized and then distilled. All the solvents were used as received.

1.2. Characterization

^{1}H NMR measurements and 2D ^{1}H NOESY NMR spectra were performed on AVANCE III HD-400 (400 MHz) spectrometer. FT-IR spectra were recorded on a Nicolet 6700 spectrometer frequencies ranging from 400–4000 cm^{-1}. The molecular weight of polymer sample was determined in formamide solution by classical light scattering using a multiangle spectrometer (AMTEC Model MM1). The UV-Vis absorption spectra of the different samples were recorded by using an Agilent Cary-60 UV-Vis spectroscopy. Isothermal titration calorimetry (ITC) experiments was conducted on a MicroCal VP-ITC system at 20.00±0.01 °C. Steady-state fluorescence spectra of pyrene were recorded on a SHIMADZU RF-5301PC luminescence spectrometer, equipped with a circulating water bath.

Rheological measurements were conducted to determine the sol-gel transition point on a HAAKE Par Rotary Rheometer (HAAKE MARS III) rheometer using a cone-plate of 40 mm diameter with cone angle of 1º. Dynamic frequency spectra were obtained in the linear viscoelastic region of the samples, as determined by dynamic

strain sweep experiments. A shear strain amplitude of 5% and an angular frequency of 1rad.s^{-1} were applied. To investigate the thermal-response property, samples were placed between the para-plate and the platform with special care to avoid evaporation of water.

1.3. The method for determination of critical micellar concentration(CMC), critical aggregate concentration (CAC) and aggregation numbers (Nagg)

A stock ethanolic solution, containing 1×10^{-3} M pyrene, was used. The final concentration of the probe was 6×10^{-7} M and the excitation wavelength was 339 nm. The intensity ratio (I_1/I_3) of the first (I_1) over the third(I_3) vibronic band of the emission spectrum of pyrene, at 373 and 384 nm, respectively, was used to detect the formation of hydrophobic microdomains.

The micelle aggregation numbers of micelles, N_{agg}, for $NaAMC_{16}S$ was determined by the steady-state fluorescence quenching technique (SSFQ). This method is based on quenching of pyrene fluorescence by a hydrophobic quencher. Benzophenone was used as the quencher. Excitation of the probe was at 335 nm and the emission was monitored at 374 nm. By changing the quencher concentration, Cq (0–0.45 mmol/L), a linear relationship between ln I_0/I and Cq was obtained, the corresponding equation is as follows:

$$In\frac{I_0}{I}=\frac{N_{agg}}{C-C_{cmc}}\times Cq \qquad (1)$$

where I_0 is the fluorescence intensity of the probe in the micellar solutions as in the absence of the quencher, and I is the fluorescence intensity of the probe in the presence of the quencher. C_{CMC} and C are the critical micellar concentration and the total concentration of the surfactant, respectively. According to the Eq. (1), the straight lines of logarithm of the intensity ratio versus the quencher concentration Cq were plotted, and the aggregation numbers (N_{agg}) of $NaAMC_{16}S$ at a given concentration were obtained.

1.4. Sample preparation.

Amounts of polymer was dissolved in DI water by heating for 2-3 h at 65 ^{o}C and

then stirred at room temperature for 12 h. α-CD was then mixed with polymer gel-like solution, and further stirred for 24 h at 20 ºC. All the samples were sealed without stirring to reach equilibrate at room temperature for at least 48 h prior to test. The glass tubes (volume 10 mL) containing the samples were immersed in a thermostatic bath with temperature increase at rate of 1ºC in order to check whether the sample flowed or not.

The photo-controllable samples were isomerized by photoirradiation using a 400 W Xe lamp equipped with a cutoff filter and a band-pass filter (360 nm UV light or 435 nm visible light, 10min). The distance between the sample cell and the lamp was fixed at 40 cm. All the samples were put in the ice bath, each batch was held in a crystallizing dish surrounded by ice. To minimize isomerization after irradiation, each batch was covered and placed in a -20 °C freezer as soon as irradiation was completed. Each sample after irradiated was kept in the dark at room temperature for 24 h prior to test.

2. Synthesis, Characterization and Preparation.

2.1 Synthesis and characterization of sodium 2-acrylamido-tetradecane sulfonate (NaAMC14S and sodium 2-acrylamido-hexadecane sulfonate ($NaAMC_{16}S$

Sodium 2-acrylamido-tetradecane sulfonate ($NaAMC_{14}S$) and sodium 2-acrylamido-hexadecane sulfonate ($NaAMC_{16}S$) were synthesized by using 1-hexadecene (1-tetradecane), acrylonitrile, acetic anhydride and oleum as raw materials. A typical synthetic method has been given as followed: tetradecene (28 mL), acrylonitrile (8 mL), acetic anhydride (25 mL) and dichloroethane (20 mL) were added to a three-neck bottle equipped with an agitator, a dropping funnel and a thermometer, and the content was cooled below 0 ºC. Oleum (9mL) in the dropping funnel was added dropwise with vigorous stirring, and the temperature was kept below -5 ºC during dropping. After finishing the addition of oleum, the temperature of the content was left to stir at room temperature for another 12 h. The product was then cooled to 4 ºC and filtrated to obtain white powder. The crude product was then washed with acetone and further dissolved in distilled water, and then neutralized with

NaOH solution. The mixture was kept static below 4 ºC for 12 h until the white crystal, $NaAMC_{16}S$, was produced. In order to pure $NaAMC_{16}S$, the white crystal was recrystallized twice from the mixed solvent of saturated Na_2CO_3 water and acetone. The ^{1}HNMR spectrum of sodium 2-acrylamido-tetradecane sulfonate ($NaAMC_{16}S$) in D_2O (Figure S1) demonstrated the successful synthesis.

