

Electronic Supplementary Information

Chemical fuel-driven gelation with dissipative assembly- induced emission

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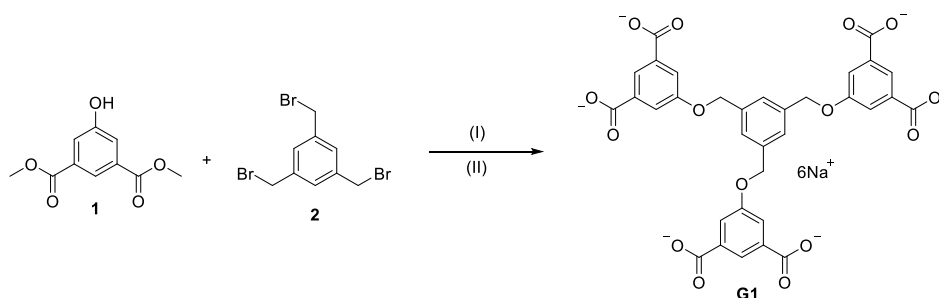
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1. General information

Unless otherwise stated, all reactions take place in the air. All reagents and solvents are obtained from commercial sources. **G1** and **G2** were synthesized according to modified procedures from the literature.^[1-2] All yields were given as isolated yields. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer with internal standard tetramethylsilane (TMS) and solvent signals as internal reference at 298 K. The fluorescence spectra were measured on an Edinburgh instrument FLS1000. UV-vis experiment was recorded in a PerkinElmer LAMBDA1050+ instrument.

2. Synthesis of G1 and G2

(1) General procedure for the synthesis of **G1**

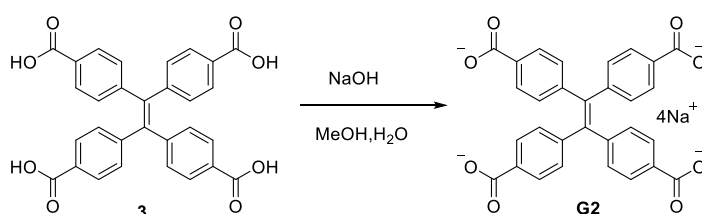


Scheme S1. Synthesis of the multiple-carboxylate-anion molecule **G1**. Reagents and Conditions: (I) DMF, K₂CO₃, 100 °C, 24 h; (II) MeOH/H₂O, NaOH, 100 °C, 2 h.

Compound **1** (1.27 g, 6.0 mmol) was dissolved in DMF (25 mL). K₂CO₃ (2.60 g, 26.0 mmol) was added to the solution. The solution was heated to 100 °C and compound **2** (0.28 g, 0.8 mmol) was added to the mixture, and then heated at 100 °C for 24 h. After cooling to room temperature, approximately 80 mL of water was added to the solution to produce a white precipitate which was filtered, washed thoroughly with ice cold water, and air-dried. No further purification is required. The methyl ester crude product

was added to around bottom flask containing methanol (25 mL). An aqueous solution of NaOH was added to this mixture and then heated to 50 °C for 2 h. Then solvent was removed and the solid was washed several times with EtOH until ^1H NMR was pure enough to get **G1** (0.15 g, 25%) as a white solid. ^1H NMR (400 MHz, D_2O , 298 K): δ (ppm) = 7.92 (s, ArH, 3H), 7.69 (s, ArH, 3H), 7.63 (s, ArH, 6H), 5.26 (s, CH_2 , 6H). ^{13}C NMR (100 MHz, D_2O , 298 K): δ (ppm) = 174.7, 157.8, 138.0, 137.5, 127.7, 122.2, 117.8, 70.2.

(2) General procedure for the synthesis of **G2**.



Scheme S2. Synthesis of the multiple-carboxylate-anion molecule **G2**.

