Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Flexible and highly transparent two-component organogels with enhanced viscoelasticity for self-healing materials and room-temperature phase-selective gelation

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1. Materials

D-Gluconic acid, 3,4-dichlorobenzaldehyde, hydrazine hydrate, 1,4-butanediamine, 1,6-hexanediamine, 1,12-Dodecanediamine and aliphatic acids, 4-dimethylaminopyridine were purchased from Shanghai Jingchen 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 300K 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.

Field Emission Scanning Electron Microscope (FESEM): The morphologies of the xerogels were obtained by a Hitachi S-4800 SEM instrument operating at 3-5 kV. Samples were prepared by dropping the diluted solution of gels on the thin aluminium sheets and then dried under vacuum for 24 h. We coated the samples with a thin layer of Au before the experiment.

FT-IR spectroscopy: IR spectra were collected by a FTS3000 spectrometer with KBr pellets. The xerogels were prepared by drying chlorobenzene gels on glass slides under vacuum for 24 h.

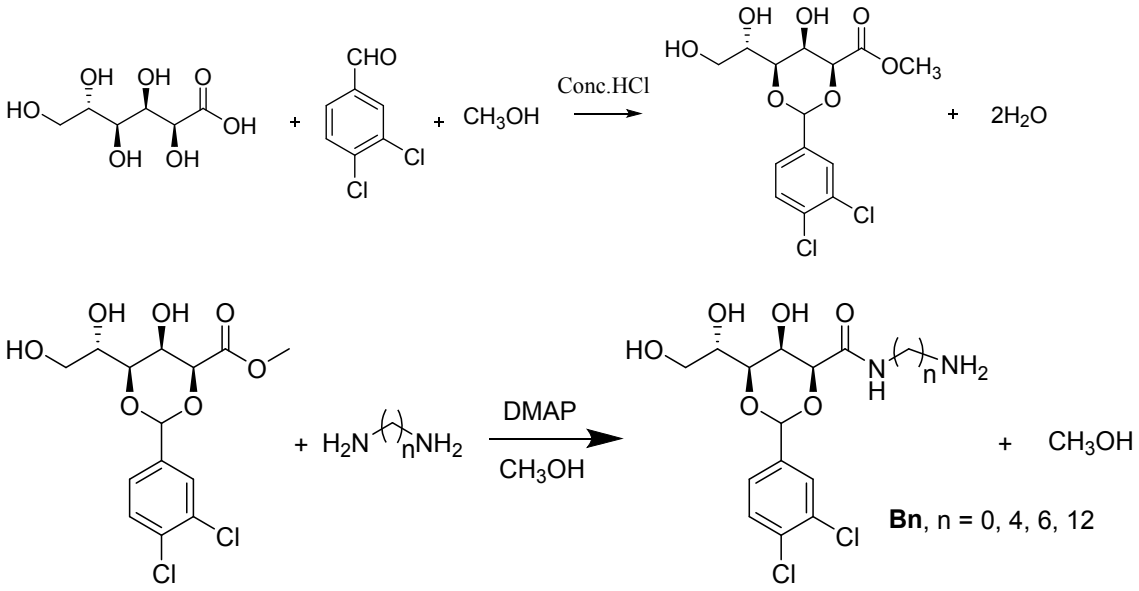
Powder X-ray diffraction (PXRD): PXRD diagrams of xerogels which were prepared from chlorobenzene gels were obtained by using a Bruker D8-S4 (CuKα radiation, λ=1.546 Å). The d spacing values were calculated by Bragg's law (nλ=2d sin θ).

Rheology measurements: Rheology experiments were carried out with a strain-controlled rheometer (Anton Paar Physica MCR 301) equipped with steel-coated parallel-plate geometry (15 mm diameter). The gap distance was fixed at 0.5 mm. A solvent trapping device was placed above the plate and measurement was set at 20 °C in order to avoid solvent evaporation. The frequency sweep at a constant strain of 0.1% was obtained from 0.1 to 100 rad⋄s^{-1}. Strain sweep was performed in the 0.01%-1000% range at a constant frequency (1 Hz). The time sweep was conducted to observe the recovery property of the gel. First, a constant strain of 0.1% was applied on the sample. Then a constant strain of 100% was applied to destroy the sample. And then a constant strain (0.1%) was applied again. The storage modulus G' and the loss modulus G'' of the sample were monitored as functions of time in this experiment.

Gelation tests: Gelation tests for Bn in organic solvents were investigated by a typical tube inversion method. Bn and aliphatic acid (molar ratio of 1:1) were mixed in an organic solvent (1 mL) in a sealed test tube, which was heated until the solid was completely dissolved and then cooled to room temperature. Finally, the test tube was inversed to observe whether the solution inside could still flow.[1] Gelation was considered to have occurred when a homogeneous substance was obtained which

exhibited no gravitational flow, and it was denoted by “G”. Solution and solid-like gel may coexist within a system as “partial gels (PG)”. Systems, in which only solution was obtained, were referred to as solution (S). If clear solutions were obtained when they are hot, but precipitation occurs when they are cooled down to room temperature, these systems are denoted by “precipitation (P)”. In an insoluble system (I), gelator could not be dissolved even at the boiling point of the solvent. The critical gelation concentrations (CGCs) means the minimum amount of gelator required to immobilize 1 mL of solvent.

3. Synthesis



Scheme S1. The synthetic route of Bn (n=0, 4, 6, 12).

The synthetic route for compounds Bn was shown in Scheme S1, the detaied synthetic methods are described below.

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

The synthesis and characterization of the precursors 2,4-(3,4-dichloro) benzylidene Methy-D-Gluconate was reported previously.[2]

(2) Synthesis of compounds Bn

5 g (0.014 mol) 2,4-(3,4-dichloro) benzylidene Methy-D-Gluconate was dissolved in 50 mL methanol, then 4.88 g (0.042 mol) 1,6-hexanediamine and 0.01 g DMAP (0.008 mmol) were added. 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 water for twice and recrystallized with methanol to obtain compound B6 with a yield of 80%. Similarly, B0, B4, B12 were obtained from 2,4-(3,4-dichloro) benzylidene Methy-D-Gluconate with hydrazine hydrate, 1,4-butanediamine and 1,12-dodecamethylenediamine respectively and purified by the same method.

(3) Chemical characterization

B0

^{1}H NMR (400MHz, DMSO-d_6, TMS, 25 °C)：δ 8.84-8.80 (s, 1H, CONH), 7.95-7.99 (d,

J=2.32 Hz, 1H, Ar-H), 7.63-7.67 (d, *J*=8.77 Hz, 1H, Ar-H), 7.53-7.57 (s, 1H, Ar-H), 5.65 (s, 1H, OCHO), 4.75 (d, *J*=7.17 Hz, 1H, OH), 4.66 (d, *J*=8.78 Hz, 1H, OH), 4.47 (d, *J*= 8.28 Hz, 1H, OH), 4.45 (s, 1H, CH), 4.31 (s, 2H, NH_2), 3.99 (d, *J*=8.78, 1H, CH), 3.77 (d, *J*=9.51, 1H, CH), 3.62 (m, 1H, CH_2), 3.55 (m, 1H, CH_2), 3.42 (m, 1H, CH).