$NaAMC_{16}S$ (yield: 42%) : ^{1}H NMR (400 MHz, D_2O, δ) : 6.12 (dt, 2H,-CH=CH-), 5.65 (d, *J* = 10.1 Hz, 1H, -CH=CH-), 4.30 (s, 1H,-CH-), 3.02 (dd, *J* = 40.4, 14.9 Hz, 2H,-CH_2-SO_3Na), 1.53 (d, *J* = 48.0 Hz, 2H,-CH-CH_2), 1.12 (s, 24H,-$(CH_2)_{12}$), 0.71 (s, 3H,-CH_3).

$NaAMC_{14}S$ (yield: 40%): ^{1}H NMR (400 MHz, D_2O, δ): 6.16 (dt , 2H, -CH=CH-), 5.63 (d, *J* = 9.8 Hz, 1H, -CH=CH-), 4.27 (s, 1H, -CH-), 3.09 – 2.87 (m, 2H, -CH_2-SO_3Na), 1.66 – 1.38 (m, 2H, -CH-CH_2-), 1.13 (d, *J* = 37.0 Hz, 20H, -$(CH_2)_{10}$), 0.69 (t, *J* = 6.3 Hz, 3H, -CH_3).

$NaAMC_{12}S$ (yield: 32%) : ^{1}H NMR (400 MHz, D_2O, δ) :6.23 (dt, 2H, -CH=CH-), 5.69 (d, *J* = 9.2 Hz, 1H, -CH=CH-), 4.35 (s, 1H, -CH-), 3.16 – 2.96 (m, 2H, -CH_2-SO_3Na), 1.59 (d, *J* = 39.8 Hz, 2H, -CH-CH_2-), 1.17 (s, 16H, -$(CH_2)_8$), 0.77 (t, *J* = 6.5 Hz, 3H, -CH_3).

$NaAMC_{10}S$(yield: 26%): ^{1}H NMR (400 MHz, D_2O, δ): 6.23 (dt, 2H, -CH=CH-), 5.69 (d, *J* = 8.8 Hz, 1H, -CH=CH-), 4.34 (d, *J* = 4.0 Hz, 1H, -CH-), 3.07 (m, 2H, -CH_2-SO_3Na), 1.58 (d, 2H,-CH-CH_2-), 1.21 (d , 12H, -$(CH_2)_6$), 0.76 (t, *J* = 6.5 Hz, 3H, -CH_3).

$NaAMC_8S$(yield: 28%): ^{1}H NMR (400 MHz, D_2O, δ): 6.34 – 6.04 (m, 2H, -CH=CH-), 5.67 (d, *J* = 9.7 Hz,1H, -CH=CH-), 4.32 (s, 1H, -CH-), 3.19 – 2.82 (m, 2H, -CH_2-SO_3Na), 1.56 (d, *J* = 45.3 Hz, 2H, -CH-CH_2-), 1.18 (d, *J* = 36.2 Hz, 8H, -$(CH_2)_4$), 0.73 (s, 3H, -CH_3).

The critical micellar concentration (CMC) of $NaAMC_{14}S$ and $NaAMC_{16}S$ have been determined as 0.2 mM and 0.8 mM at 60 ºC using steady-state fluorescence probe (Figure S2), and the micelle aggregation numbers of micelles, N_{agg}, for $NaAMC_{14}S$ of 16CMC was determined as 50 and $NaAMC_{16}S$ of 8CMC was determined as 10 at 60 ºC by the steady-state fluorescence quenching technique (Figure S3).

