

Supporting Information

One-step-synthesized D-gluconic acetal-based supramolecular organogelators with effective phase-selective gelation

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1. Materials

D-Gluconic acid, benzaldehyde and methyl p-formylbenzoate were purchased from Shanghai Jingchun Scientifical Co., Ltd. The chemical reagents were commercially available and directly utilized without further purification.

2. Instrumentation

NMR experiments: NMR spectra were measured on Bruker DPX 400 MHz Spectrometer. The chemical shifts were reported as δ values (ppm) relative to the residual peak of the solvent.

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 aluminum 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: FTIR spectroscopic measurements were conducted using Nicolet 5700 FT-IR. A resolution of 4 cm^{-1} was used, and read between 400 and 4000 cm^{-1} . The xerogels were prepared by drying gels on glass slides under vacuum for 24 h.

X-Ray diffraction (XRD): Using a Rigaku D/Max 2200-PC diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.15418\text{ nm}$), the patterns were obtained at the ambient temperature and the samples were scanned in the 2θ range of 3 - 30° at a scan rate of 0.2 s/step . Data processing and analyses were performed using Materials Date JADE XRD pattern processing software. The samples were dried for 2 weeks at room conditions.

Gelation test: Gelation tests in organic solvents were investigated by a typical tube inversion method. These tests were performed by adding the weighed amount of gelators 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. 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". A small glass ball with a diameter of 5 mm (0.15 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. $1.5\text{ }^\circ\text{C/min}$. 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.

Determination of Critical gelator concentration (CGC): CGCs were determined at $20\text{ }^\circ\text{C}$ by the stable to inversion test tube method using a series of gels in which the gelator concentrations were changed in 0.01wt% increments. The solution was cooled to room temperature to form gel.

Rheological Study: Measurements were performed using 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 25°C in order to avoid solvent evaporation. The frequency sweep at a constant strain of 0.1% was obtained from 0.1 to $100\text{ rad}\cdot\text{s}^{-1}$. Strain sweep was performed in the 0.01%-1000% range at a constant frequency (1 Hz).

The time-temperature superposition (TTS) procedure was carried out to observe the temperature dependence of the mechanical properties of the viscoelastic materials. In these experiments, the Storage modulus (G') and Loss modulus (G'') were monitored as a function of frequency in the linear viscoelastic region at various temperatures by means of isothermal frequency sweep tests.

The water surface waves test: Intelligent multifunctional water wave experiment instrument

(Beijing Yaou Depeng Technology Co., Ltd., model DP-FD-WPB, frequency range of water wave = 1-200 Hz, amplitude range of water wave = 0.001–100 mm) were used to detect the oscillating frequency and amplitude of water waves. The cylindrical gel samples (10 cm in diameter, 0.2 cm in height) are placed on the surface of a water bath (h ~ 5 cm). The amplitude of the water wave is slowly increased while maintaining a constant frequency.

3.Synthesis

Gelators GAA-1 and GAA-2 was synthesized as the methods reported previously.¹ The detailed synthetic methods are described below.

0.5 mol benzaldehyde (or methyl p-formylbenzoate) was dissolved in 400 mL methanol at room temperature and then 215.8 g (0.55mol) 50wt% aqueous solution of D-gluconic acid was added to this solution followed by the addition of 100 mL hydrochloride (12mol/L) under vigorously stirring. The reaction mixture was stirred for 12h and the white solid was collected by filtration. The filtrate was washed with water for three time and hot dichloromethane for twice respectively.

Chemical Identification

2,4-benzylidene Methy-D-Gluconate (gelator GAA-1).

