Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

A novel multi-stimuli responsive gelator based on D-gluconic acetal and its potential applications

Xidong Guan[a,b], Tongyang Gao[a], Anping Ma[a], Bao Zhang*[a] and Jian Song*[a,b]

[a] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China.

[b] The Co-Innovation Center of Chemistry and Chemical Engineering of Tianjin, Tianjin 300072, China.

Table of contents: **Pages**

Experimental Section

1. Materials

D-Gluconic acid, 3,4-dichlorobenzaldehyde, ethylamine, butylamine, n-octylamine and dodecylamine, DMAP (4-dimethylaminopyridine), were purchased from Shanghai Jingchun Scientifical Co., Ltd. The chemical reagents were commercially available and directly utilized without further purification.

2. Instrumentation

NMR experiments: All 400 MHz NMR studies were carried out on a Bruker DPX 400 MHz spectrometer at 300 K using cryo probe in DMSO-d_6 maintaining the concentration 4-10 mM.

Mass spectrometry: Mass spectra were recorded on a TOF-QII high-resolution mass spectrometer.

Scanning electron microscopy (SEM): Samples were prepared and dried under the ambient conditions for 10 days. After coating the samples with the gold, the images of the samples were obtained by a Hitachi S-4800 SEM. The accelerating voltage was 5 kV, and the emission current was 10 mA.

Gelation test: These tests were performed by adding the weighed amount of G8 into the measured volume of solvent in the tube (10 mm diameter) and then heating the tube until the gelators were dissolved or could not be

dissolved ever. A “stable to inversion test tube method” was adopted.[1] Each experiment was done in duplicate.

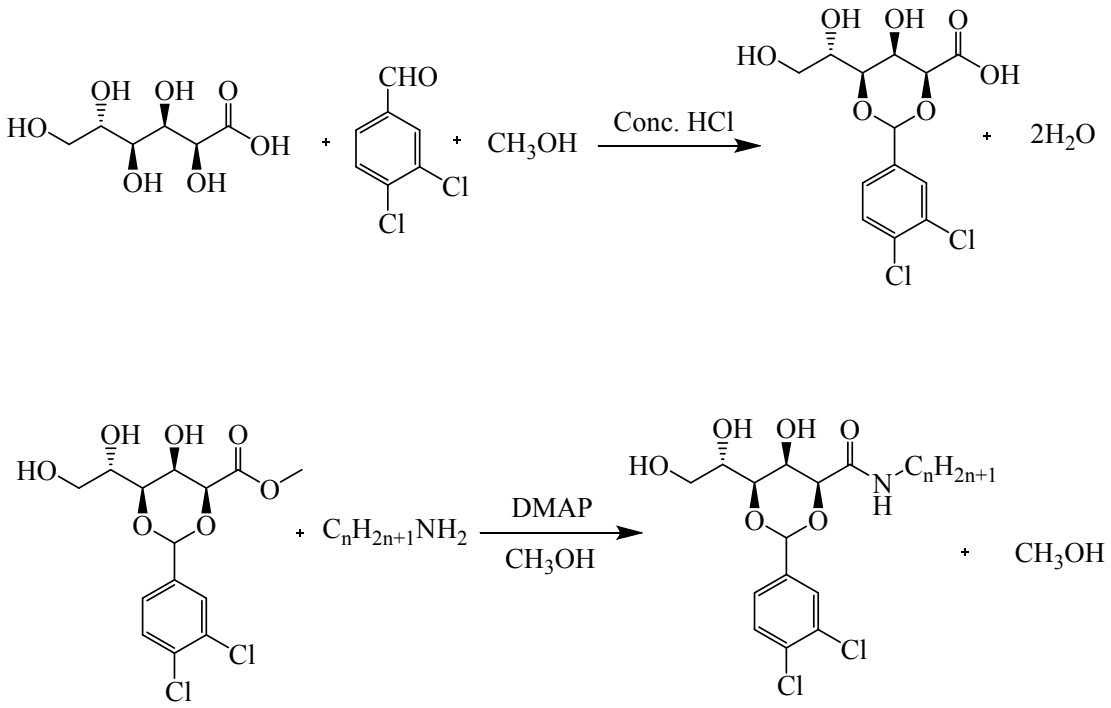
Gel-sol phase transition temperature measurements (T_{gel}): The gel-sol transition temperature was determined by a conventional “ball-drop method”.[2] A small glass ball with a diameter of 5 mm (0.24 g) was placed on the top of the gel in a test tube (10 mm diameter) which was in a thermostated oil bath and was heated at ca. 1.5 °C/min. The temperature corresponding to submersion in the solution was regarded as the T_{gel} of the gel. The measured experiments were carried out in duplicate.