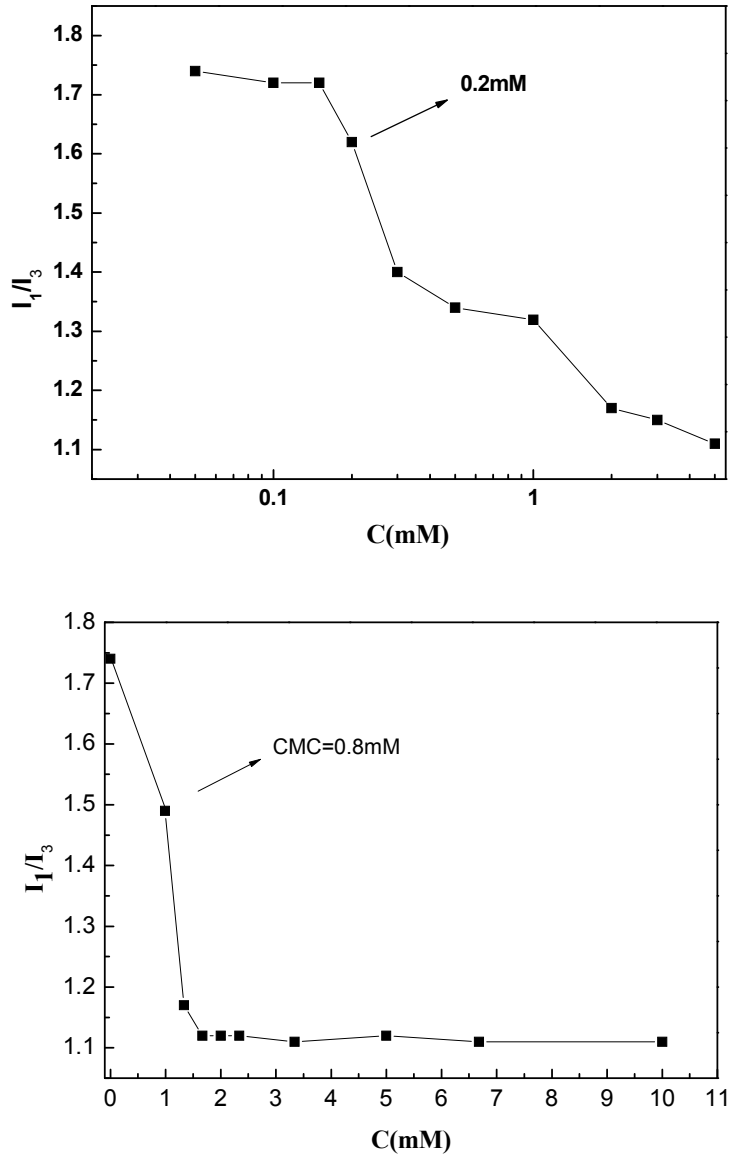


Figure S1. Varying of the I_1/I_3 ratio of pyrene in $NaAMC_{14}S$ and $NaAMC_{16}S$ solutions in pure water with monomer concentration.

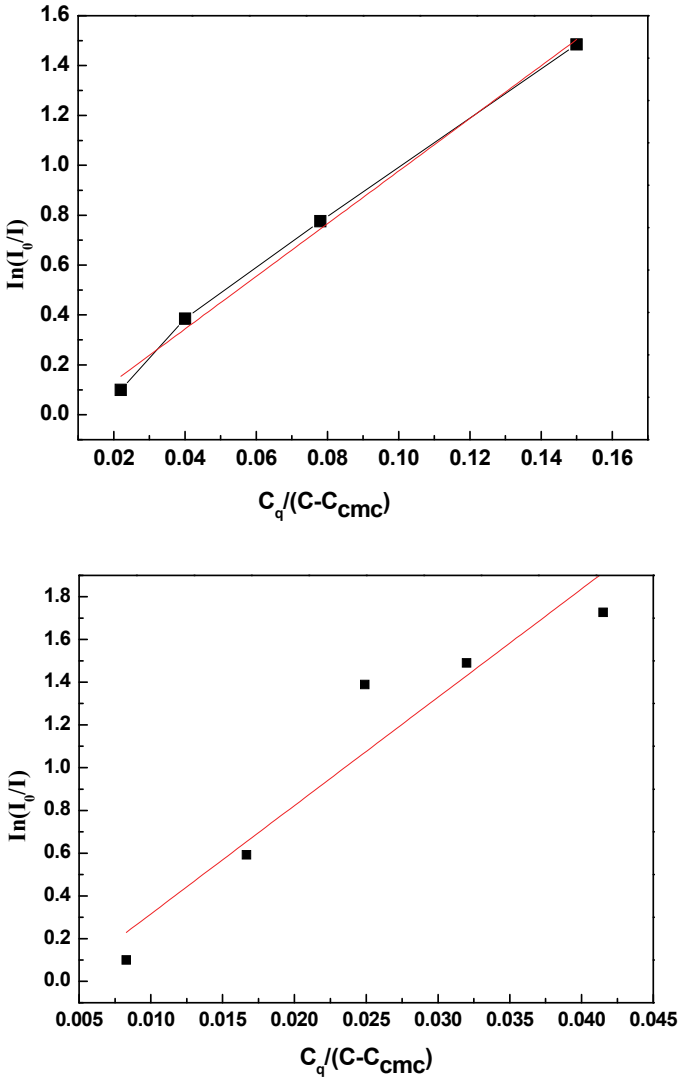


Figure S2. Plot of ln(I_0/I) vs. $Cq/(C - C_{CMC})$. Concentration of $NaAMC_{16}S$: 8CMC, Concentration of $NaAMC_{14}S$: 16CMC.

2.2. Synthesis and characterization of hydrophobically modified polyacrylamide of blocky structure

Hydrophobically modified polyacrylamide of blocky structure were synthesized by the free-radical micellar copolymerization of acrylamide and surfmer in an aqueous medium. To illustrate the synthetic procedure, we give details for the preparation of PCnAM by micellar copolymerization: $NaAMC_{14}S$ (0.3 g, 1.5 mol%) was dissolved in 85.0 mL deionized water at 50 ^oC to obtain a transparent solution. After adding and dissolving acrylamide (9.823 g, 97.5 mol%), nitrogen was bubbled

through for another 1 hour. Finally, 2 mL of an APS stock solution (6.5 mM) was added to initiate the reaction. The reaction was carried out at 60 ºC for 12 h. After polymerization, the product was dialyzed against pure water for 1 week. Finally, the polymer was recovered by freeze drying and white powder was obtained. The chemical structure of the $PC_{14}AM$ was characterized by FTIR.