The methyl ester compound **3** (0.40 g, 0.78 mmol) was added to around bottom flask containing methanol (25 mL). An aqueous solution of NaOH was added to this mixture and stirred for 2 h. Then solvent was removed and the solid was washed several times with EtOH until ^1H NMR was pure enough to get **G2** (0.083 g, 20%) as a white solid. ^1H NMR (400 MHz, D_2O , 298 K): δ (ppm) = 7.62 (d, J = 8.39 Hz, ArH, 8H), 7.15 (d, J = 8.39 Hz, ArH, 8H). ^{13}C NMR (100 MHz, D_2O , 298 K): δ (ppm) = 175.2, 145.9, 141.2, 134.4, 130.9, 128.4.

3. ^1H NMR and ^{13}C NMR of G1 and G2

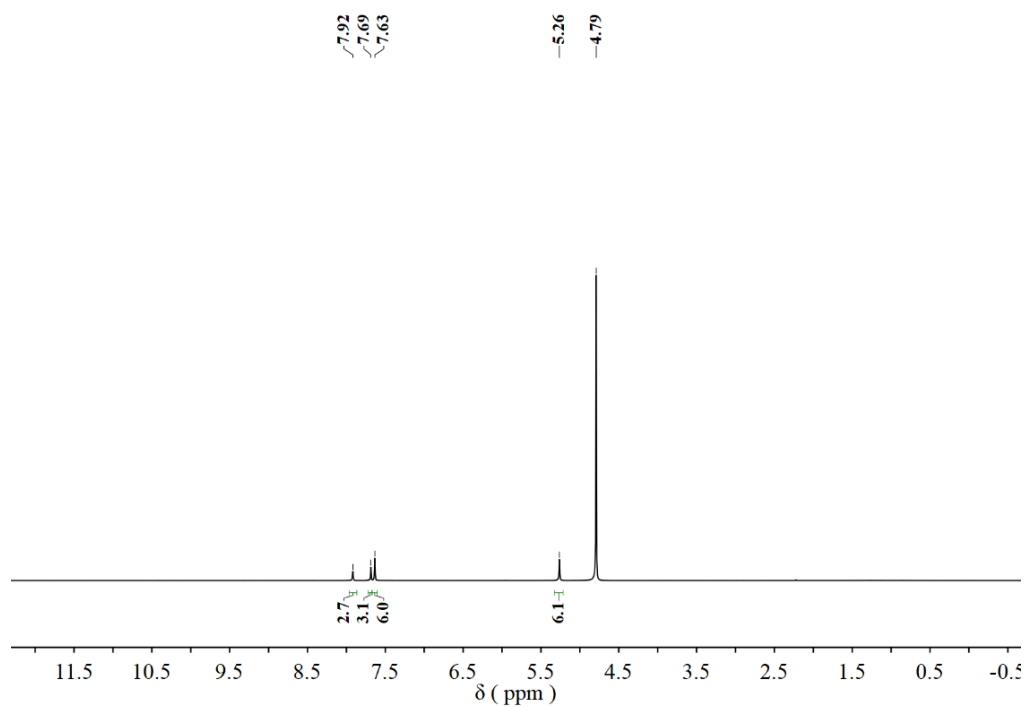


Fig. S1 ^1H NMR spectrum (400 MHz, D_2O , 298 K) of G1.