Yield: 84%. MP: 174.3-175.4°C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.53–7.51 (m, 2H, Ar-H), 7.42-7.40 (m, 3H, Ar-H), 5.64 (s, 1H, OCHO), 4.93 (d, *J* = 8.1 Hz, 1H, OH), 4.76 (d, *J* = 5.8 Hz, 1H, OH), 4.75 (s, 1H, OH), 4.46 (t, *J* = 5.8 Hz, 1H, CH), 4.03 (d, *J* = 8.1 Hz, 1H, CH), 3.81 (d, *J* = 8.9 Hz, 1H, CH), 3.70 (s, 3H, CH₃), 3.60-3.58 (m, 1H, CH), 3.43 (s, 1H, CH₂), 3.34 (s, 1H, CH₂); ¹³C NMR (400 MHz, DMSO-*d*₆) δ 169.29, 138.51, 129.23, 128.36, 126.98, 100.04, 79.37, 79.14, 69.44, 63.56, 62.92, 52.03.

2,4-(methyl formate) benzylidene Methy-D-Gluconate (gelator GAA-2).

Yield: 75%. MP: 179.3-180.9°C; ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.01 (d, *J* = 6.9 Hz, 2H, Ar-H), 7.66 (d, *J* = 7.7 Hz, 2H, Ar-H), 5.71 (s, 1H, OCHO), 5.09-5.06 (m, 1H, OH), 4.83 (t, *J* = 5.8 Hz, 1H, OH), 4.76 (d, *J* = 3.8 Hz, 1H, OH), 4.53-4.51 (m, 1H, OH), 4.01 (d, *J* = 8.2 Hz, 1H, CH), 3.87 (s, 3H, CH₃), 3.83-3.81 (m, 1H, CH), 3.69 (s, 3H, CH₃), 3.57-3.55 (m, 1H, CH), 3.44-3.42 (m, 1H, CH), 3.41 (d, *J* = 5.1 Hz, 1H, CH), 3.36 (s, 1H, CH₂); ¹³C NMR (400 MHz, DMSO-*d*₆): δ 169.45, 138.11, 136.32, 129.35, 128.04, 124.45, 100.35, 79.45, 79.15, 69.44, 63.54, 62.92, 52.00, 19.82, 19.66.

¹H NMR and ¹³C NMR spectra of GAA-1 and GAA-2. (Figure S1- Figure S4)