Critical gelator concentrations (CGCs): CGCs were determined at 20 °C by the stable to inversion test tube method using a series of gels in which the gelator concentrations were changed in 0.1wt% increments.

Rheological Study: Measurements were performed using a strain-controlled rheometer (Anton Paar Physica MCR 301) equipped with stainless coaxial cylinder rheometer (cup diameter, 16 mm; bob diameter, 15 mm). To study the thixotropic behavior, a simple step strain experiment was performed for all gels in several steps. At first gels were subjected to a constant strain of 0.1% (step 1). Then a constant strain (25%) was applied to destroy the samples (step 2). Then a small constant strain was applied (0.1%) again and the storage modulus G′ and the loss modulus G" of the sample were monitored as functions of time (step 3). The angular frequency was kept at a constant angular frequency of 10

rad/s. Experiments were performed with gels having a concentration of 1% w/v, and an environmental temperature of 20 ℃.

3. Synthesis



Scheme S1. The synthetic route of low-molecular-weight gelators Gn.

The synthetic route for gelators Gn was shown in Scheme S1, and the detailed synthetic methods are described below.

(1) Synthesis of 2,4-(3,4-dichloro) benzylidene Methy-D-Gluconate.

87.5 g (0.5 mol) 3,4-dichlorobenzaldehyde was dissolved in 400 ml methanol at room temperature and then 215.8 g (0.55 mol) 50wt% aqueous solution of D-gluconic acid was added to this solution followed by the addition of 200 mL hydrochloride acid (12 mol/L) under vigorously stirring. The reaction mixture was stirred for 36 h and the

white solid was collected by filtration. The filter cake was washed with water for five times and hot dichloromethane for twice respectively.

Yield: 140 g (0.38 mol, 76%).

(2) Synthesis of 2,4-(3,4-dichloro) benzylidene-N-octyl-D-gluconamide (G8).

The synthesis of gelator G8 was described as follows. To a solution of 5 g (0.014 mol) 2,4-(3,4-dichloro) benzylidene Methy-D-Gluconate in 50 mL methanol was added 5.42 g (0.042 mol) n-octylamine and 0.01 g DMAP (0.008 mmol). The reaction mixture was stirred for 12 h and then 20 ml water was added. Subsequently，the white solid was collected by filtration. The filter cake was washed with hot dichloromethane for twice to obtain gelator G8. Other gelators were prepared similarly.

Yield: 4.0 g (8.6 mmol, 62%).

(3) Chemical Identification

2,4-(3,4-dichloro) benzylidene Methy-D-Gluconate.

^{1}H NMR (400 MHz, DMSO-d_6, TMS, 25 °C): δ 7.90-7.92 (s, 1H, CONH), 7.65-7.80 (d, 1H, Ar-H), 7.54-7.58 (d, 1H, Ar-H), 7.46-7.51 (s, 1H, Ar-H) , 5.67 (s, 1H, OCHO), 4.74 (t, 2H, OH) , 4.47 (t, 1H, OH)，4.35 (s, 1H, CH_2), 4.01 (d, 1H, CH), 3.76 (d, 1H, CH_2), 3.65 (m, 1H, CH_2), 3.53 (m, 1H, CH), 3.42 (m, 1H, CH), 2.65 (m, 3H, CH_3).

2, 4-(3,4-dichloro) benzylidene-N-octyl-D-gluconamide (G8).