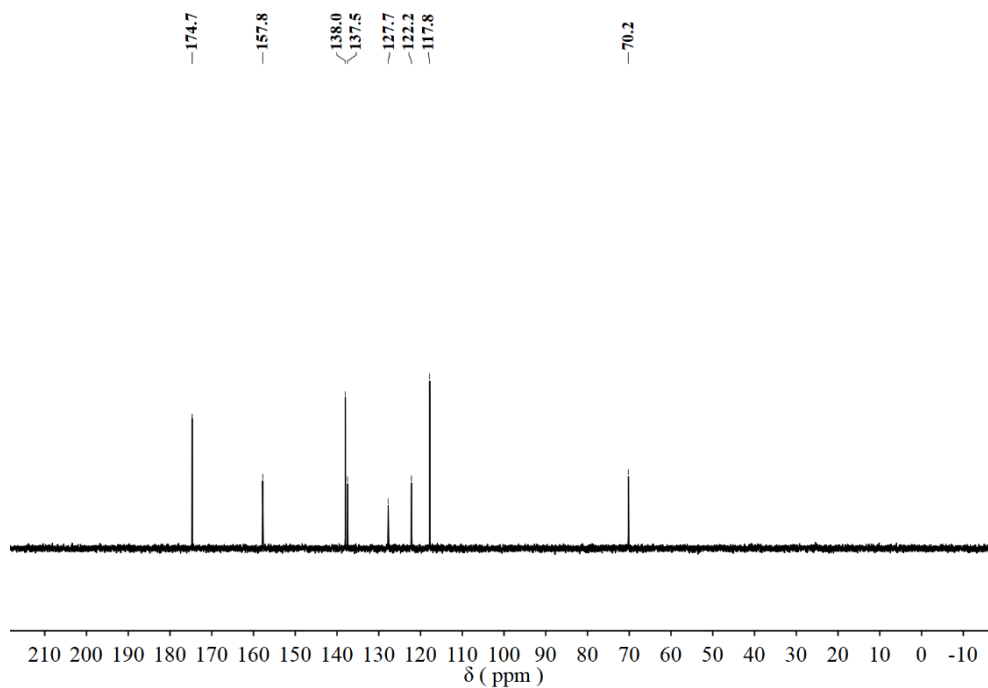


Fig. S2 ^{13}C NMR spectrum (100 MHz, D_2O , 298 K) of G1.

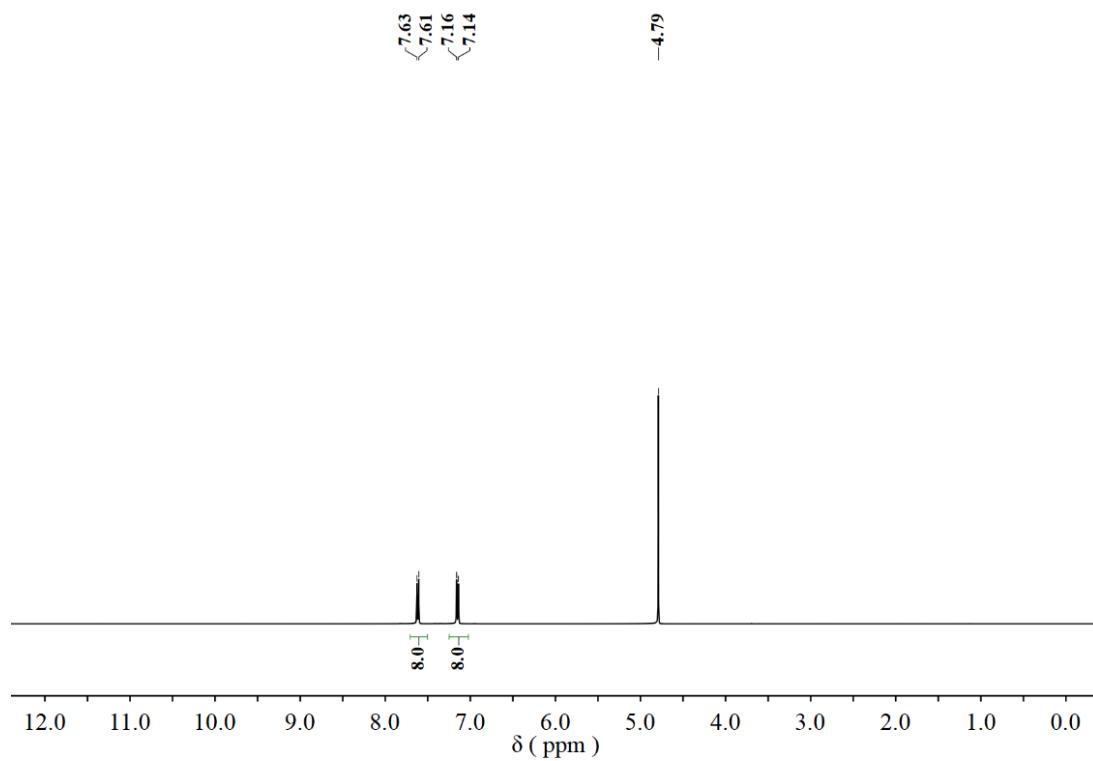


Fig. S3 ^1H NMR spectrum (400 MHz, D_2O , 298 K) of **G2**.