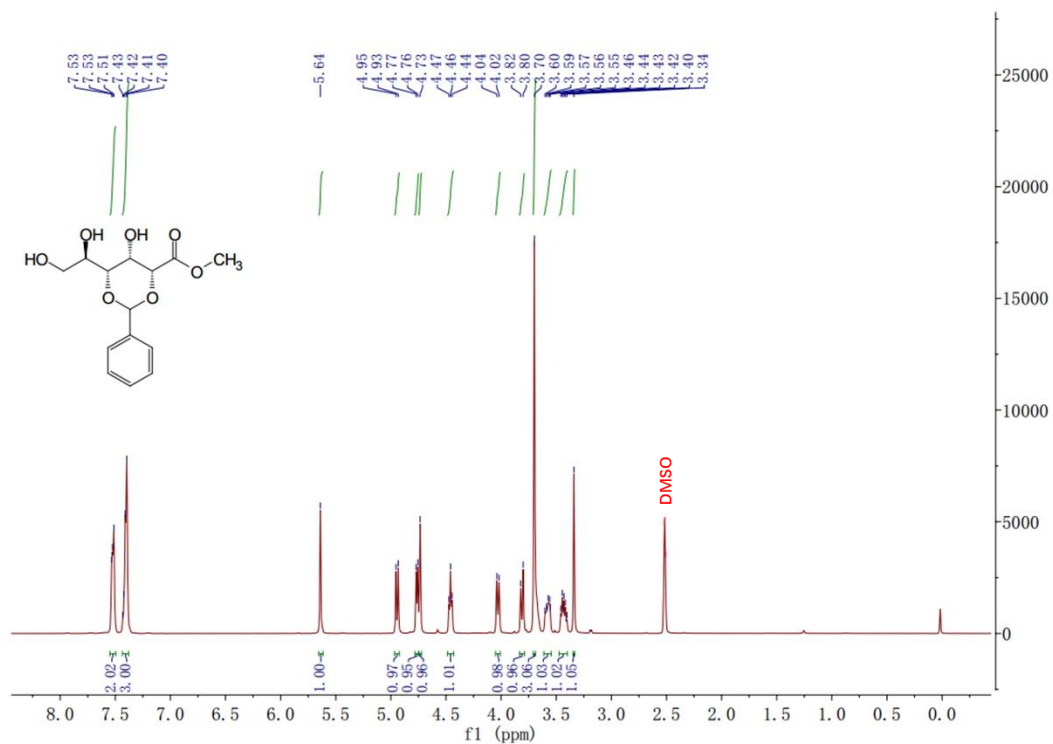


Figure S1 ^1H NMR (400 MHz) Spectra of GAA-1 in DMSO-d₆.

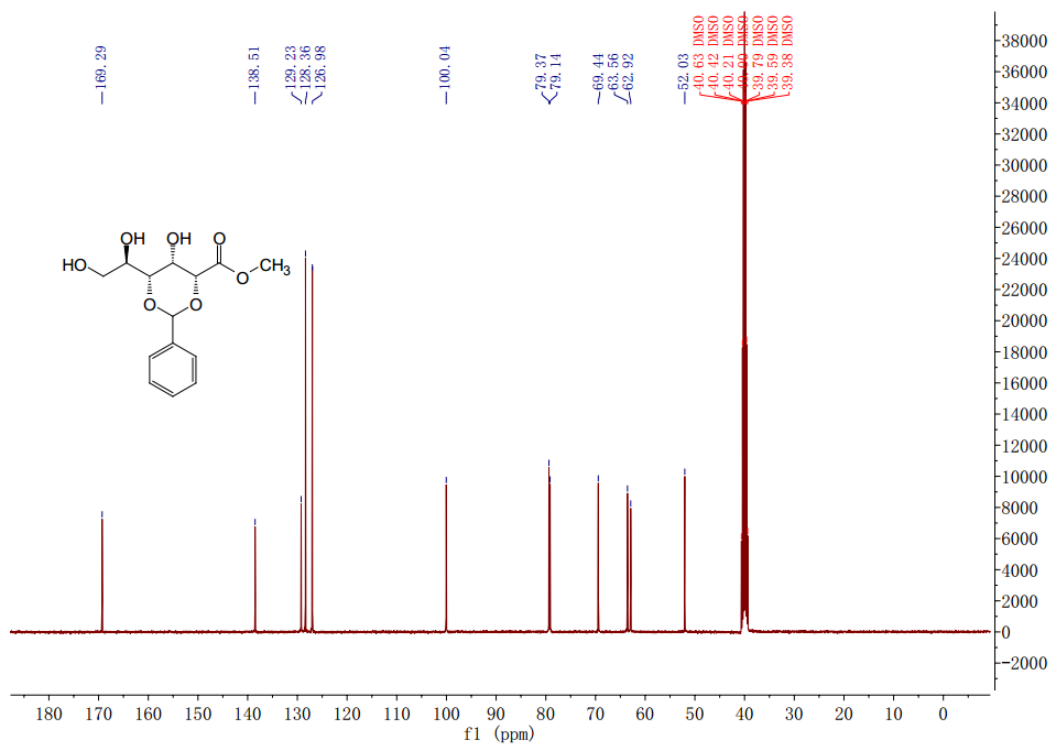


Figure S2 ^{13}C NMR (400 MHz) Spectra of GAA-1 in DMSO-d₆.