FT-IR (ATR mode): 3410 cm^{-1} ($-NH_2$), 1675 cm^{-1} (-C=O-), 2870 cm^{-1}, 1425 cm^{-1}, 1375 cm^{-1} ($-CH_3$),1203 cm^{-1}, 1048 cm^{-1} ($-SO_3Na-$), 2925 cm^{-1}, 620 cm^{-1} ($-CH_2-$).

The molecular weight of polymer sample was determined in formamide solution by classical light scattering using a multiangle spectrometer (AMTEC Model MM1). Biggs et al. showed that the presence of a small amount of a hydrophobic comonomer (5 mol%) does not significantly affect the refractive index increment, dn/dc, of polyacrylamide in formamide solution (dn/dc = 0.111). The molecular weight of polymer sample (M_w) has been determined as 50×10^4.

The critical aggregate concentration (CAC) of the $PC_{14}AM$ and $PC_{16}AM$ were measured by steady-state fluorescence probe method，and the CAC have been determined as 0.02 wt% and 0.05 wt%, respectively.

2.3. None of thermo-response behavior of $PC_{16}AM$ solution

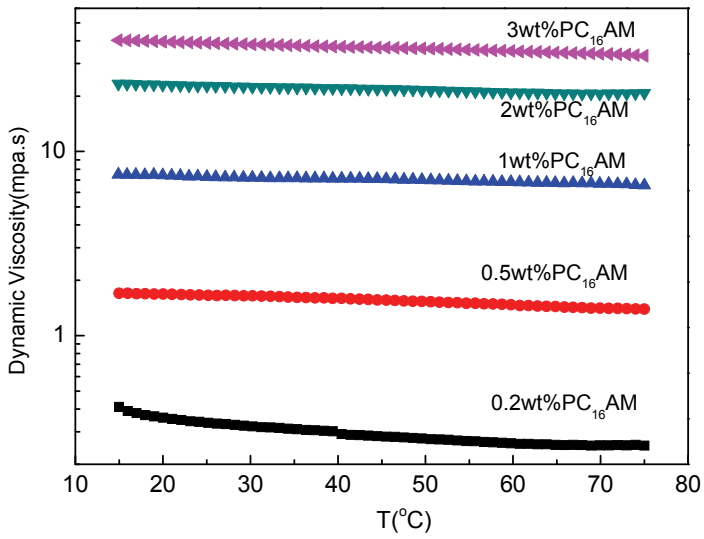


Figure S3. The thermothinning behavior of $PC_{16}AM$ solution

2.4. Phase angle and complex viscosity thermos-response behavior

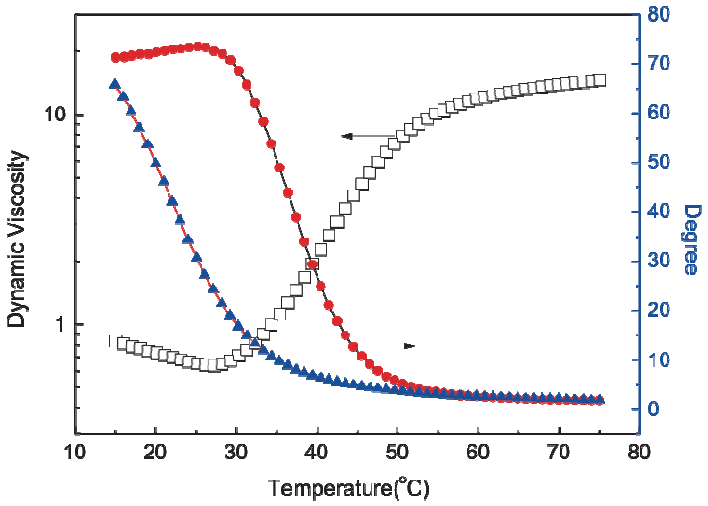


Figure S4. The thermo-response behavior of Phase angle and complex viscosity

2.5. 2D ^{1}H NMR study of the NaAMC$_{14}$S/α-CD and NaAMC$_{16}$S/α-CD mixture

Investigated by 2D ^{1}H NOESY spectra at 50ºC and 60ºC, it can be seen that the signals of inner protons (H3, H6, and H5) of α-CD were correlated with the resonance of the alkyl chain of NaAMC$_{14}$S (NaAMC$_{16}$S), indicating that the inclusion complex was stable with temperature increasing.