^{1}H NMR (400 MHz, DMSO-d_6, TMS, 25 °C): δ 7.90-7.92 (s, 1H, CONH), 7.65-7.80 (d, 1H, Ar-H), 7.54-7.58 (d, 1H, Ar-H), 7.46-7.51 (s, 1H, Ar-H), 5.67 (s, 1H, OCHO), 4.72 (dd, 2H, OH), 4.47 (t, 1H, OH), 4.35 (s, 1H, CH_2)，4.00 (d, 1H, CH), 3.76 (d, 1H, CH_2), 3.64 (m, 1H, CH_2), 3.55 (m, 1H, CH), 3.41 (m, 1H, CH), 3.11 (m, 2H, CH_2), 1.42 (m, 2H, CH_2), 1.24 (s, 10H, CH_2), 0.83 (t, 3H, CH_3).

^{13}C NMR (400 MHz, DMSO-d_6, 25 °C): δ 168.47, 139.50, 132.08, 131.56, 130.91, 129.47, 127.82, 98.73, 80.89, 79.89, 69.65, 63.12, 62.99, 38.99, 31.96, 29.99, 29.49, 29.38, 27.09, 22.80, 14.66.

HRMS: (m/z) 464.1622 $(M+H)^+$, 486.1441 $(M+Na)^+$.

^{1}H NMR (400 MHz, $CDCl_3$-d_1 (gel), TMS, 25 °C): δ 7.54 (CONH), 7.43 (Ar-H), 7.26 (Ar-H), 6.41 (Ar-H), 5.54 (OCHO), 4.35 (OH), 3.97 (OH), 3.90-3.6 (CH, CH_2), 3.24 (CH_2), 1.53 (CH_2), 1.19 (CH_2), 0.80 (CH_3).

2,4-(3,4-dichloro) benzylidene-N-ethyl-D-gluconamide (G2).

^{1}H NMR (400 MHz, DMSO-d_6 TMS, 25 °C): δ 7.90-7.92 (s, 1H, CONH), 7.65-7.80 (d, 1H, Ar-H), 7.54-7.58 (d, 1H, Ar-H), 7.46-7.51 (s, 1H, Ar-H), 5.67 (s, 1H, OCHO), 4.72 (dd, 2H, OH), 4.47 (t, 1H, OH), 4.36 (s, 1H, CH_2) , 4.00 (d, 1H, CH), 3.76 (d, 1H, CH_2), 3.64 (m, 1H, CH_2), 3.55 (m, 1H, CH), 3.43 (m, 1H, CH), 3.11 (m, 2H, CH_2), 0.83 (t, 3H, CH_3).

^{13}C NMR (400 MHz, DMSO-d_6, 25 °C): δ 168.39, 139.49, 132.08, 131.57, 130.91, 129.50, 127.84, 98.77, 80.88, 79.89, 69.64, 63.11, 62.98, 33.81, 15.67.

HRMS: (m/z) 380.1104 $(M+H)^+$, 402.1209 $(M+Na)^+$.

2,4-(3,4-dichloro) benzylidene-N-butyl-D-gluconamide (G4).

^{1}H NMR (400 MHz, DMSO-d_6 TMS, 25 °C): δ 7.90-7.92 (s, 1H, CONH)，7.65-7.80 (d, 1H, Ar-H), 7.54-7.58 (d, 1H，Ar-H), 7.46-7.51 (s, 1H，Ar-H)，5.67 (s,1H, OCHO), 4.73 (dd, 2H, OH), 4.47 (t, 1H, OH), 4.36 (s, 1H, CH_2), 4.00 (d, 1H, CH), 3.76 (d, 1H, CH_2), 3.64 (m, 1H, CH_2), 3.56 (m, 1H, CH), 3.41 (m, 1H, CH), 3.12 (m, 2H, CH_2), 1.40 (m, 2H, CH_2), 1.27 (m, 2H, CH_2), 0.83 (t, 3H, CH_3).

^{13}C NMR (400 MHz, DMSO-d_6, 25 °C): δ 168.50, 139.49, 132.08, 131.56, 130.91, 129.48, 127.82, 98.75, 80.90, 79.89, 69.64, 63.12, 62.98, 38.64, 32.15, 20.22, 14.45.

HRMS: (m/z) 408.0993 $(M+H)^+$, 430.0810 $(M+Na)^+$.

2,4-(3,4-dichloro) benzylidene-N-dodecyl-D-gluconamide (G12).