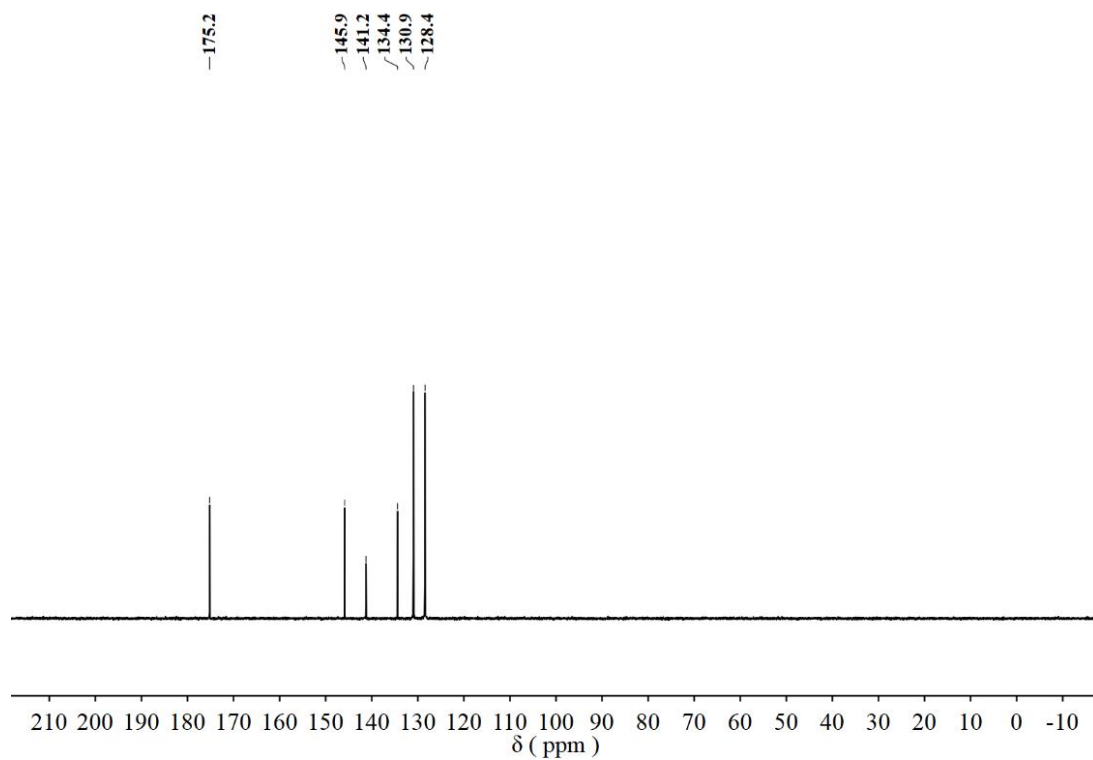


Fig. S4 ^{13}C NMR spectrum (100 MHz, D_2O , 298 K) of **G2**.