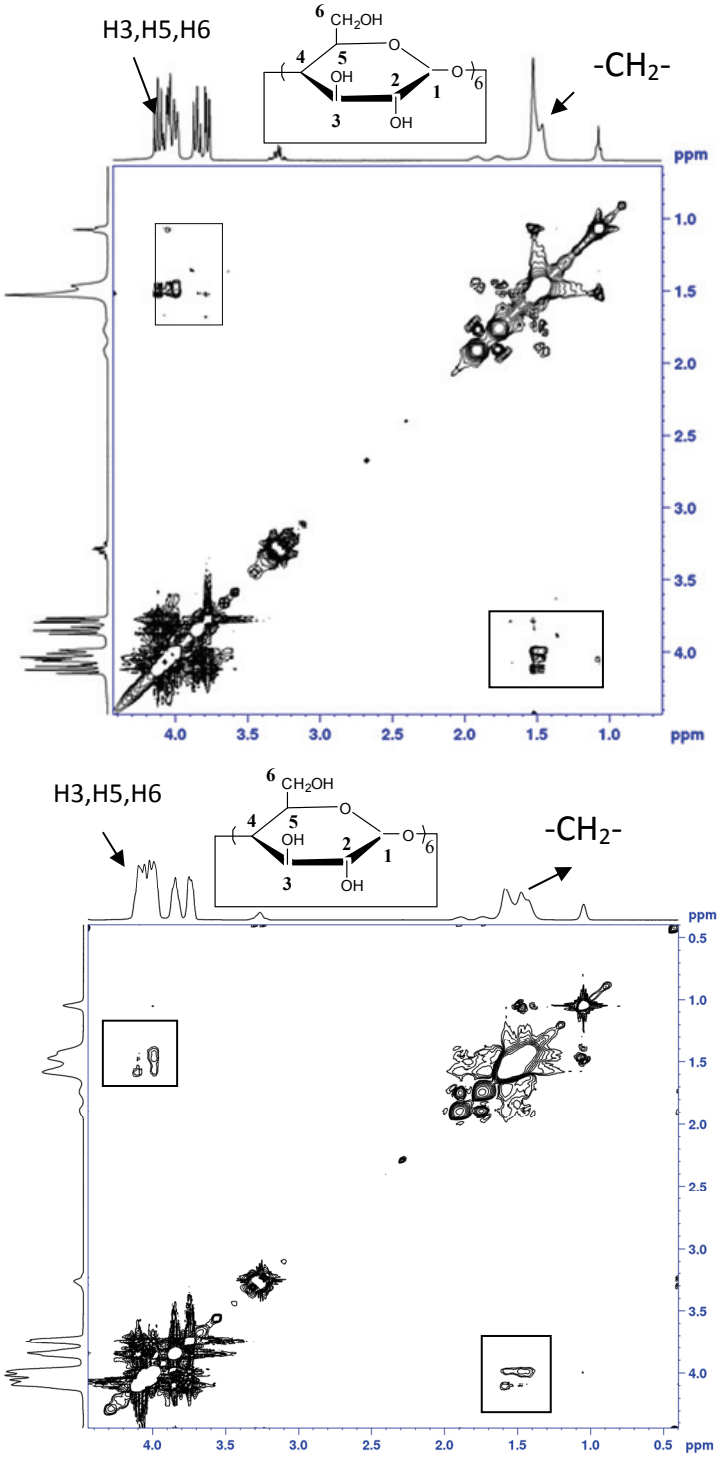


Figure S5. Two-dimensional NOESY spectra of $NaAMC_{14}S$/α-CD and $NaAMC_{16}S$/α-CD mixture in D_2O at temperature of 50 ºC and 60 ºC, respectively.

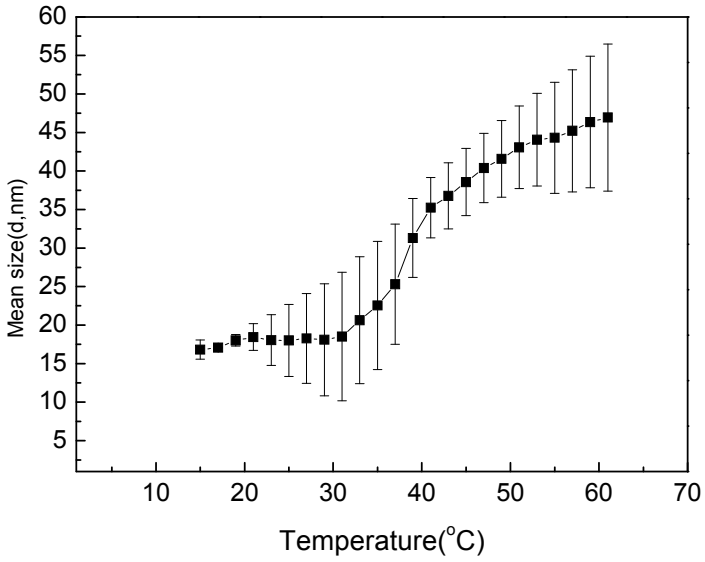


Figure S6. The DLS data for temperature dependence of 2% $PC_{14}AM$/ 4mM α-CD mixture.

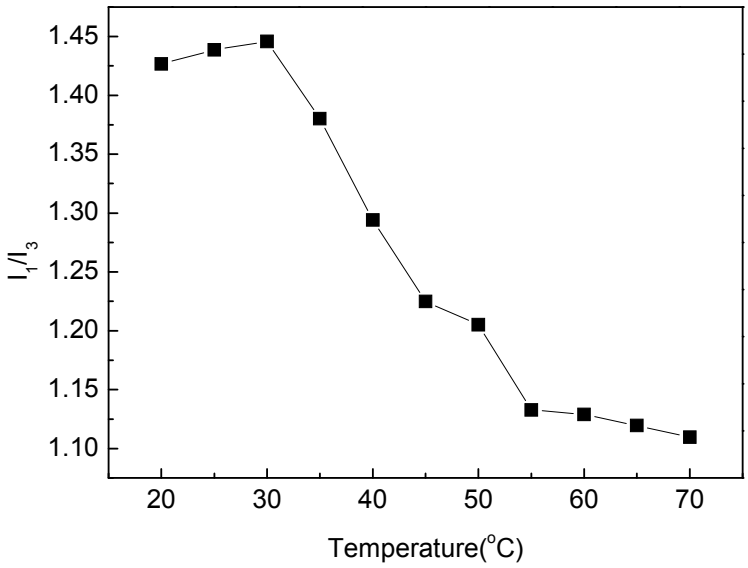


Figure S7. The fluorescence data for temperature dependence of 2% $PC_{14}AM$/ 4mM α-CD mixture.