^{1}H NMR (400 MHz, DMSO-d_6, TMS, 25 °C)**:** δ 7.90-7.92 (s, 1H, CONH), 7.65-7.80 (d, 1H, Ar-H), 7.54-7.58 (d, 1H, Ar-H), 7.46-7.51 (s, 1H, Ar-H), 5.67 (s, 1H, OCHO), 4.72 (dd, 2H, OH), 4.47 (t, 1H, OH), 4.35 (s, 1H, CH_2)，4.00 (d, 1H, CH), 3.76 (d, 1H, CH_2), 3.63 (m, 1H, CH_2), 3.55 (m, 1H, CH), 3.42 (m, 1H, CH), 3.12 (m, 2H, CH_2), 1.42 (m, 2H, CH_2), 1.24 (s, 18H, CH_2), 0.83 (t, 3H, CH_3).

^{13}C NMR (400 MHz, DMSO-d_6, 25 °C): δ 168.49, 139.50, 132.08, 131.56, 130.91, 129.47, 127.82, 98.73, 80.89, 79.89, 69.65, 63.12, 62.99, 38.99, 31.96, 29.99, 29.49, 29.38, 27.09, 22.80, 20.21, 18.63, 16.52, 15.65, 14.66, 14.45.

HRMS: (m/z) 520.2249 $(M+H)^+$, 542.2061 $(M+Na)^+$.

(4) ^{1}H NMR, ^{13}C NMR and HRMS Spectra of G8.

Figure S1: ^{1}H NMR (400 MHz) Spectra of G8 in DMSO-d_6.

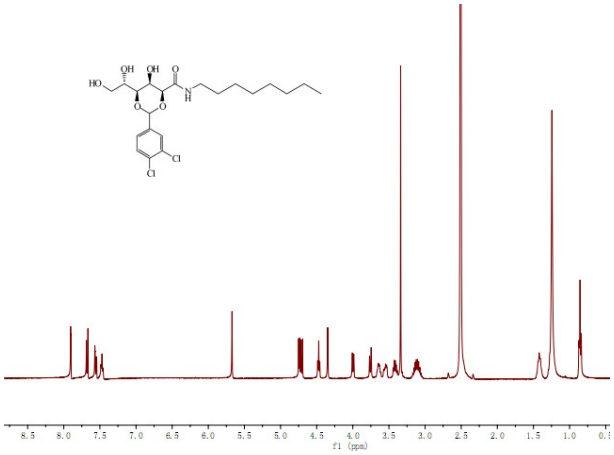


Figure S2: ^{1}H NMR (400 MHz) Spectra of chloroform gel of G8.

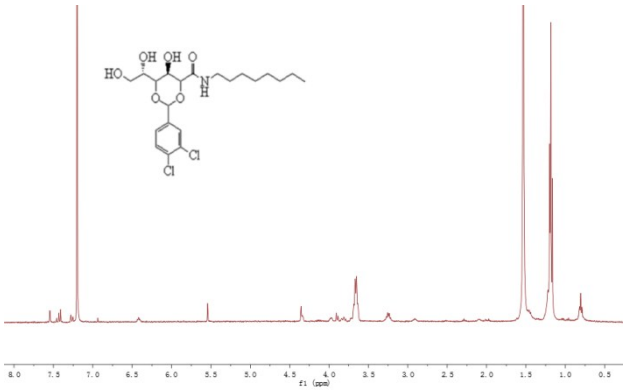


Figure S3: ^{13}C NMR (400 MHz) Spectra of G8 in DMSO-d_6.

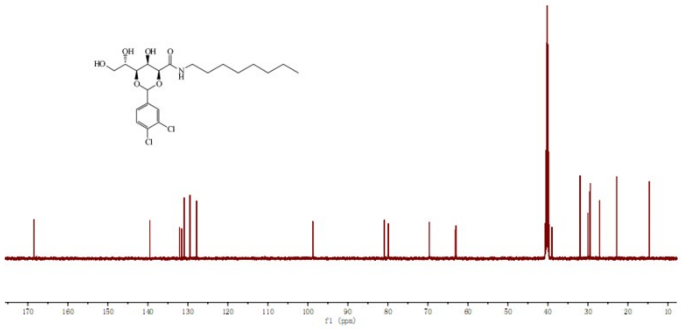


Figure S4: HRMS Spectra of G8 in CH_3OH.