4. ^1H NMR of G1 and G2 upon the addition of DMS

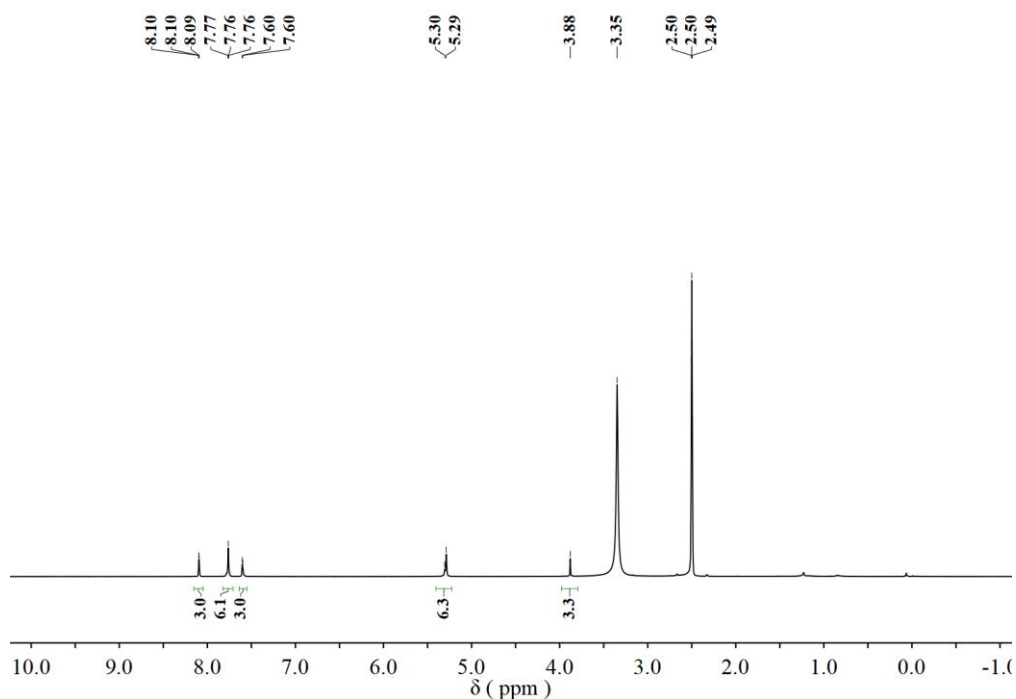


Fig. S5 ^1H NMR spectra (400MHz, $\text{DMSO-}d_6$, 298 K) of **G1** (5.0 mmol) + DMS (150 mmol). The sample was freeze-dried and the resulting solids were thoroughly washed with water before NMR measurement.