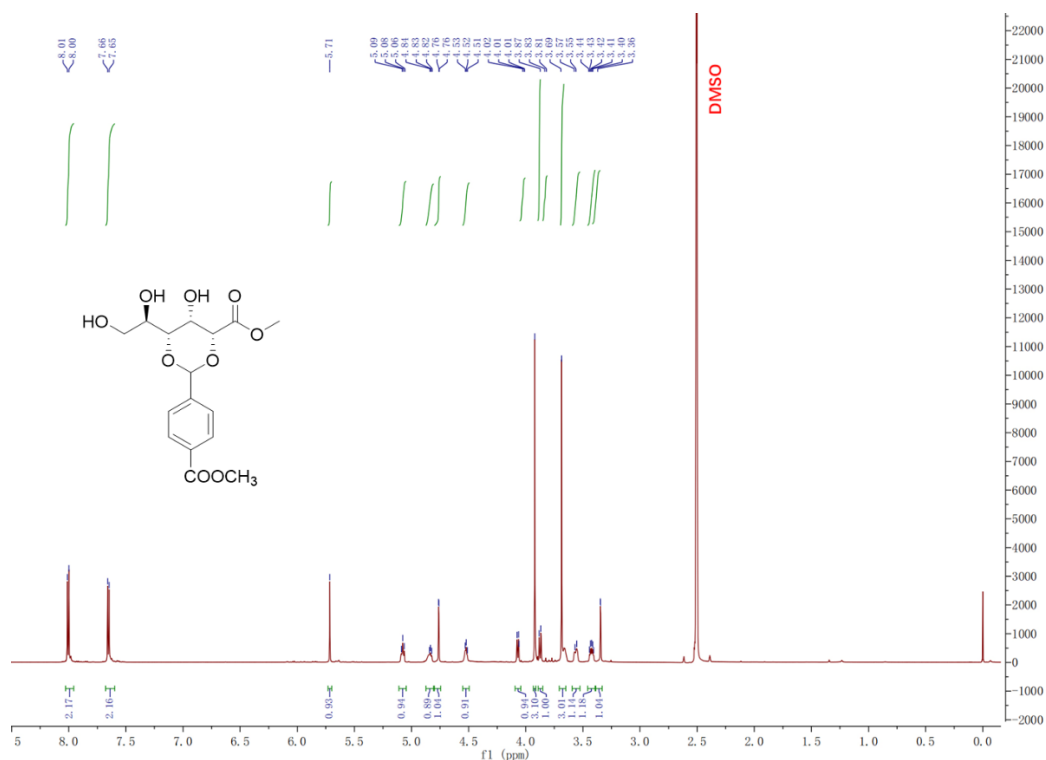


Figure S3 ^1H NMR (400 MHz) Spectra of GAA-2 in DMSO-d₆.

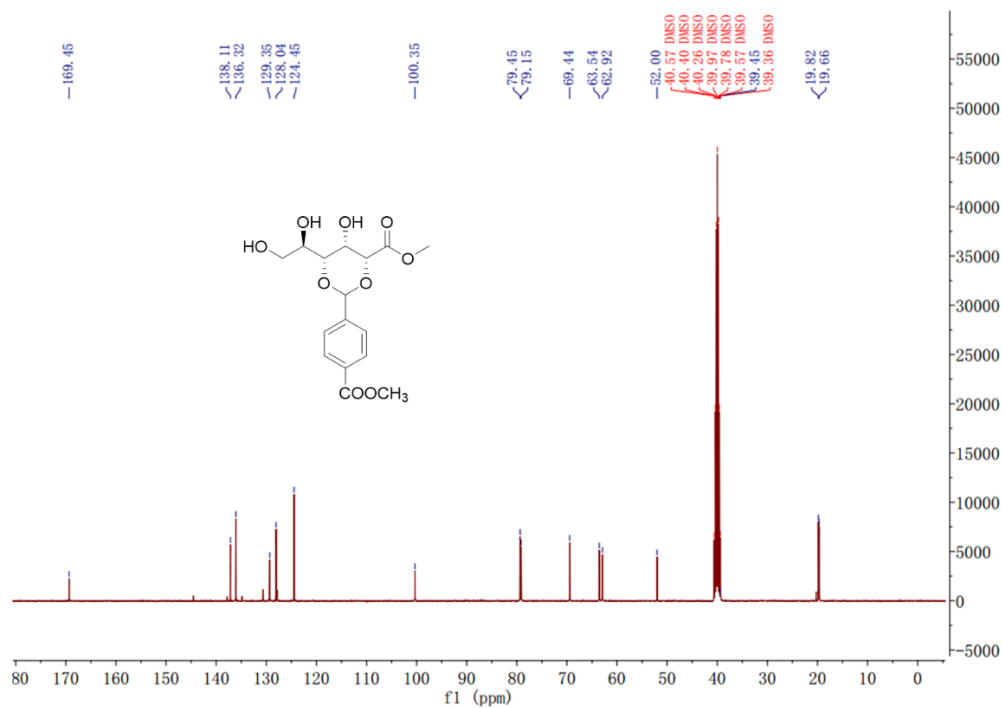


Figure S4 ^{13}C NMR (400 MHz) Spectra of GAA-2 in DMSO-d₆.