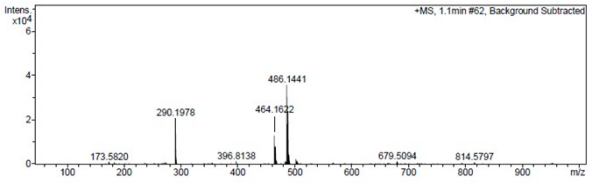


Table S1: Gelation ability of gelators Gn (n=2, 4, 8, 12) in various solvents.

	Solvent	G2	G4	G8			G12
				Phase	T_{gel} (℃)	CGC (wt%)	
	n-Octanol	OG	OG	OG	56.8	0.90	OG
2	Iso-octanol	OG	OG	OG	70.5	0.75	OG
3	n-Butyl acetate	OG	OG	OG	80.8	0.20	OG
4	Acetone	I	I	TG	52.2	0.72	TG
5	Acetonitrile	I	OG	OG	79.6	0.67	OG
6	Toluene	I	I	TG	110.3	0.07	TG
7	o-Dichlorobenzene	OG	TG	TG	115.4	0.02	TG
8	o-Xylene	I	I	TG	117.0	0.13	TG
9	Nitrobenzene	OG	TG	TG	137.1	0.08	TG
10	Hexadecane	S	OG	TG	186.9	0.08	TG
11	Liquid paraffin	S	OG	TG	202.1	0.07	TG
12	Pump oil	S	OG	TG	196.9	0.04	TG
13	Chloroform	I	OG	TG	116.2	0.06	TG
14	Chloroform(RT)	I	I	OG	80.5	0.28	OG
15	NMP/H_2O=1:1	I	I	OG	63.9	0.49	TG
16	NMP/H_2O=1:1(RT)	I	I	OG	66.6	0.83	OG
17	EG: H_2O=8:2	I	OG	OG	97.1	0.66	OG
18	Pyridine	S	S	S			S
19	DMF	S	S	S			S
20	DMSO	S	S	S			S
21	Water	I	I	I			I

Gelator concentration: 1.0% w/v, RT: gel formed at room temperature, OG: opaque gel, TG: transparent gel, S: solution, I: insoluble, EG: ethylene glycol, NMP: n-methyl-2-pyrrolidinone.

Figure S5: FTIR spectras of chloroform solution (0.1 mM) of G8 and chloroform xerogel (1.0% w/v) of G8.