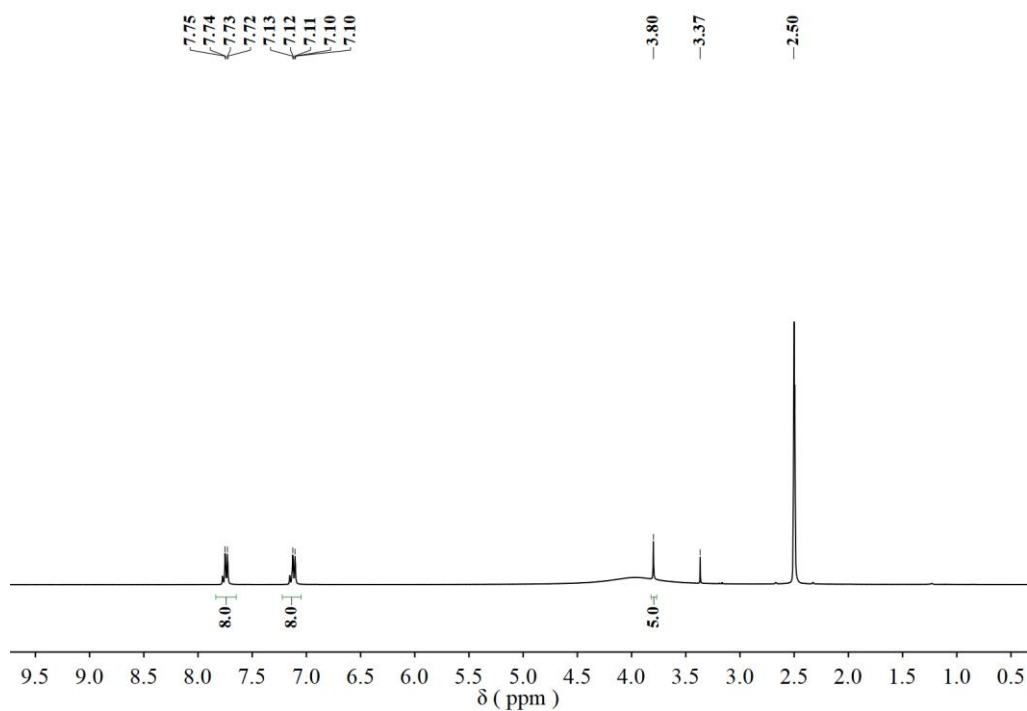


Fig. S6 ^1H NMR spectra (400MHz, $\text{DMSO-}d_6$, 298 K) of **G2** (5.0 mmol) + DMS (150 mmol). The sample was freeze-dried and the resulting solids were thoroughly washed with water before NMR measurement.

In order to confirm how many carboxylate groups are transformed into ester units, we characterized the system of (**G1** + DMS) and (**G2** + DMS) by ^1H NMR measurements. According to the spectra integration results, about 1.1 carboxylate groups of **G1** and 1.6 carboxylate groups of **G2** are transformed into ester units. The number of methylated groups both in **G1** and **G2** are between 1 and 2, suggesting that some of the molecules are equipped with two methyl groups which should be the main factor for hydrogelation. Therefore, we depicted two methyl groups in both **G1'** and **G2'** in Scheme 1.

5. Fatigue test of the sol-gel transition

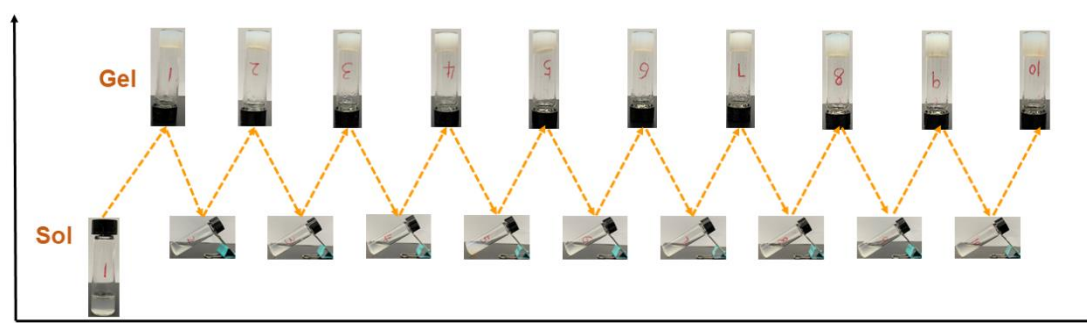


Fig. S7 The photos of sol-gel transition process. A vortex was used to speed up the gel-to-sol transition in order to shorten the time for repeat experiments.

We have performed the Sol-Gel transition experiments in 10 cycles. Normally, the gel-to-sol process takes 48 h. Therefore, a vortex was used to speed up the gel-to-sol transition in order to shorten the time for repeat experiments. However, no obvious fatigue phenomenon was observed in 10 cycles, as shown in Fig. S7.