Table S1: The SBCGC value of gelator GAA-2 powder in different solvents at room temperature.

Solvent	SBCGC (wt%)	Gelation time (min)	recovery rate (%)
Benzene	2.6	74	80
Toluene	2.2	63	82
o-Xylene	1.9	56	85
P-Xylene	1.8	54	87
m-Xylene	2.0	59	84

^a The SBCGC (stirring biphasic critical gelation concentration) values were determined using a biphasic system containing aromatic solvents and water (0.5 mL/ 2 mL). ^b Gelation time was tested for each liquid under mild stirring at room temperature.

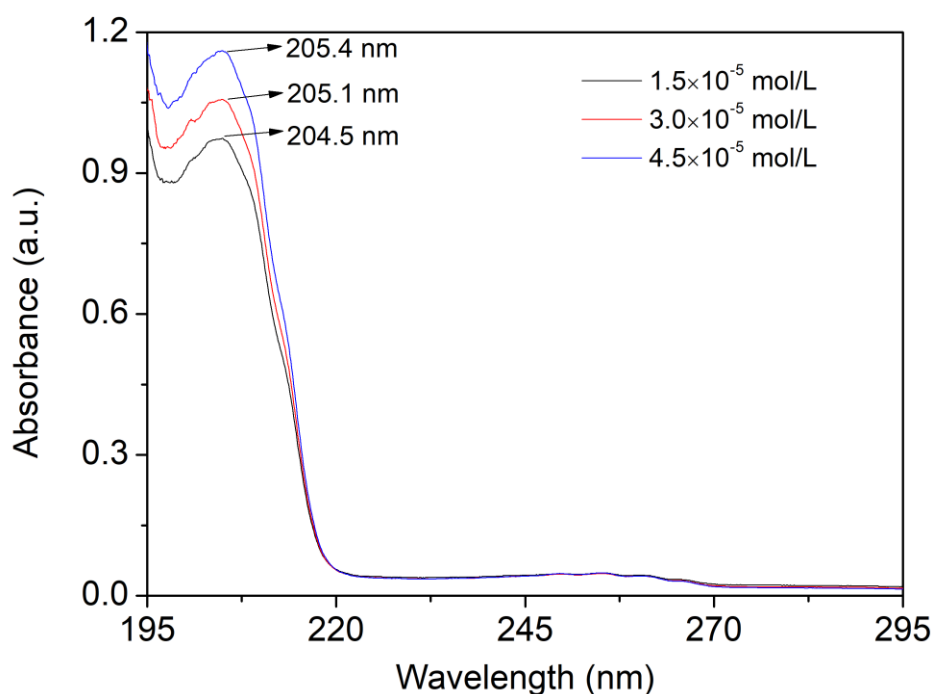


Figure S5 UV spectra of GAA-2 in acetonitrile as the concentration was increased from 1.5×10^{-5} mol/L to 4.5×10^{-5} mol/L.