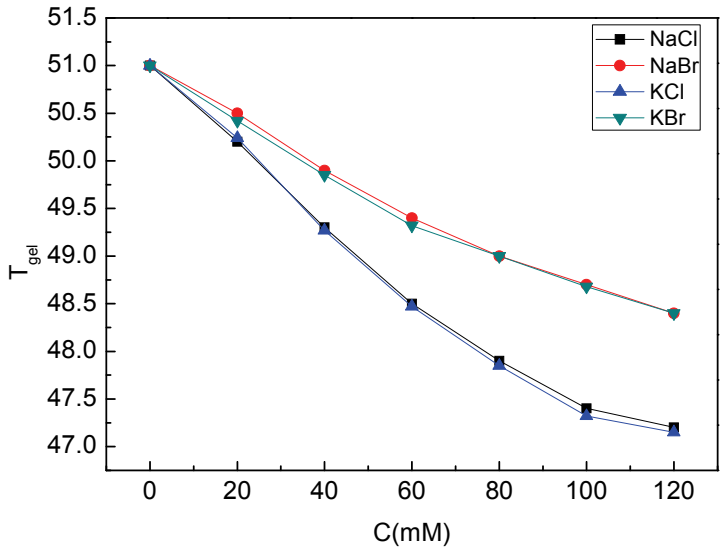
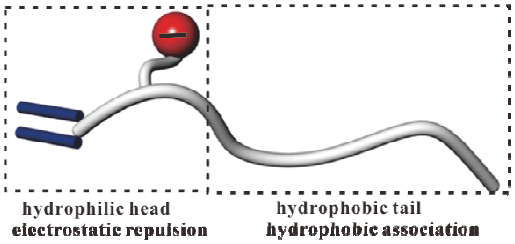


Figure S8. The salt effect on the gelation temperature of 2.5 wt%$PC_{14}AM$/8 mM α-CD mixture solution.

2.6 The effect of side chain

Table.S1. The effect of side chain on the thermos-response behavior

CH_2 in side chain	Thermogelling
8	No thermogelling
10	No thermogelling
12	slight thermo-thickening
14	thermogelling
16	thermogelling



2.7. The thermo-response behavior of $PC_{14}AM$/α-CD and $PC_{14}AM$/α-CD/Azo mixture

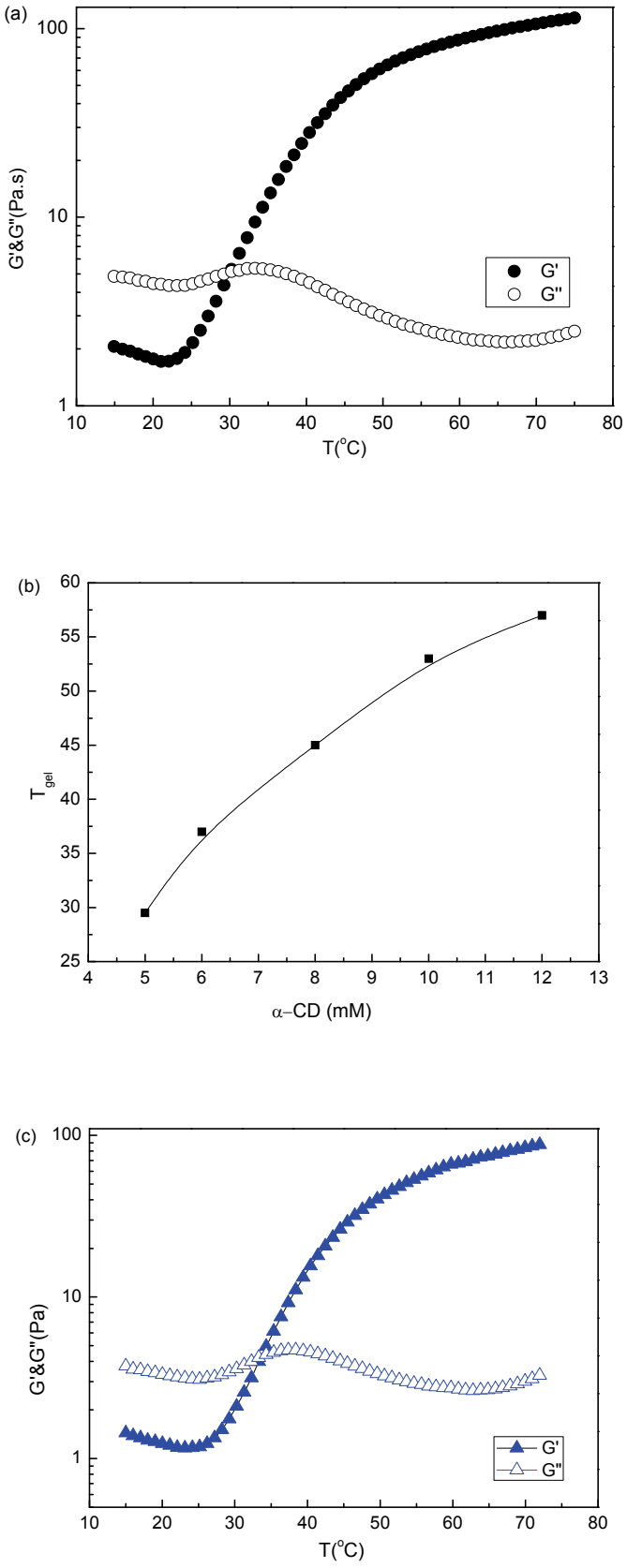


Figure S9. (a) Reology study of thermogelling behaviour of 3w t% $PC_{14}AM$/5 mM

α-CD. (b) Dependence of sol–gel transition temperature for $PC_{14}AM$/α-CD solution as a function of the α-CD (c) Reology study of thermogelling behaviour of 3 wt% $C_{14}AM$/25 mM PBA/30mM α-CD.