6. Photophysical properties of the sol and gel

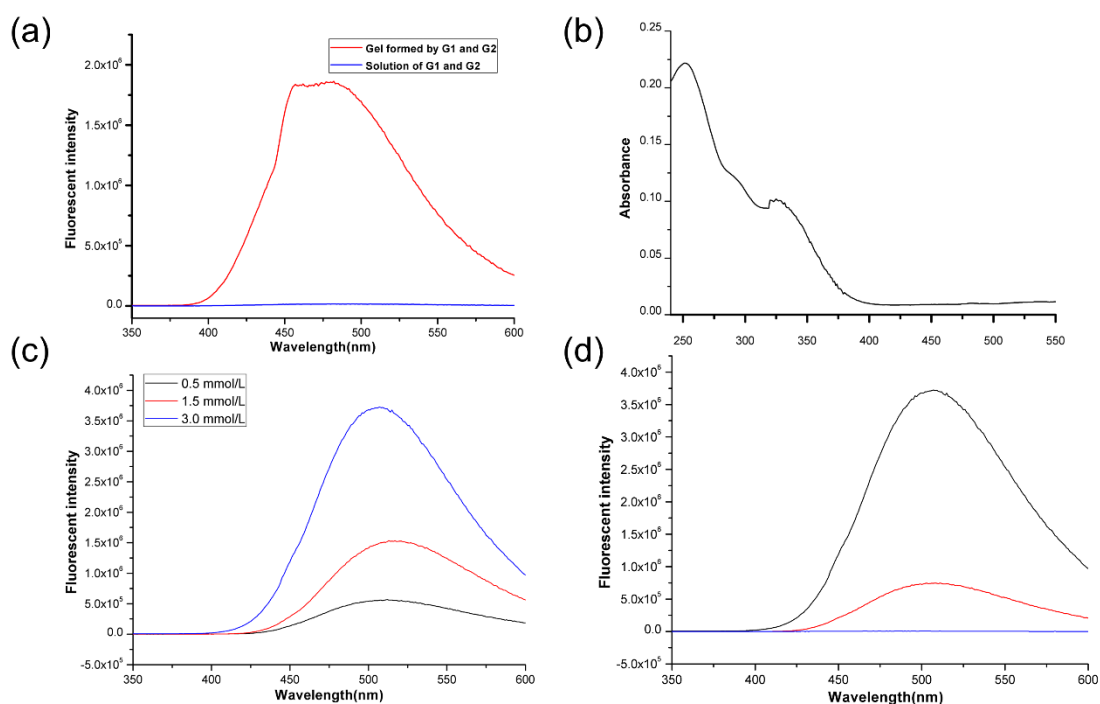


Fig. S8 (a) Fluorescence spectra of the aqueous solution of **G1** and **G2**, and the gel of **G1** and **G2** ($\lambda_{\text{ex}} = 315 \text{ nm}$, $25 \text{ }^\circ\text{C}$). (b) UV-vis absorption spectrum of **G2**. (c) The fluorescence emission spectra of gels. The concentration of starting solution for **G1** is 3.0 mmol/L . The concentration of starting solution for **G2** are 3.0 mmol/L , 1.5 mmol/L , 0.5 mmol/L respectively. (d) The fluorescence emission spectra of gel and sol (black line is the spectrum of starting gel, red line is the spectrum of gel after 24 hours, blue line is the sol solution obtain through a vortex). The concentration of starting solution for **G1** and **G2** are both 3.0 mmol/L .

As shown from the Fig. 8c, the more amount of the material, the higher the fluorescence intensity. Since **G2** is the main factor for fluorescence, we kept the concentration of **G1** constant (3.0 mmol/L), and varied the concentration of **G2** (0.5 mmol/L , 1.5 mmol/L , 3.0 mmol/L). During the fluorescence increase process (accompanied by gelation), this period is very short (in 20 s), we can observe the fluorescence was greatly enhanced from solution (blue line) to gel (red line) (Fig. S8a). As the hydrogel breaks down, we can see the fluorescence gradually quenched (Fig. S8d).