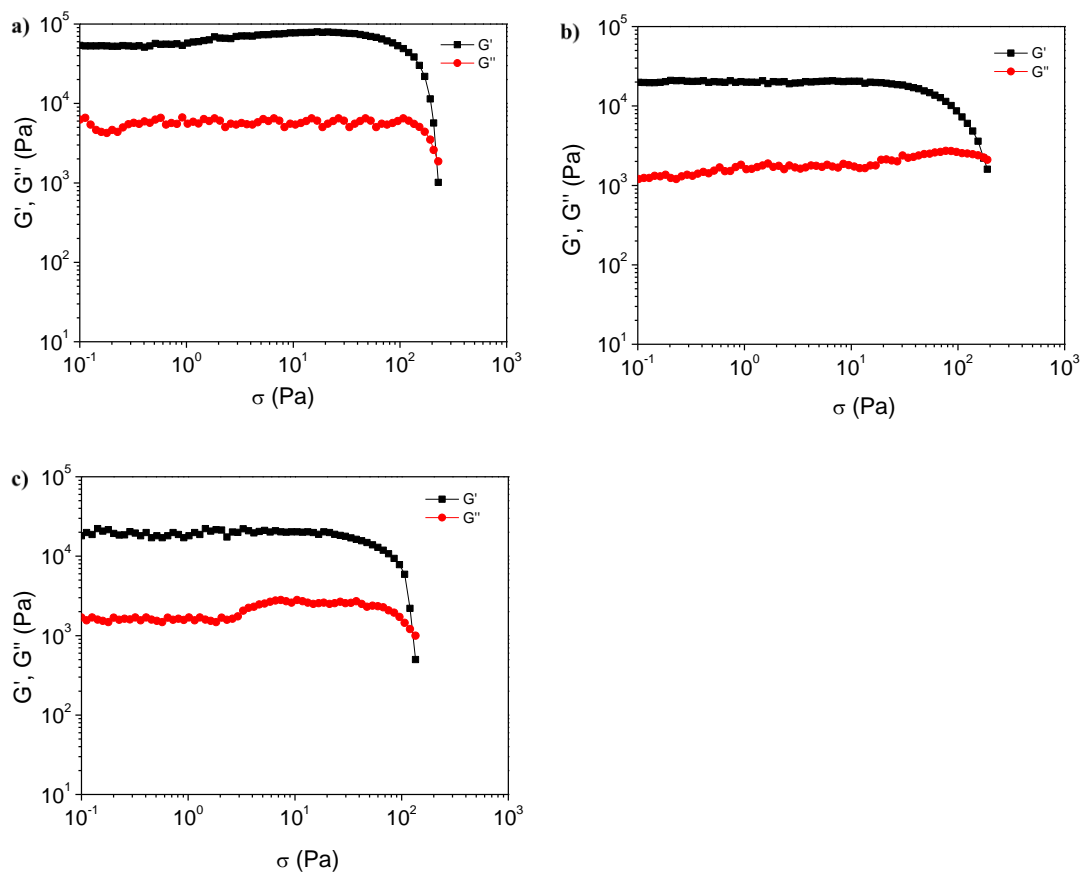


Figure S6 Strain sweep of GAA-2 gels with a fixed frequency (1 Hz) in different solvents: a) o-xylene, b) toluene, c) benzene.

Table S2. Summary of breaking amplitudes at different applied frequencies for gel film on Water.

Gels	Applied frequency (Hz)	Breaking amplitude (mm) (min)
Benzene gel	10	0.86
	20	0.49
	30	0.07
Toluene gel	10	0.97
	20	0.69
	30	0.10
o-Xylene gel	10	1.25
	20	0.77
	30	0.21