^{13}C NMR (400 MHz, DMSO-d_6, 25 °C)：δ 167.33, 139.21, 131.88, 131.35, 130.57, 129.21, 127.50, 98.50, 80.52, 79.60, 69.38, 62.99, 52.10. HRMS calcd for $C_{13}H_{16}Cl_2N_2NaO_6$ $[M+Na]^+$: 389.0278; Found: 389.0192.

B4

^{1}H NMR (400MHz, DMSO-d_6, TMS, 25 °C)：δ 7.99-8.01(d, *J*=1.82 Hz, 1H, Ar-H), 7.69-7.75 (dd, *J*=3.81, 8.70 Hz, 1H, Ar-H), 7.54-7.58 (d, *J*=1.91 Hz, 1H, Ar-H), 7.46-7.51 (d, *J*=5.31 Hz, 1H, CONH), 5.67 (s, 1H, OCHO), 4.34 (s, 2H, OH), 4.00 (s, 1H, OH), 3.75 (d, *J*=9.12 Hz, 1H, CH), 3.64(m, 1H, CH), 3.55(dd, *J*=2.65Hz, 12.00Hz, 1H, CH_2), 3.41 (dd, *J*=5.72 Hz, 11.44Hz, 1H, CH_2), 3.12 (m, 2H, CH_2), 2.53 (m, 2H, CH_2), 1.45 (m, 2H, CH_2), 1.32(m, 2H, CH_2).

^{13}C NMR (400 MHz, DMSO-d_6, 25 °C)：δ 168.56, 139.53, 132.09, 131.57, 130.93, 129.45, 127.79, 98.74, 80.95, 79.96, 69.69, 63.15, 63.02, 40.41, 38.77, 31.09, 27.46. HRMS calcd for $C_{17}H_{24}Cl_2N_2NaO_6$ $[M+Na]^+$: 445.0904; Found: 445.0966

B6

^{1}H NMR (400MHz, DMSO-d_6, TMS, 25 °C)：δ 7.89 (d, *J*=1.8Hz, 1H, Ar-H), 7.67(d, *J*=6.9Hz, 1H，Ar-H), 7.54-7.58 (dd, *J*=1.8Hz, 9.0Hz, 1H, Ar-H), 7.47 (t, *J*=6.3Hz, 1H, CONH), 5.67 (s, 1H, OCHO), 4.34 (s, 1H, OH), 4.00 (s, 1H, OH), 3.75 (d, *J*=9.2 Hz, 1H, CH), 3.62-3.64 (m, 1H, CH), 3.55 (dd, *J*=3.2Hz, 10.8 Hz, 1H, CH_2), 3.41 (dd, *J*=5.0 Hz, 11.7 Hz, 1H, CH), 3.17-3.21 (m, 2H, CH_2), 3.12 (m, 2H, CH_2), 2.52 (t, *J*=6.5 Hz, 2H, CH_2), 1.38 (m, 2H, CH_2), 1.34 (m, 2H, CH_2), 1.32 (m, 2H, CH_2), 1.29 (m, 2H, CH_2).

^{13}C NMR (400 MHz, DMSO-d_6, 25 °C)：δ 168.31, 139.31, 131.89, 131.37, 130.72, 129.25, 127.59, 98.54, 80.73, 79.75, 69.48, 62.94, 62.82, 40.69, 38.76, 33.68, 29.80, 26.77, 26.64. HRMS calcd for $C_{19}H_{28}Cl_2N_2NaO_6$ $[M+Na]^+$: 473.1217; Found: 473.1244

B12

^{1}H NMR (400MHz, DMSO-d_6, TMS, 25 °C)：δ7.89 (d, *J*=1.22 Hz, 1H, Ar-H), 7.67 (d, *J*=8.32 Hz, 1H, Ar-H), 7.55 (dd, *J*=1.48 Hz, 9.26 Hz, 1H, Ar-H), 7.46 (t, *J*=5.85 Hz, 1H, CONH), 5.67 (s, 1H, OCHO), 4.34 (s, 1H, OH), 4.00 (s, 1H, OH), 3.76 (d, *J*=8.53 Hz, 1H, CH), 3.64 (m, 1H, CH), 3.56 (dd, *J*=4.01Hz, 12.67Hz, 1H, CH_2), 3.41 (dd, *J*=4.52 Hz, 11.54 HZ, 2H, CH), 3.07-3.15 (m, 3H, CH_2), 1.4 2(s, 2H, CH_2), 1.32 (s, 2H, CH_2), 1.24 (s, 14H, CH_2).

^{13}C NMR (400 MHz, DMSO-d_6, 25 °C)：δ 168.47, 139.52,132.09, 131.57, 130.91, 129.44, 127.78, 98.73, 80.93, 79.96, 69.69, 63.15, 63.02, 40.24, 39.00, 29.96, 29.76, 29.69, 29.49, 27.06. HRMS calcd for $C_{25}H_{40}Cl_2N_2NaO_6$ $[M+Na]^+$: 557.2156; Found: 557.2195

Table S1: Gelation abilities of compounds Bn (n=0, 4, 6, 12) in solvents.

	Solvent	B0	B4	B6	B12
1	DMSO	S	S	S	S
2	NMP	S	S	S	S
3	DMF	S	S	S	S
4	Methanol	I	S	S	OG
5	Ethanol	I	S	S	OG
6	n-Octanol	I	TG	TG	TG
7	Toluene	I	PG	PG	OG
8	o-Xylene	I	OG	OG	OG
9	Chlorobenzene	I	OG	OG	OG
10	1,4-dioxane	I	PG	OG	OG
11	Chloroform	I	I	I	I
12	Acetonitrile	I	I	I	I
13	n-hexane	I	I	I	I

Gelator concentration: 2.0 wt%, Gels were formed by heating-cooling method. OG: opaque gel, TG: transparent gel, PG: partial gel, S: solution, I: insoluble.

Table S2: Gelation abilities of B0 with aliphatic acids in solvents.

Solvent	B0	B0-A10	B0-A12	B0-A14	B0-A16	B0-A18	B0-HSA	B0-LA
DMSO	S	S	S	S	S	S	S	S
Methanol	I	I	I	I	I	I	I	I
n-Octanol	I	I	I	I	I	I	I	I
Toluene	I	I	I	I	I	I	I	I
Chlorobenzene	I	I	I	I	I	I	I	I
o-Xylene	I	I	I	I	I	I	I	I
1,4-dioxane	I	I	I	I	I	I	I	I
Chloroform	I	I	I	I	I	I	I	I
Acetonitrile	I	I	I	I	I	I	I	I
n-hexane	I	I	I	I	I	I	I	I

Gelator concentration: 2.0 wt%, Gels were formed by heating-cooling method. S: solution, I: insoluble.

Table S3: Gelation abilities of B4 with aliphatic acids in solvents.

Solvent	B4	B4-A10	B4-A12	B4-A14	B4-A16	B4-A18	B4-HSA	B4-LA
DMSO	S	S	S	S	S	S	S	S
Methanol	S	S	S	S	S	S	S	S
n-Octanol	1.5	S	S	S	S	S	S	S
Toluene	PG	I	PG	PG	PG	PG	PG	I
Chlorobenzene	G(0.6)	G(1.5)	G(0.6)	G(0.5)	G(0.5)	G(0.5)	G(0.6)	G(1.0)
o-Xylene	G(0.5)	G(4.7)	G(3.8)	G(0.5)	G(0.5)	G(0.5)	G(0.5)	G(0.8)
1,4-dioxane	PG	G(2.5)	G(2.4)	G(2.6)	G(2.5)	G(2.5)	G(2.6)	G(2.7)
Chloroform	I	PG	PG	PG	PG	PG	PG	I
Acetonitrile	I	I	I	I	I	I	I	I
n-hexane	I	I	I	I	I	I	I	I

Gels were formed by heating-cooling method. G: gel with critical gelation concentrations (CGCs); PG: partial gel; I: insoluble; S: solution.