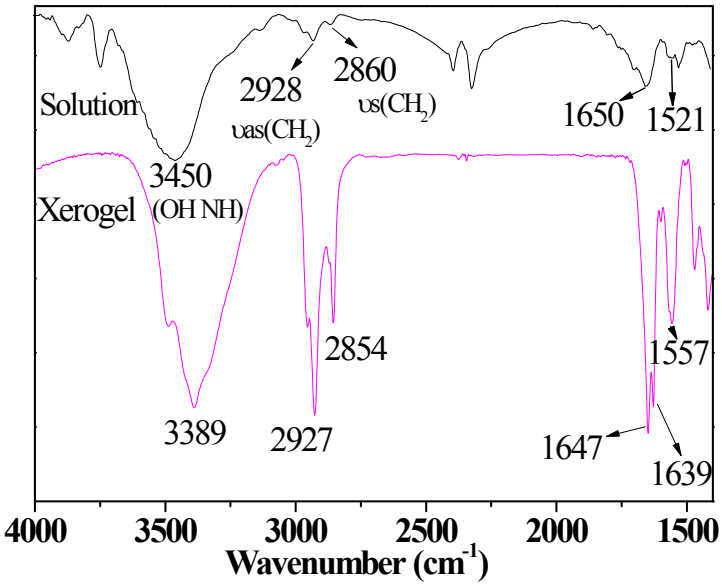
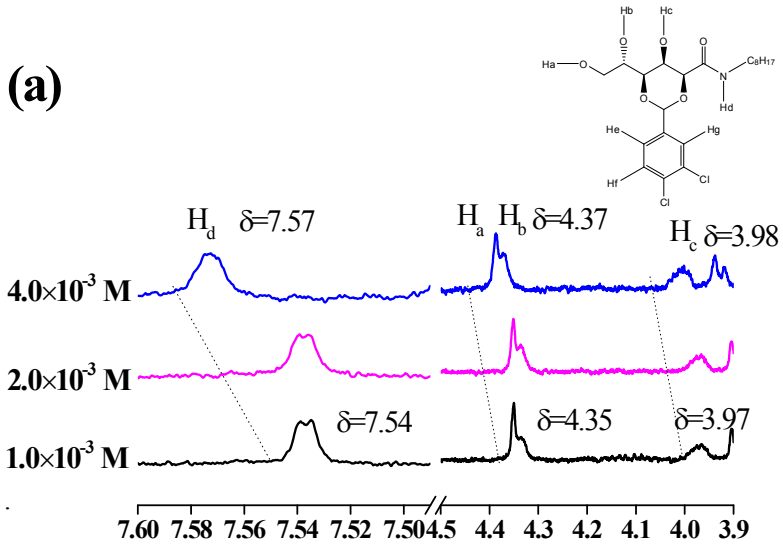
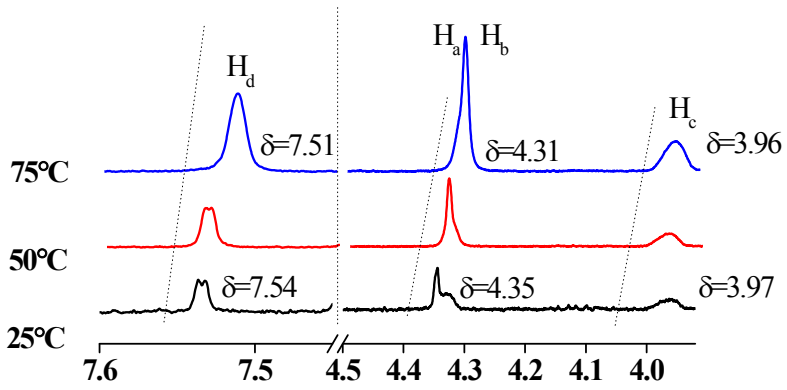


Figure S6: Change in ^{1}H NMR chemical shift of hydroxyl and amide protons of gelator G8 in chloroform at different concentrations and temperatures.



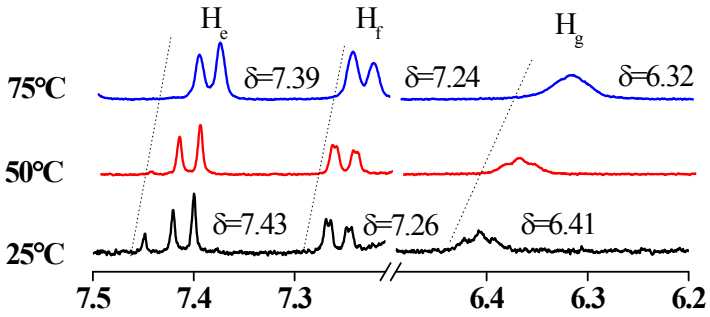
(a) Change in ^{1}H NMR chemical shift of hydroxyl and amide protons of gelator G8 in chloroform as concentrations increases from 1.0 x10^{-3} M to 4.0 x10^{-3} M at 25 ℃.

(b)



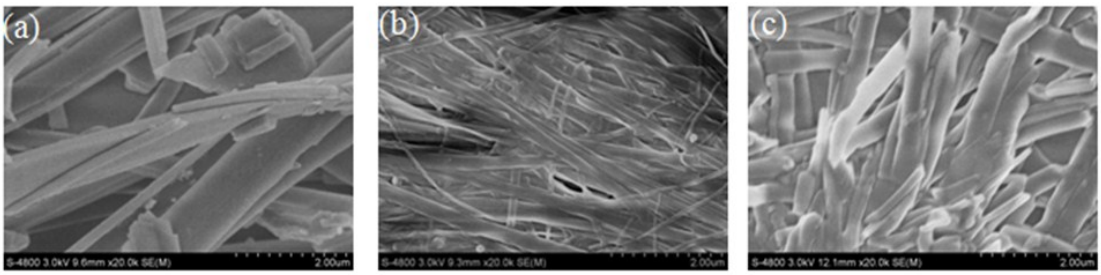
(b) Change in ^{1}H NMR chemical shift of hydroxyl and amide protons of gelator G8 in chloroform (1.0% w/v) as temperature increases from 25 to 75 ℃.