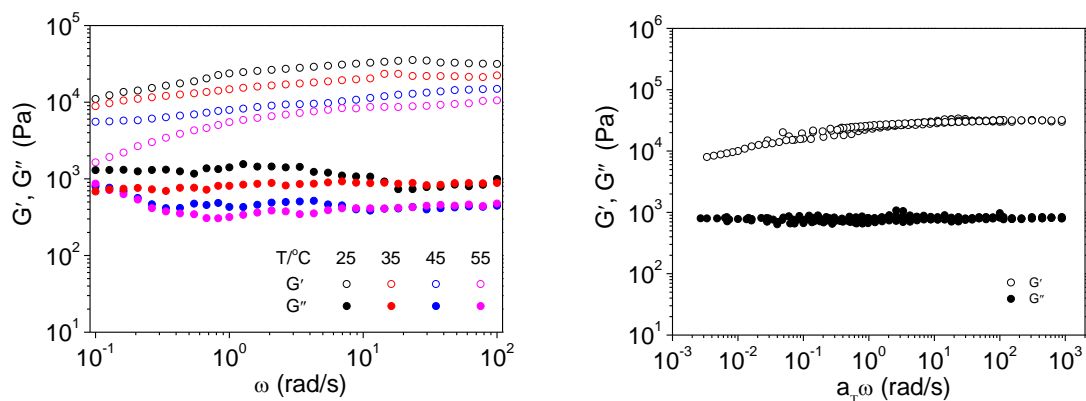


Figure S7. Frequency sweep curves at temperatures from 25 to 55 °C (left) and the final master curve (right) for the benzene gel of GAA-2 with 3 wt %.

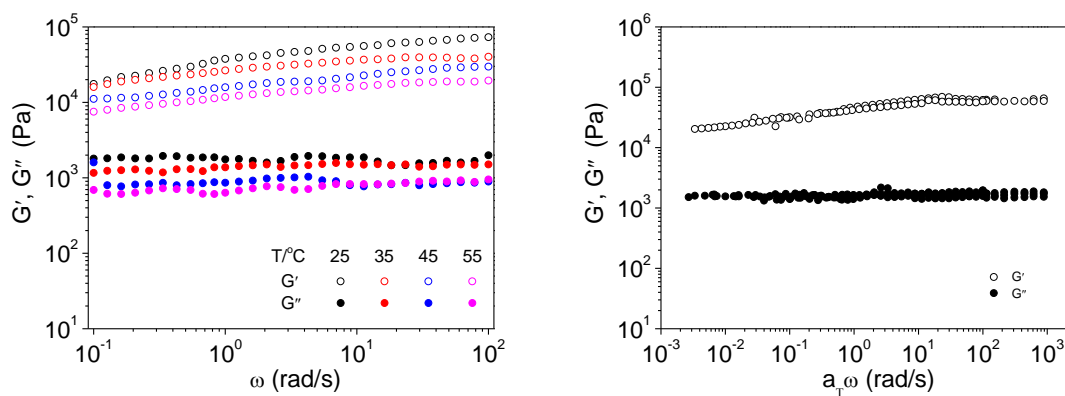


Figure S8. Frequency sweep curves at temperatures from 25 to 55 °C (left) and the final master curve (right) for the toluene gel of GAA-2 with 3 wt %.

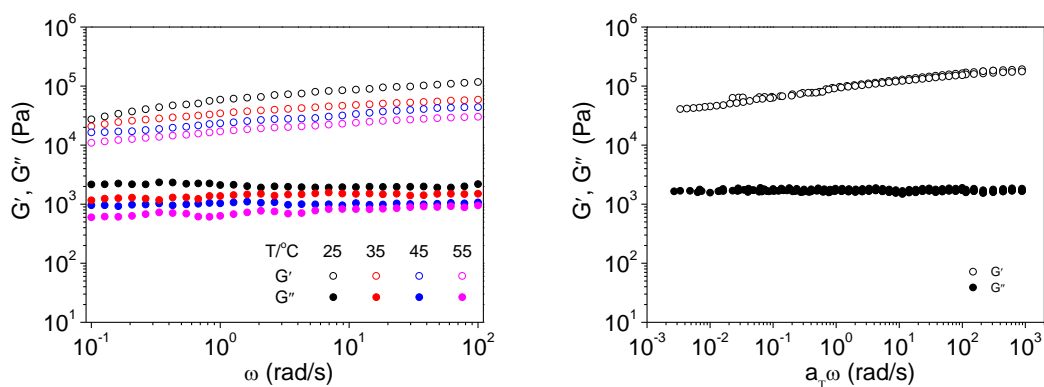


Figure S9. Frequency sweep curves at temperatures from 25 to 55 °C (left) and the final master curve (right) for the o-xylene gel of GAA-2 with 3 wt %.

References:

1. X. Guan, K. Fan, T. Gao, A. Ma and B. Zhang, Chem Commun., 2016, 52, 962-965.