Table S4: Gelation abilities of B6 with aliphatic acids in solvents.

Solvent	B6	B6-A10	B6-A12	B6-A14	B6-A16	B6-A18	B6-HSA	B6-LA
DMSO	S	S	S	S	S	S	S	S
Methanol	S	S	S	S	S	S	S	S
n-Octanol	G(1.3)	G(0.8)	G(0.8)	G(0.8)	G(0.8)	G(0.8)	G(1.0)	G(1.3)
Toluene	I	PG	PG	PG	PG	PG	PG	PG
Chlorobenzene	G(0.5)	G(0.04)	G(0.04)	G(0.05)	G(0.04)	G(0.04)	G(0.3)	G(0.7)
o-Xylene	G(0.3)	G(0.06)	G(0.07)	G(0.08)	G(0.07)	G(0.07)	G(0.2)	G(0.5)
1,4-dioxane	G(1.5)	G(0.5)	G(0.5)	G(0.4)	G(0.4)	G(0.3)	G(1.3)	G(1.8)
Chloroform	I	PG	PG	PG	PG	PG	PG	I
Acetonitrile	I	PG	PG	PG	PG	PG	PG	I
n-hexane	I	I	I	I	I	I	I	I

Gels were formed by heating-cooling method. G: gel with critical gelation concentrations (CGCs); PG: partial gel; I: insoluble; S: solution.

Table S5: Gelation abilities of B12 with aliphatic acids in solvents.

Solvent	B12	B12-A10	B12-A12	B12-A14	B12-A16	B12-A18	B12-HSA	B12-LA
DMSO	S	S	S	S	S	S	S	S
Methanol	G(1.2)	P	P	P	P	P	P	P
n-Octanol	G(0.7)	G(1.2)	G(1.2)	G(1.2)	G(1.2)	G(1.2)	G(1.4)	G(1.0)
Toluene	G(0.2)	I	G(1.4)	G(1.4)	G(1.2)	G(1.4)	G(1.4)	I
Chlorobenzene	G(0.3)	G(0.4)	G(0.4)	G(0.4)	G(0.3)	G(0.3)	G(0.4)	G(0.7)
o-Xylene	G(0.2)	G(0.4)	G(0.4)	G(0.4)	G(0.4)	G(0.3)	G(0.3)	G(0.8)
1,4-dioxane	G(1.0)	G(3.5)	G(3.5)	G(2.0)	G(1.9)	G(1.8)	G(1.9)	G(3.6)
Chloroform	I	I	I	I	I	I	I	I
Acetonitrile	I	I	I	I	I	I	I	I
n-hexane	I	I	I	I	I	I	I	I

Gels were formed by heating-cooling method. G: gel with critical gelation concentrations (CGCs); PG: partial gel; I: insoluble; S: solution; P: precipitate.

Pictures of mechanical response of 1.0 wt% of gels in chlorobenzene:

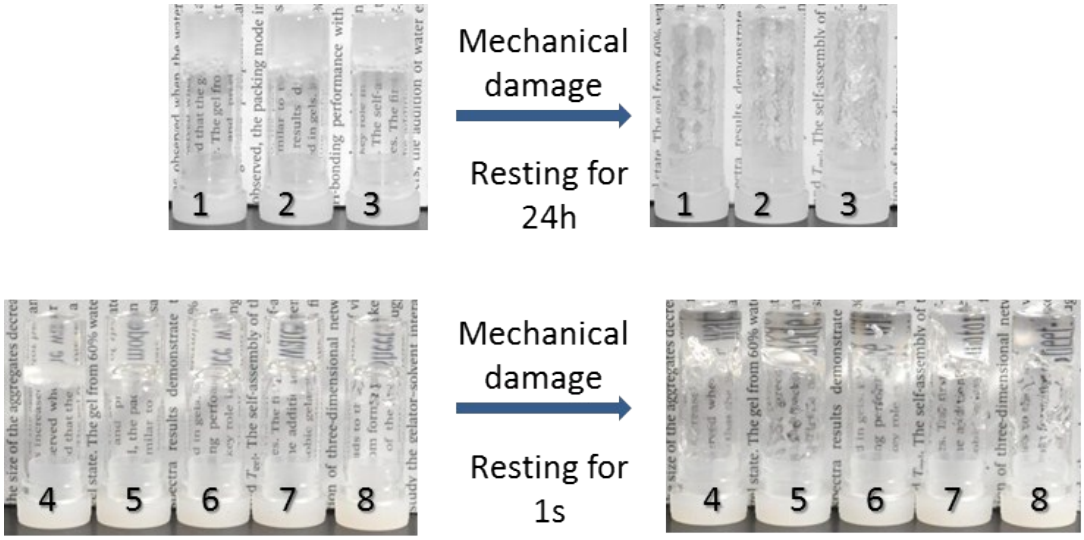


Figure S1. Pictures of mechanical response of 1.0 wt% of gels in chlorobenzene (1) B6, (2) B6-HSA, (3) B6-LA, (4) B6-A10, (5) B6-A12, (6) B6-A14, (7) B6-A16, (8) B6-A18.

Frequency sweep of chlorobenzene gel (2 wt%) with a fixed strain (0.1%):