(c)



(c) Change in ^{1}H NMR chemical shift of aromatic protons of gelator G8 in chloroform (1.0% w/v) as temperature increases from 25 to 75 ℃.

Figure S7: SEM images of the xerogels of G8 in different solvents (1.0% w/v).



(a) Chloroform. (b) n-Butyl acetate. (c) o-Dichlorobenzene.

Figure S8: ^{1}H NMR spectra of G8 in chloroform (1.0% w/v) with different anions.

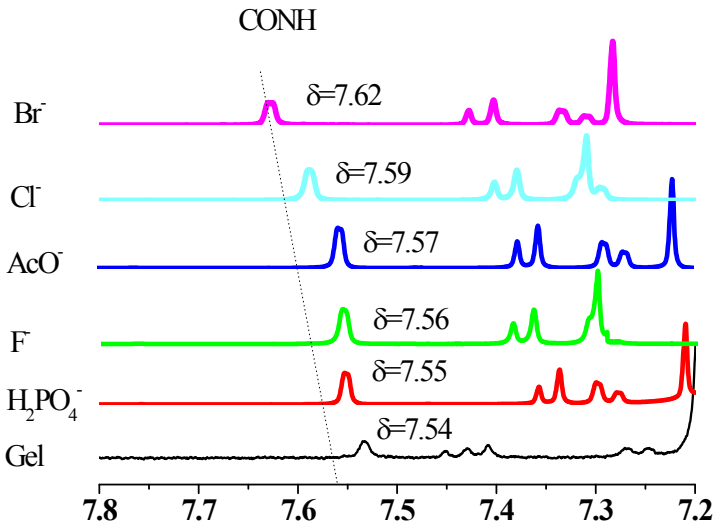


Figure S9: ^{1}H NMR spectra of G8 in chloroform (1.0% w/v) with base.