2.8 ^{1}H NMR study of PBA before UV irradiation, after UV irradiation and after visible light.

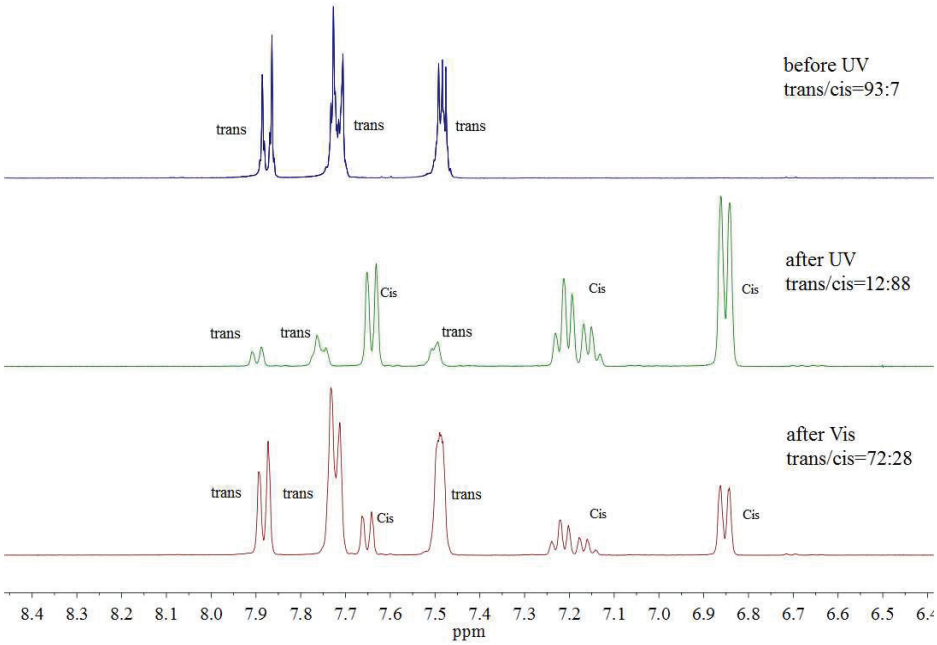


Figure S10. ^{1}H NMR spectra of a) Azo before irradiation, and b) after irradiation at 365 nm for 5 min, then c) irradiation at 430 nm for 5min.

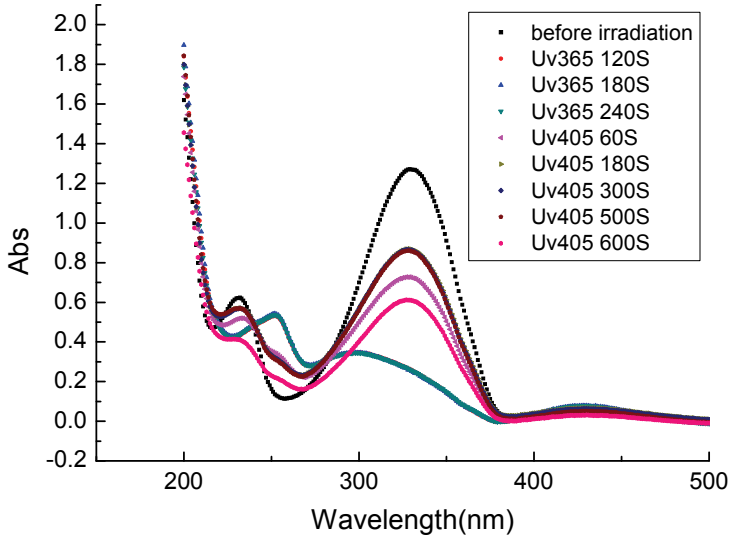
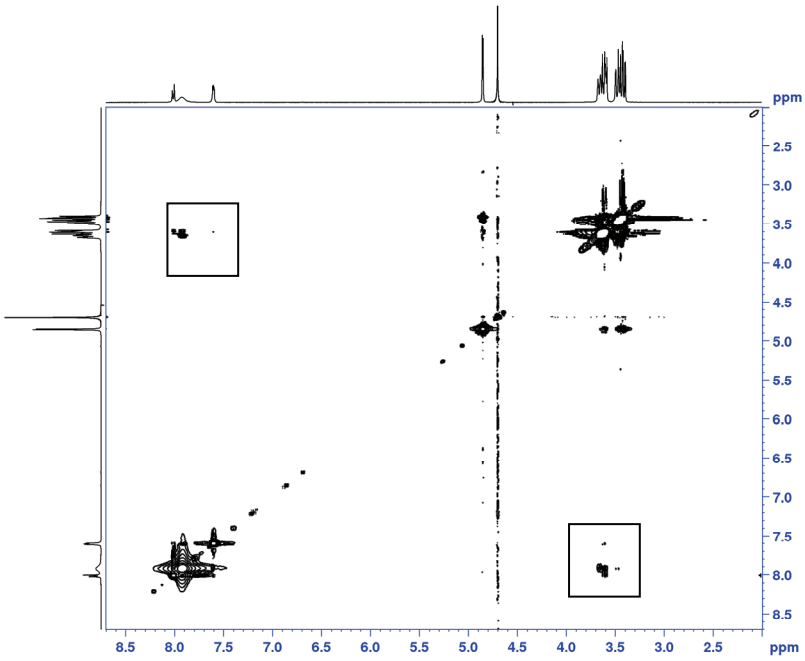