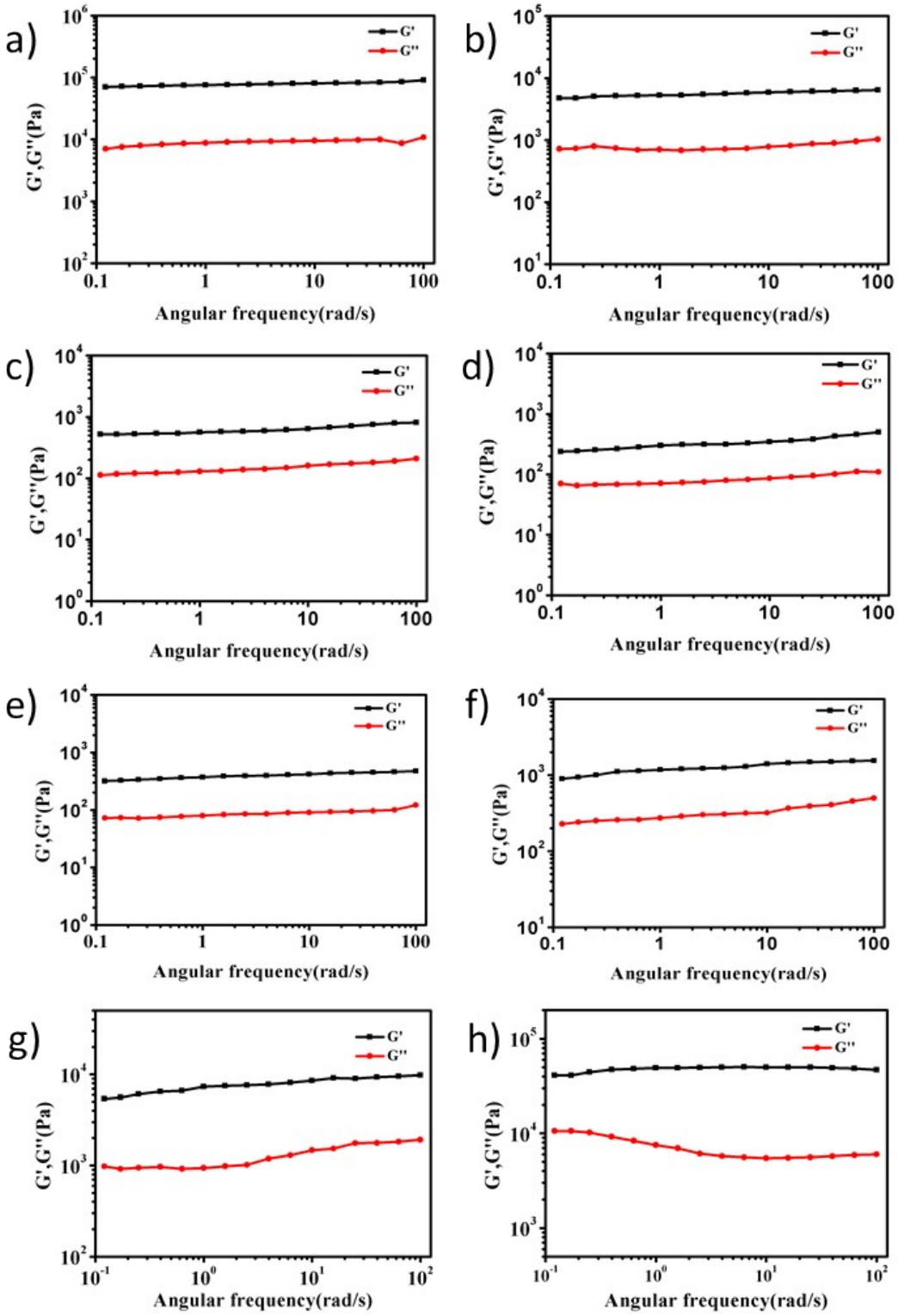


Figure S2. Frequency sweep of chlorobenzene gel (2 wt%) with a fixed strain (0.1%). (a) B6; (b) B6-A10; (c) B6-A12; (d) B6-A14; (e) B6-A16; (f) B6-A18; (g) B6-HSA; (h) B6-LA.

Strain sweep of chlorobenzene gel (2 wt%) with a fixed frequency (1 Hz):

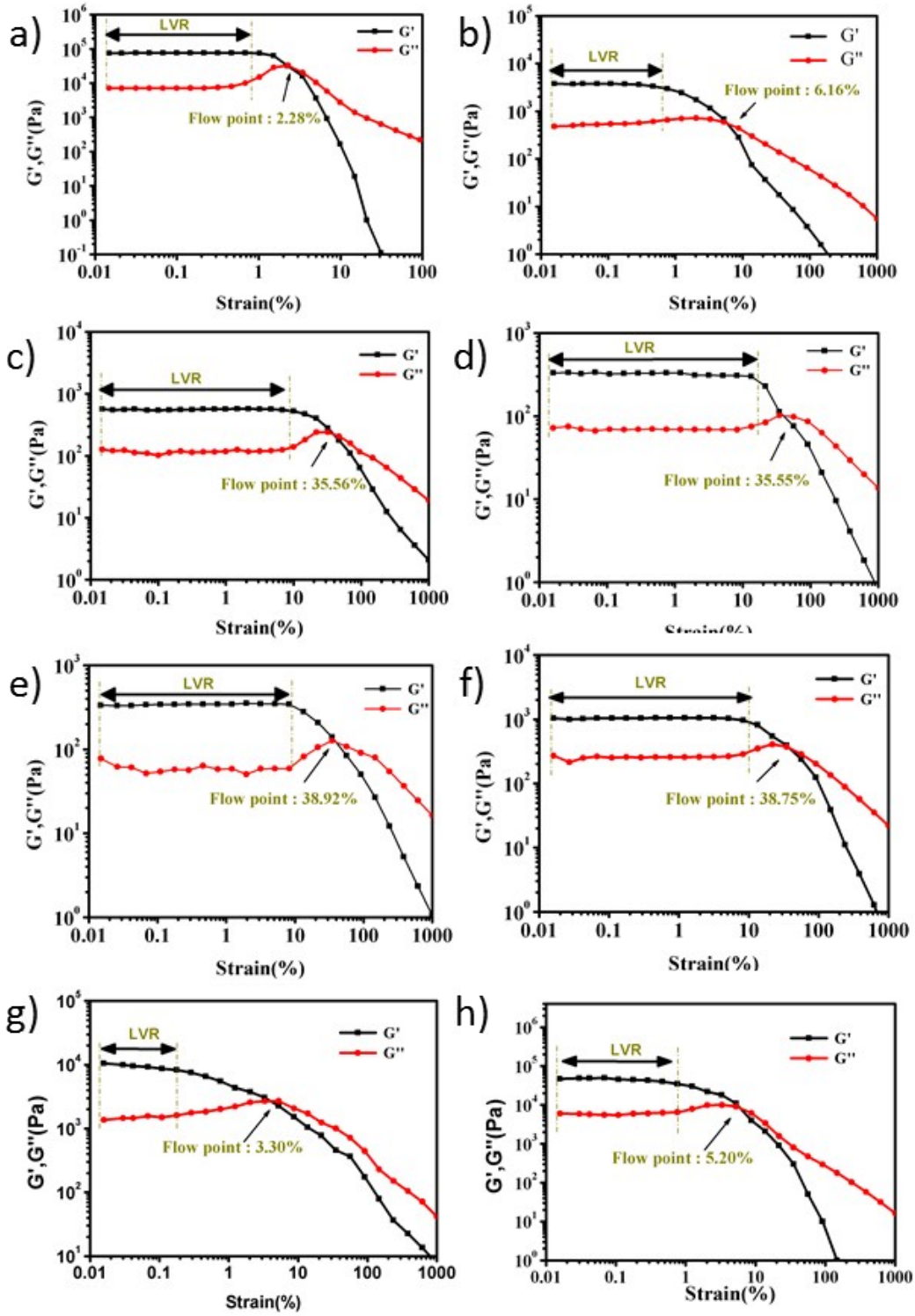


Figure S3. Strain sweep of chlorobenzene gel (2 wt%) with a fixed frequency (1 Hz). (a) B6; (b) B6-A10; (c) B6-A12; (d) B6-A14; (e) B6-A16; (f) B6-A18; (g) B6-HSA; (h) B6-LA.