7. Hydrolysis of the gel monitored by ^1H NMR

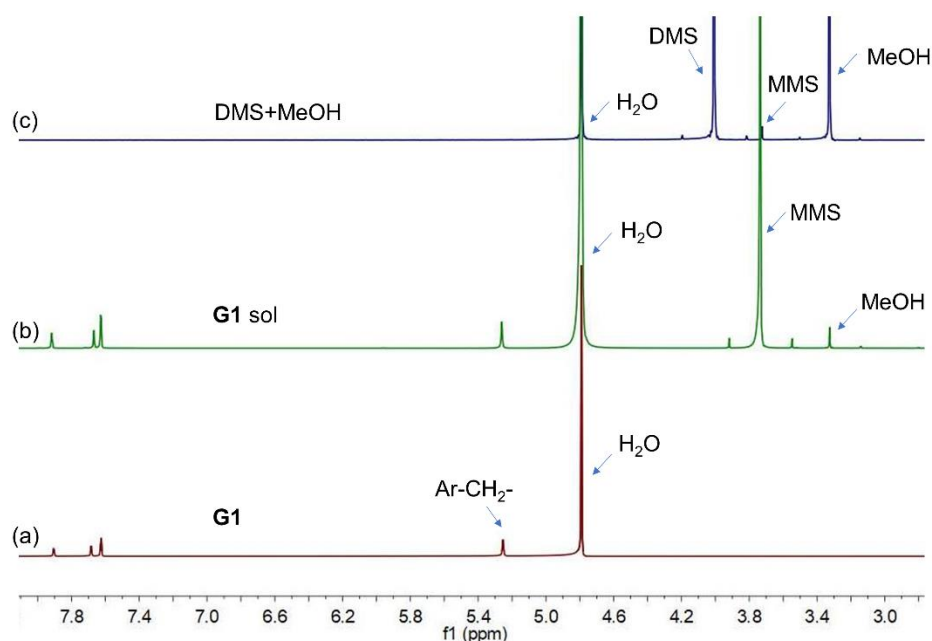


Fig. S9 ^1H NMR spectra (400MHz, D_2O , 298 K) of (a) **G1**, (b) **G1 sol** ($[\text{G1}] = 5.0$ mmol, $[\text{DMS}] = 150$ mmol), and (c) DMS and methanol. Note: DMS is dimethyl sulfate, MMS is monomethyl sulfate (also call methyl bisulfate), MeOH is methanol. The sample (c) was subjected to ^1H NMR experiment immediately after preparation.

As **G1'** plays the main role for gelation and to make the spectrum more concise, we investigated the **G1 sol** (obtained by a gel-to-sol transition from the mixture of **G1** and DMS) sample by ^1H NMR. The **G1 sol** sample was first freeze-dried and subjected to ^1H NMR by using $\text{DMSO-}d_6$. However, no signal was observed, which might be due to the large amount of salt in the sample. Therefore, we used D_2O as deuterated solvent to do ^1H NMR. As **G1'** (methylated **G1**) shows poor solubility in D_2O , we could not use **G1'** in D_2O as a direct comparison. Then we studied ^1H NMR of **G1**, **G1 sol**, and “DMS+MeOH” in D_2O (Fig. S9). As shown in Fig. S9, compared with **G1**, there is no methyl group peak in **G1 sol**, indicating that the methyl group in **G1'** was hydrolyzed. The hydrolyzed product should be MeOH. Compared with the “DMS+MeOH” sample, there is indeed a MeOH signal in **G1 sol** spectrum ($\delta = 3.32$ ppm). Moreover, a large peak at $\delta = 3.74$ ppm was observed, accompanied with two small symmetric satellite peaks. In the “DMS+MeOH” sample, there is also a small peak at $\delta = 3.74$ ppm. However, it does not belong to DMS. The methyl peak

in DMS is at $\delta = 4.00$ ppm, also accompanied with two small symmetric satellite peaks. Therefore, the peak at $\delta = 3.74$ ppm should be monomethyl sulfate (MMS), which was hydrolyzed from DMS. The sample “DMS+MeOH” was subjected to ^1H NMR experiment immediately after preparation, resulting in only a small amount of DMS hydrolysis and the observation of a small MMS peak. However, in **G1** sol sample, all DMS was hydrolyzed, leading to a large peak of MMS. All these observations suggest that the **G1**’ and DMS were completely hydrolyzed after the gel transformed into the sol state.

8. Gelation temperature test



Fig. S10 Temperature measured after heating the mixture of **G1**, **G2** and DMS with a heat gun for 30 seconds. The test was repeated for 3 times.

9. Reference

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- [2] S. Lee, K. Y. Kim, S. H. Jung, J. H. Lee, M. Yamada, R. Sethy, T. Kawai and J. H. Jung, Finely Controlled Circularly Polarized Luminescence of a Mechano-Responsive Supramolecular Polymer, *Angew. Chem. Int. Ed.*, 2019, **58**, 18878-18882.