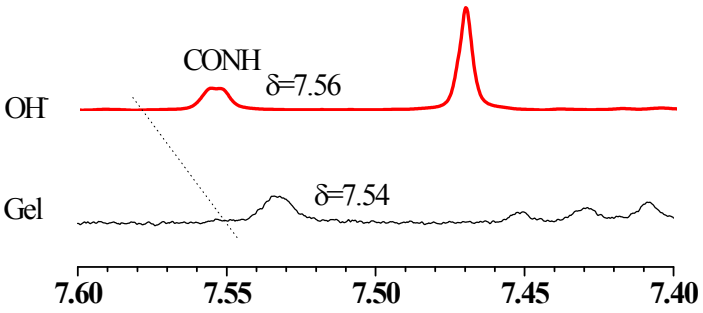
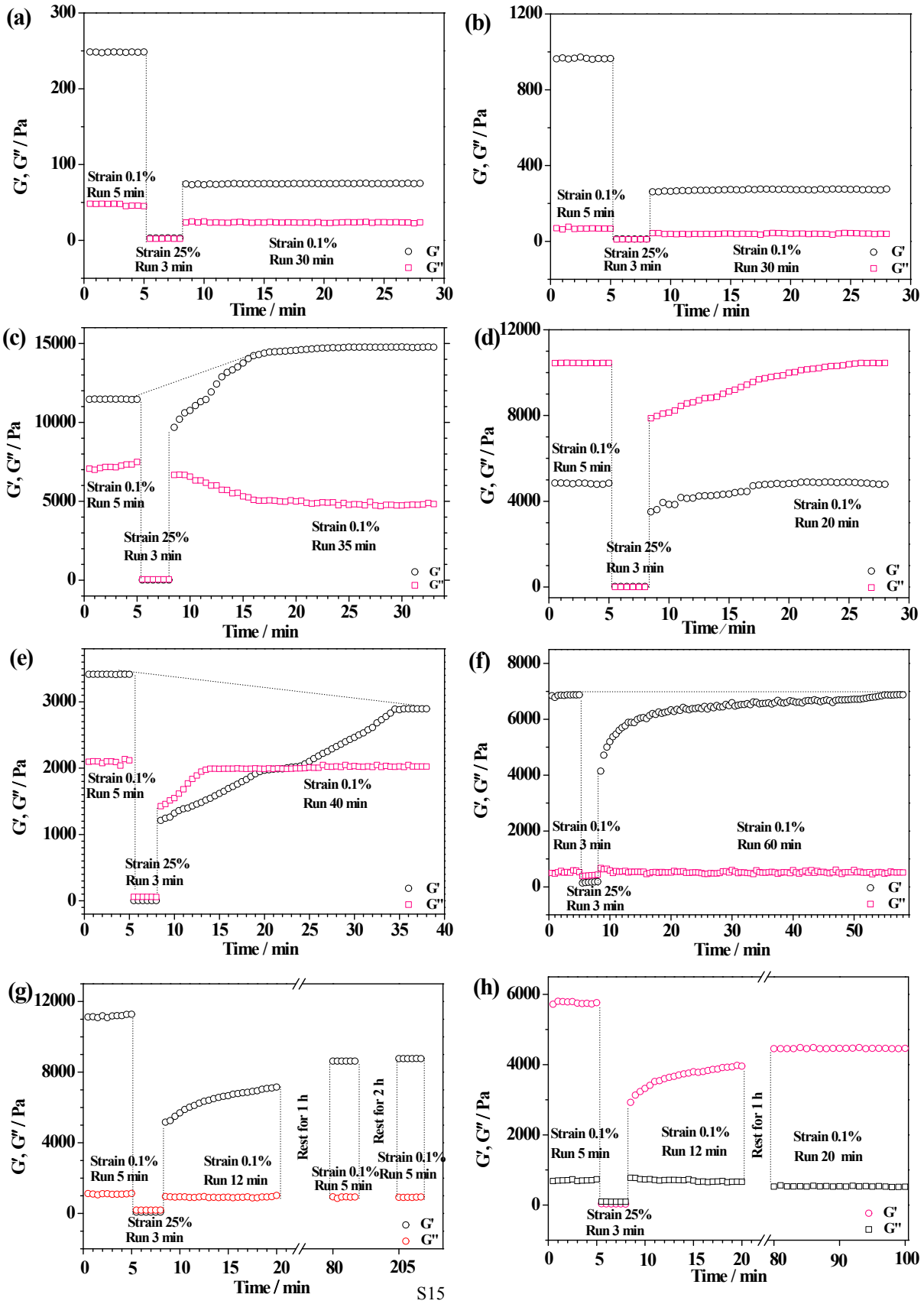


Figure S10: The step strain experimental data obtained from the gels of G8 in various organic solvents (1.0% w/v).

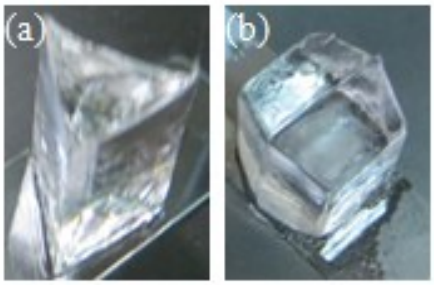


(a) Toluene gel. (b) o-Dichlorobenzene gel. (c) n-Butyl acetate gel. (d) Chloroform gel. (e) o-Xylene gel. (f) Pump oil gel. (g) EG/H_2O=8:2 gel. (h) NMP/H_2O=1:1 gel.

Figure S11: Iodine-adsorption study.

Following submergence of the n-butyl acetate xerogel (20 mg) of G8 into 7 ml saturation aqueous solutions of iodine, it efficiently adsorbed most of the iodine molecules from water within 12 h.

Figure S12: Moldability of the o-dichlorobenzene gel of G8.



(a) A gel triangular prism. (b) A gel hexagonal prism. All gels are made from o-dichlorobenzene gel of G8 at 0.5% w/v.

References

1 H. Wang, F. F. Wang, H. T. Tang, J .Y Zhang and Y. J. Yang, *Acta Chim. Sin*., 2007, **65**, 1057-1063.

2 G. Zhu and J. S. Dordick, *Chem. Mater*., 2006, **18**, 5988-5995.