Time scan tests under alternating strain of 0.1% and 100% of chlorobenzene gel (2 wt%) with a fixed frequency at 1 Hz:

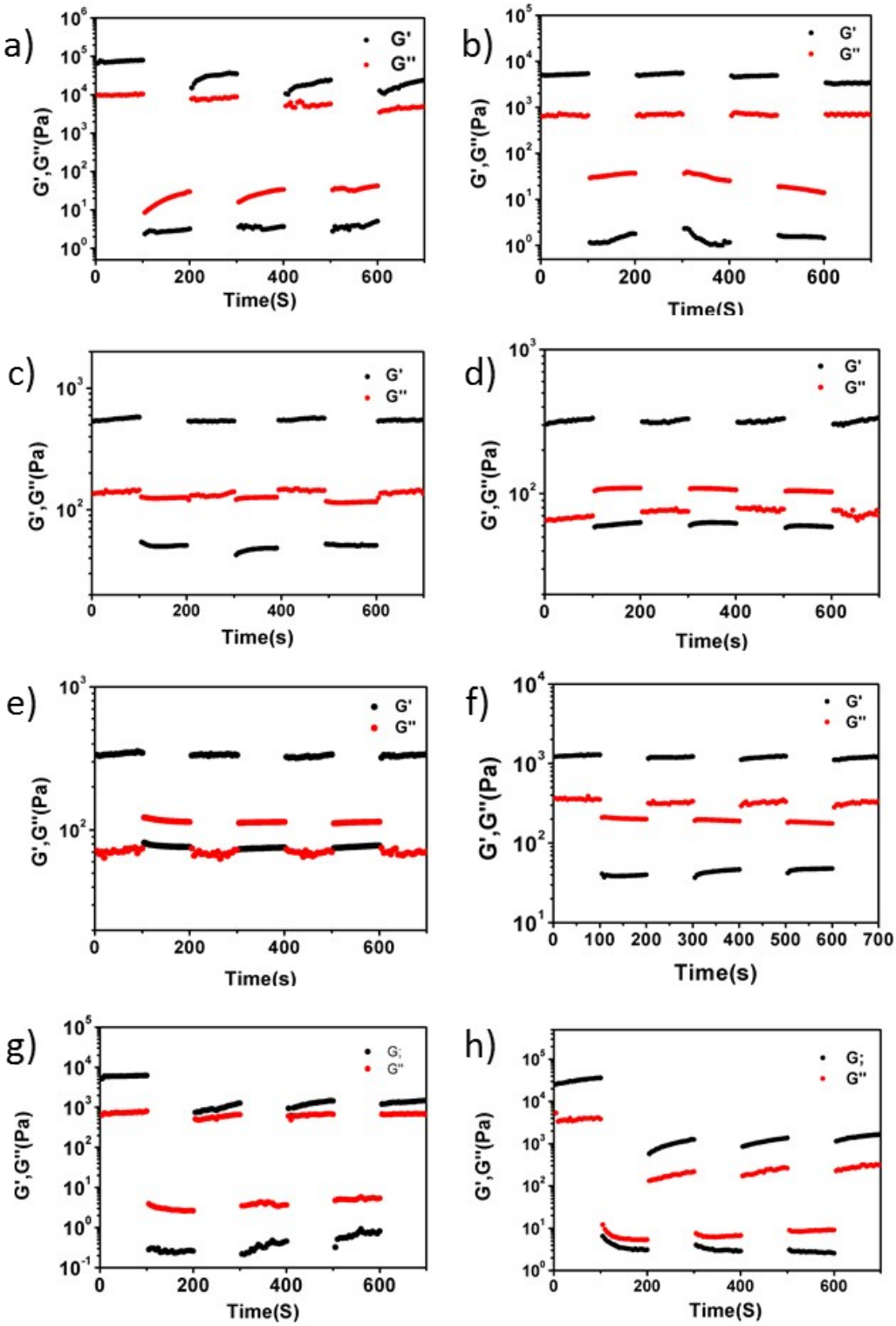


Figure S4. Time scan tests under alternating strain of 0.1% and 100% of chlorobenzene gel (2 wt%) with a fixed frequency at 1 Hz. (a) B6; (b) B6-A10; (c) B6-A12; (d) B6-A14; (e) B6-A16; (f) B6-A18; (g) B6-HSA; (h) B6-LA.

Pictures of B6-A18 gel showing self-healing behaviour:

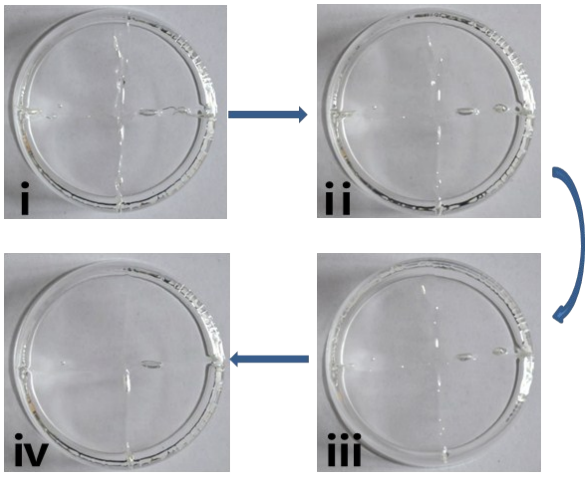


Figure S5. Pictures of sliced B6-A18/CB gel (ⅰ) after free standing for 5min, 10min and 15min, respectively (ⅱ-ⅳ).

Process of the xerogels absorbing the Methylene Blue aqueous solution (initial stage and after 24h):

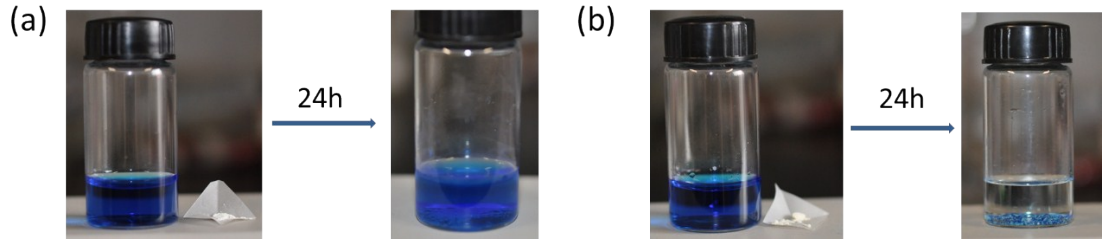


Figure S6. Process of the xerogels absorbing the Methylene Blue aqueous solution (initial stage and after 24h) (a) B6 xerogel; (b) B6-A18 xerogel.

Time-dependent UV-Vis spectroscopy measurement of the single/two-component xerogel-treated Methylene Blue aqueous solution.

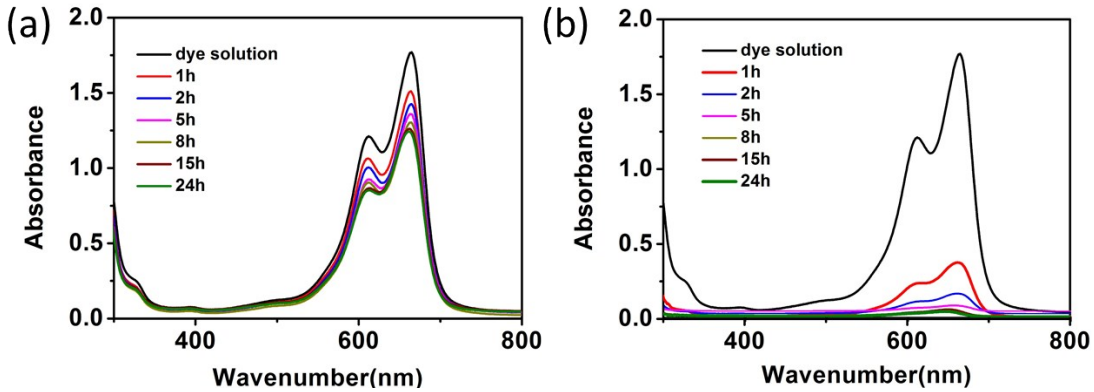


Figure S7. Time-dependent UV-Vis spectroscopy measurement of the single/two-component xerogel-treated Methylene Blue aqueous solution. (a) B6; (b) B6-A18.