Figure S11. The irradiation time effect on the Azo configuration changes.

2.9. 2D ^{1}H NOESY study of α-CD/Azo mixture before UV and after UV

Before UV



After UV

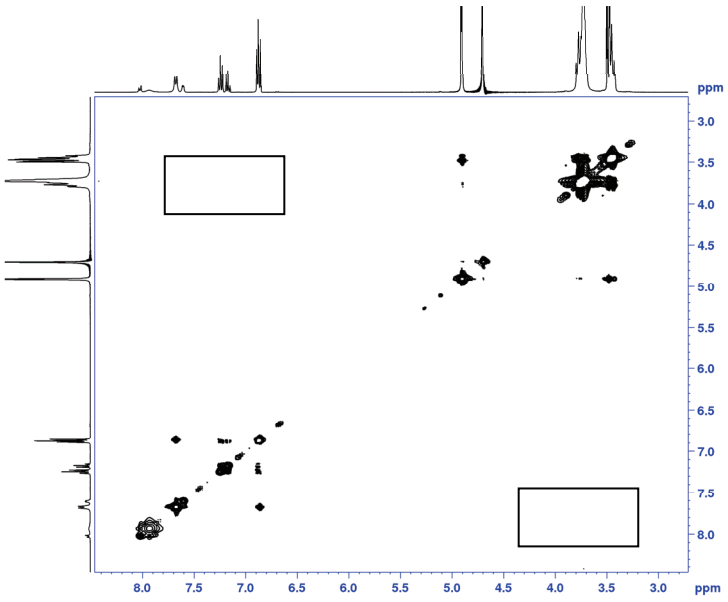


Figure S12. 2D ^{1}H NMR spectra of a) 1mM α-CD/1mM Azo before irradiation, and b) 1mM α-CD/1mM PBA after irradiation at 365 nm for 10min

2.10. The isothermal titration calorimetry (ITC) result of α-CD/PBA

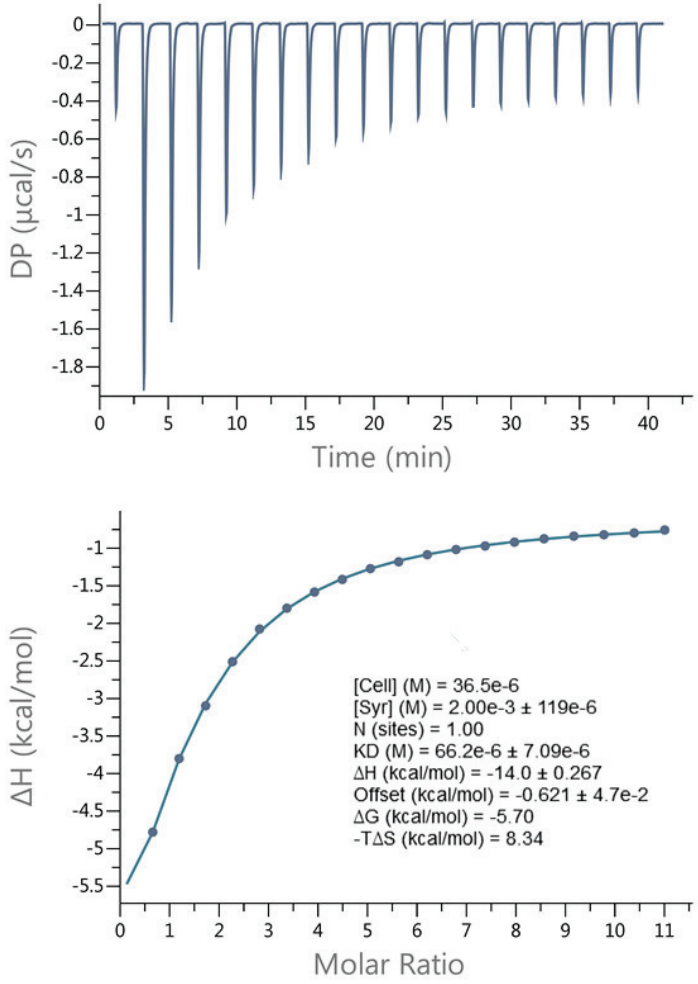


Figure S13. The isothermal titration calorimetry result of α-CD/Azo determined at 20 ^{o}C.

2.11. The competitive effect between α-CD/PC$_n$AM and α-CD/PBA

Figure S14. The competitive effect between α-CD/PC$_n$AM and α-CD/Azo .The mole ratio of α-CD:Azo is 1:1.