FTIR spectra:

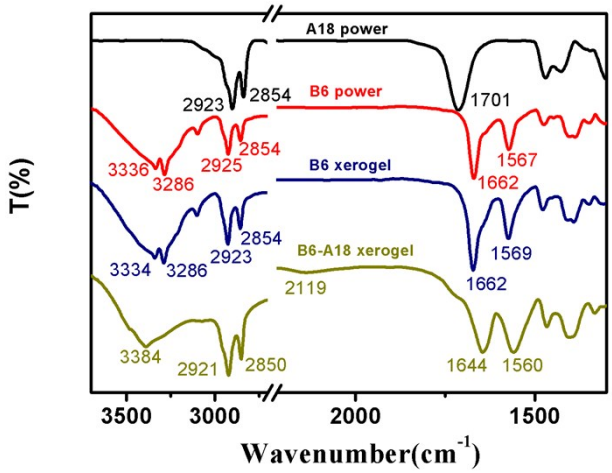


Figure S8. FTIR spectra of A18, B6, B6 xerogel and B6-A18 xerogel obtained from chlorobenzene gel (2.0 wt%).

X-ray diffraction pattern of the xerogel:

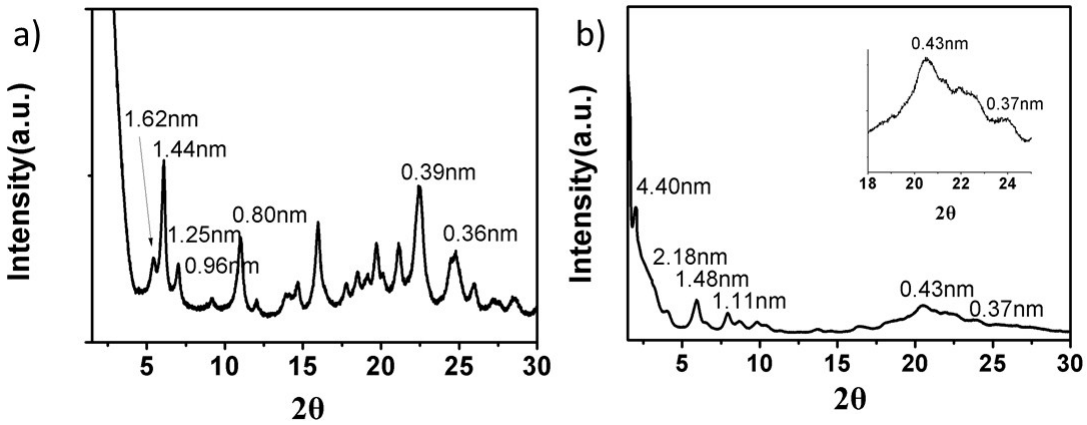


Figure S9. X-ray diffraction pattern of the xerogel of B6 (a) and B6-A18 (b) obtained from chlorobenzene gel (2.0 wt%).

SEM images of xerogel:

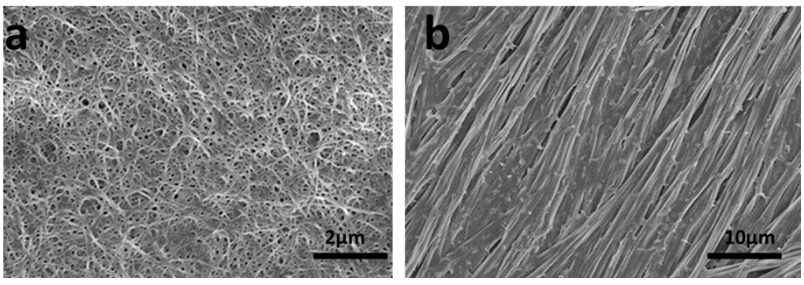


Figure S10. SEM images of xerogel of B6 (a) and B6-A18 (b) obtained from chlorobenzene gel (2.0 wt%).

Supporting Video:

Video S1: B6-A18/CB gel instantly repaired itself after destructed by vigorous stirring.

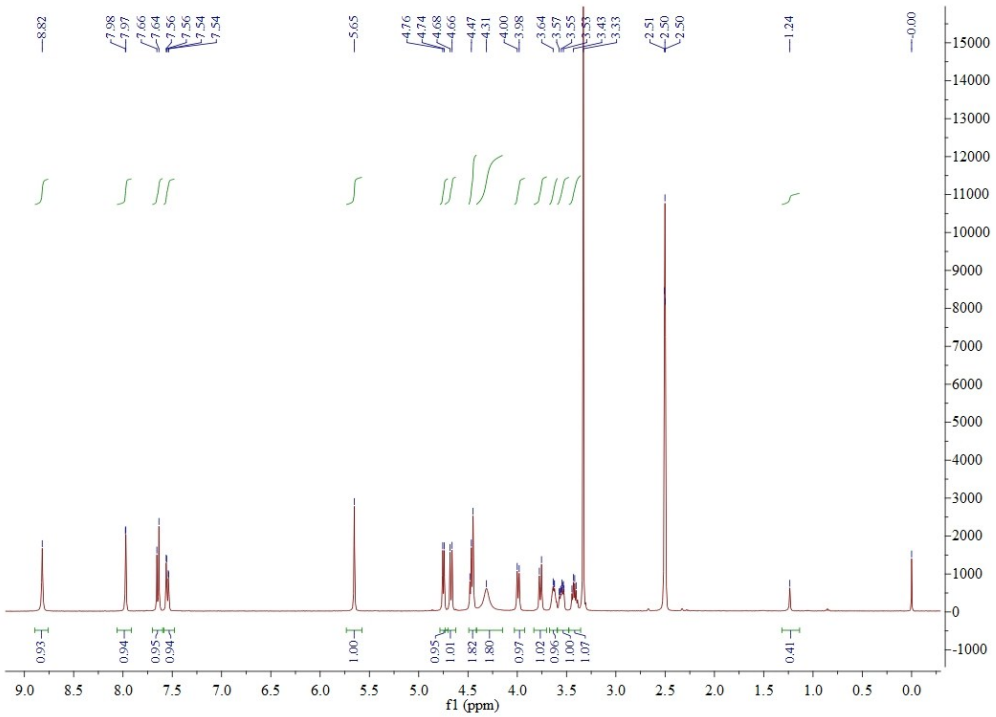
5 mL of B6-A18/CB gel (1 wt%) was prepared in a vial via the heating-cooling method. Then a stirring bar was added into the vial and the gel was stirred vigorously with a rate of 1500 rap/min for 1 min on a magnetic stirring apparatus. After stirring, the gel repaired itself instantly (within 1s).

Reference

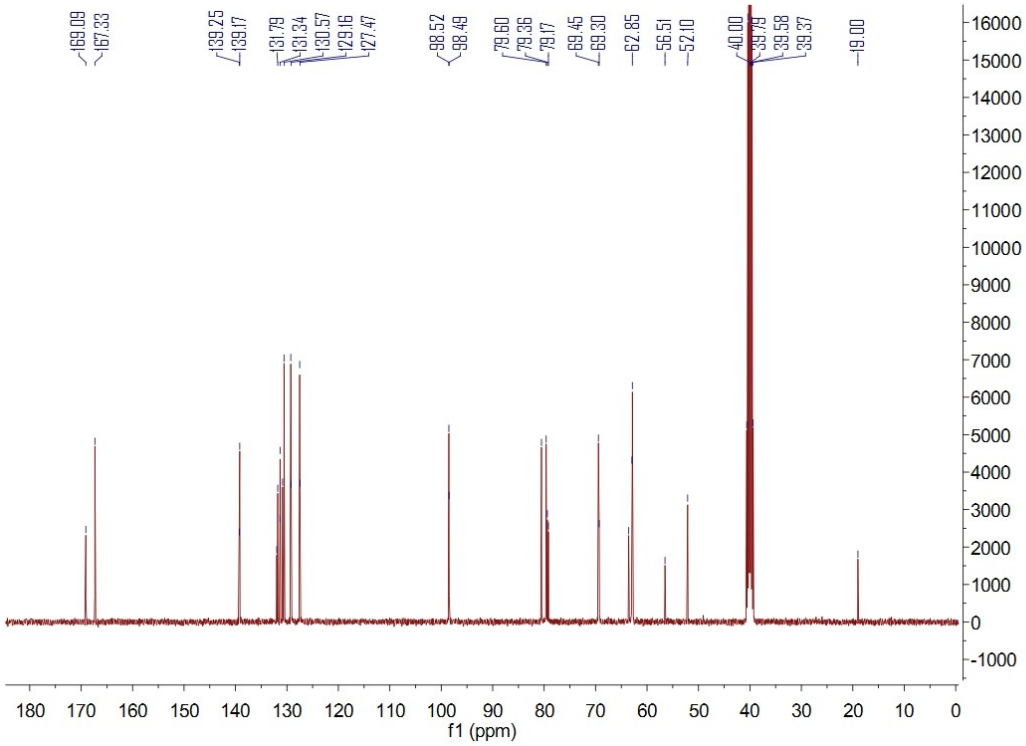
1 H. Wang, F. F. Wang, H. T. Tang, J .Y Zhang and Y. J. Yang, *Acta Chim. Sin.,* 2007, **65**, 1057-1063.

2 X. D. Guan, K. Q. Fan, T. Y. Gao, A. P. Ma, B. Zhang and J. Song, *Chem. Commun.,* 2016, **52**, 962-265.

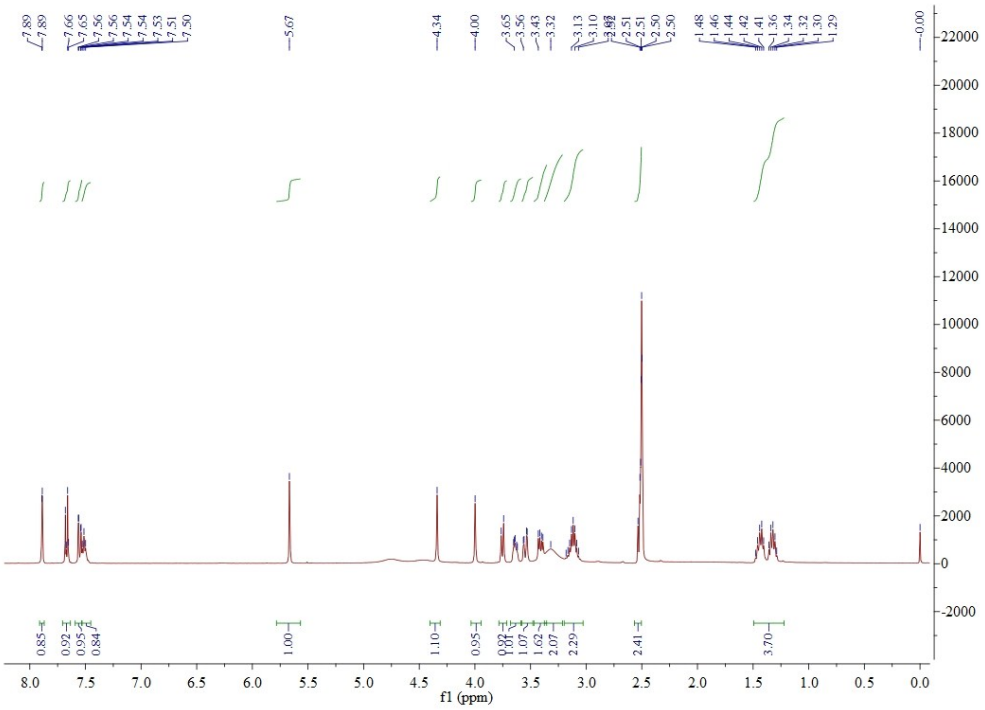
^{1}H NMR (400MHz) Spectra of B0 in DMSO-d_6:



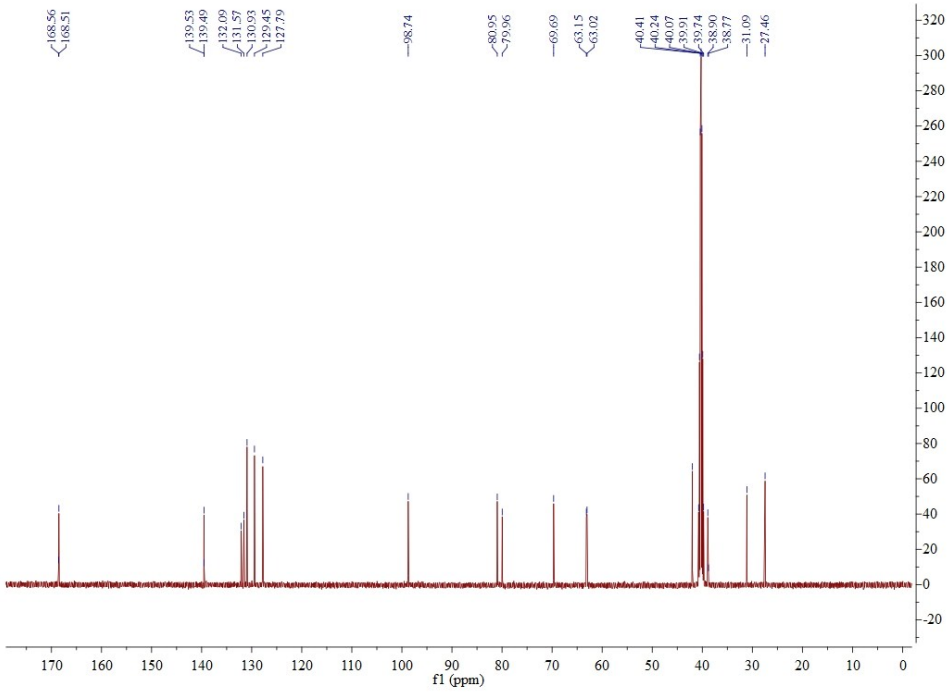
^{13}C NMR (400MHz) Spectra of B0 in DMSO-d_6:



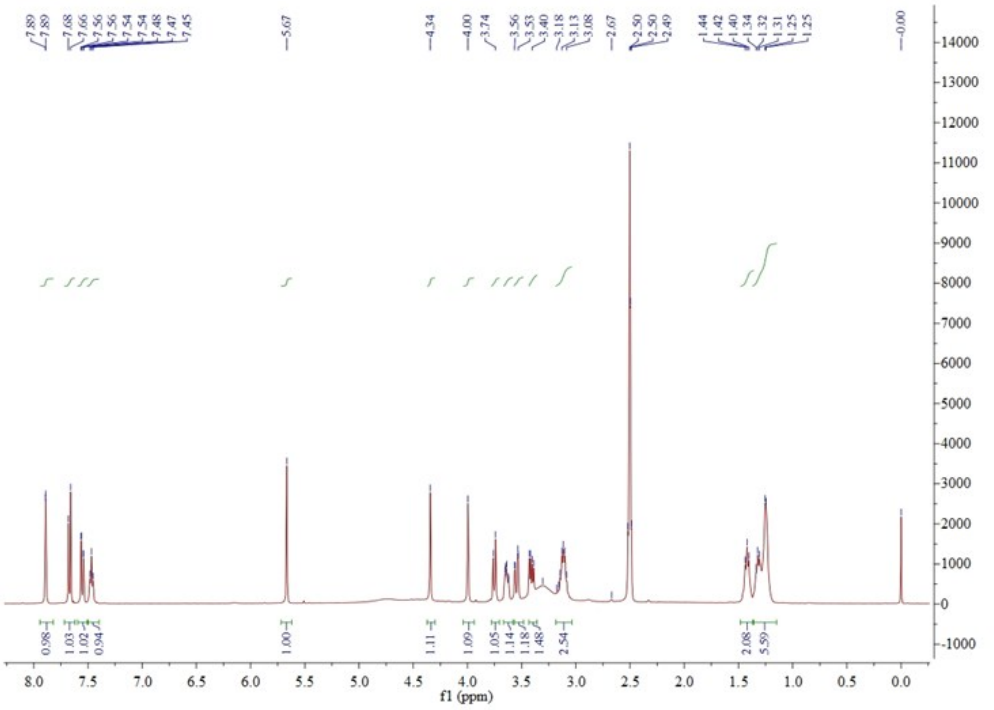
^{1}H NMR (400MHz) Spectra of B4 in DMSO-d_6:



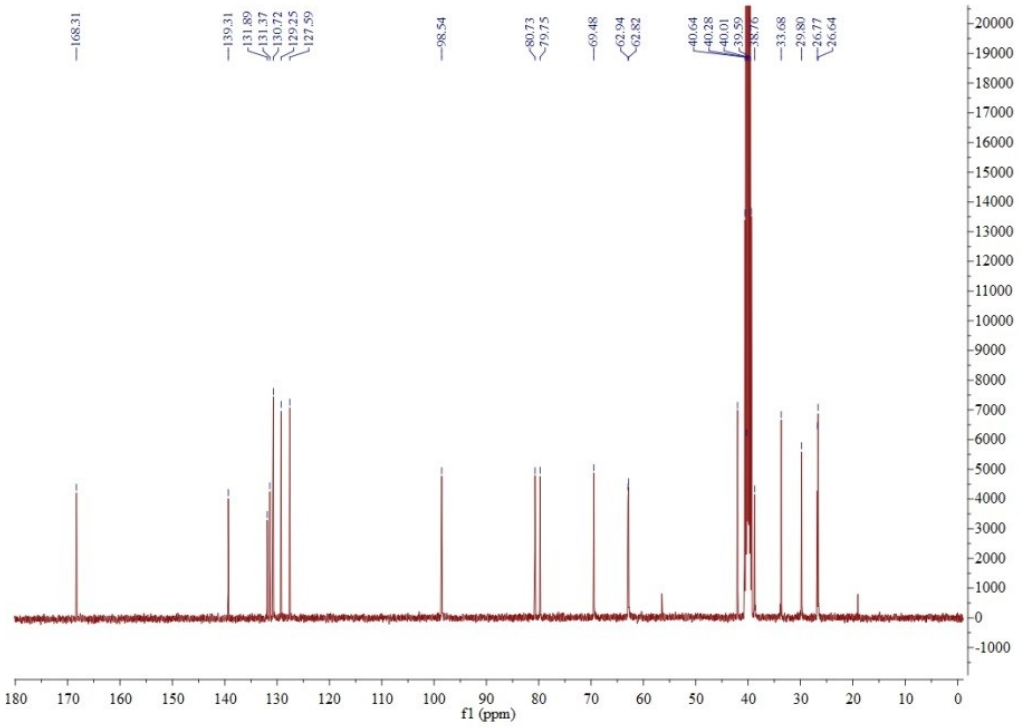
^{13}C NMR (400MHz) Spectra of B4 in DMSO-d_6:



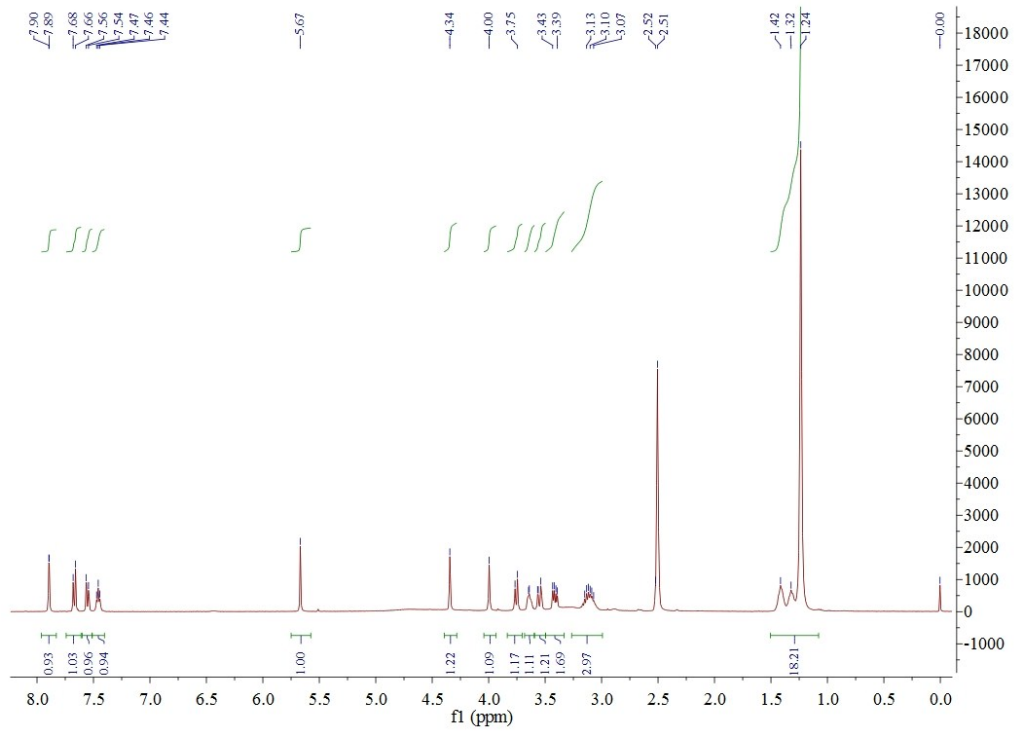
^{1}H NMR (400MHz) Spectra of B6 in DMSO-d_6:



^{13}C NMR (400MHz) Spectra of B6 in DMSO-d_6:



^{1}H NMR (400MHz) Spectra of B12 in DMSO-d_6.



^{13}C NMR (400MHz) Spectra of B12 in DMSO-d_6.