Electronic Supplementary Information

Thixotropic and self-healing triggered reversible rheology switching in a peptide-based organogel with a cross-linked nano-ring pattern

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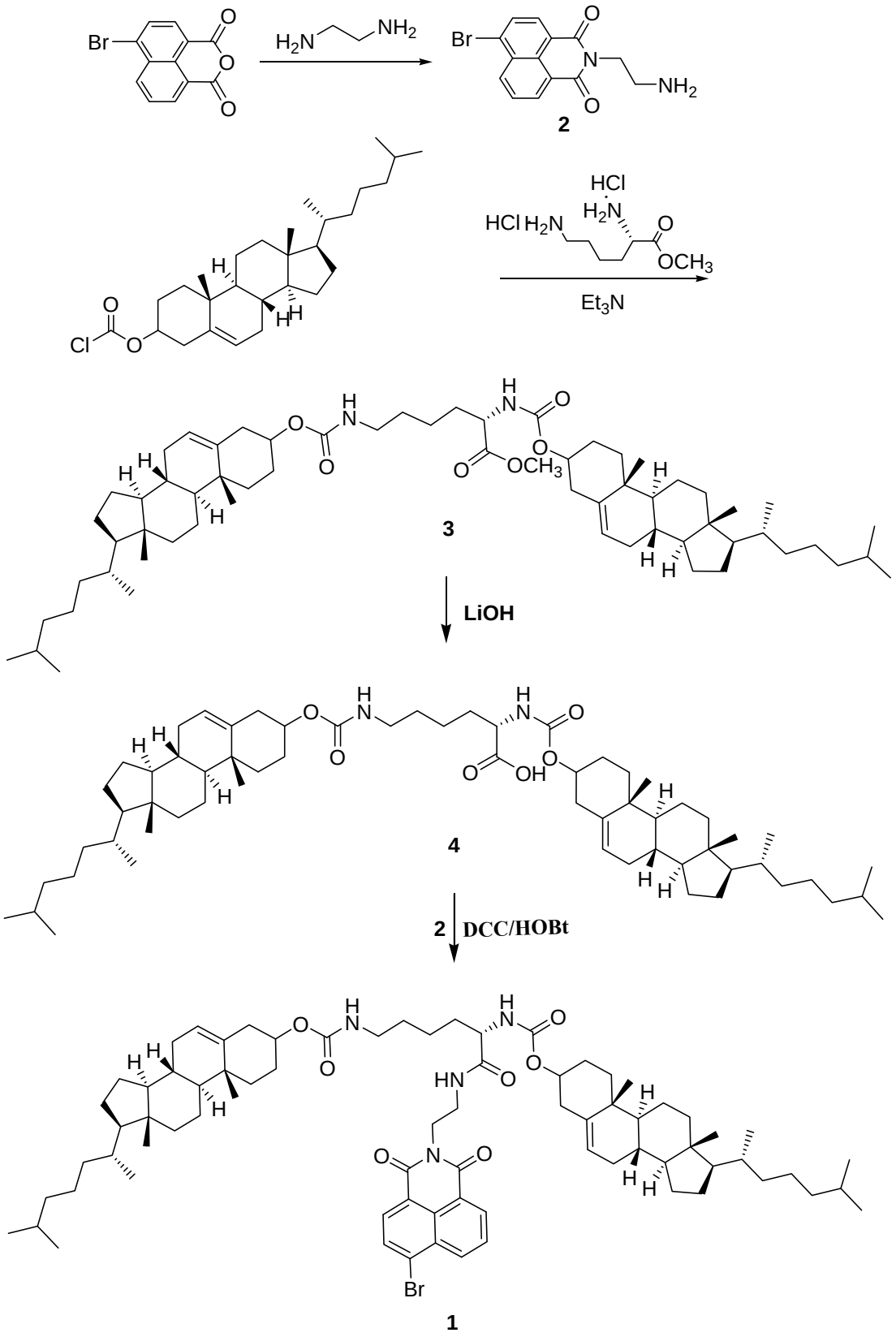
1. Synthesis detail



Scheme S1 Synthesis of compound **1**

The synthesis of N-ethyl amine-4-Br-1, 8- naphthalic anhydride **(2)** was according to the literature 1.

Synthesis of di-3-β-cholest-5-en-3-yl-ester-N-Lysine acid ethyl ester (3): Cholesteryl choroformate (2 g, 45 mmol), H-Lys-OMe·2HCl (464 mg, 20 mmol) and 2 mL Et_3N were stirred in dry CH_2Cl_2 (150 mL) for 24 hours, the mixture was concentrated and purified by column chromatography (CH_2Cl_2/ CH_3OH = 100: 1), 952 mg white solid was obtained (yield: 48.3%). Mp: 165-167°C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.70 (s, 6H, CH_3), 0.88-0.90 (m, 12H, CH_3), 0.93-0.94 (d, 6H, J = 6 Hz, CH_3), 1.01-2.36 (m, 68H, cholesterol), 3.18-3.19 (m, 2H, CH_2), 3.76 (s, 3H, OCH_3), 4.34-4.72 (m, 3H, CH), 5.39 (m, 2H, =CH). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 11.87, 19.36, 21.06, 22.57, 22.84, 23.89, 24.30, 28.00, 28.13, 28.22, 28.25, 31.88, 32.13, 35.84, 36.21, 36.55, 37.00, 38.50, 38.61, 39.53, 39.77, 42.33, 49.99, 52.32, 53.44, 56.21, 56.72, 74.35, 74.83, 122.52, 122.62, 139.73, 139.81, 155.82, 156.44, 173.13. HRMS calc. for $C_{63}H_{104}N_2NaO_6$ ($M+Na^+$): 1007.7787, found: 1007.7731.

Synthesis of di-3-β-cholest-5-en-3-yl-ester-N-Lysine acid (4): Compound **3** (800 mg, 81.3 mmol) and 1.5 g $LiOH·H_2O$ were stirred in the mixed solvent (10 mL H_2O, 10 mL THF) for 48 hours at rt, and concentrated. Then the mixture was acidified with HCl to pH = 2. White solid **4** was obtained by filtration (700 mg, 89%). Mp: 156-158°C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.70 (s, 6H, CH_3), 0.88-0.90 (m, 12H, CH_3), 0.93-0.95 (d, 6H, J = 5.6 Hz, CH_2), 1.03-2.35 (m, 68H, cholesterol), 3.13-3.14 (m, 2H, CH_2), 4.31-4.97 (m, 3H, CH), 5.38-5.60 (m, 2H, =CH). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 11.88, 18.74, 19.37, 21.08, 22.57, 22.83, 23.94, 24.31, 28.01, 28.26, 31.89, 35.86, 36.23, 36.56, 37.01, 38.51, 39.79, 42.34, 50.00, 56.24, 56.72, 74.50, 74.97, 122.56, 139.73, 156.28, 176.00. HRMS calc. for $C_{62}H_{102}N_2NaO_6$ ($M+Na^+$): 993.7636, found: 993.7616.

Synthesis of 1: Compound **4** (727 mg, 75 mmol), compound **2** (238 mg, 75 mmol)，Dcc (102.6 mg, 3 equiv) and HOBt (150 mg) were stirred in dry $CHCl_3$ for 24 h. The

mixture was concentrated and purified by chromatography (SiO_2, $CHCl_3$/ CH_3OH = 20: 1) to give **1** as a pale gray solid (428 mg, yield: 45%). Mp: 186-188°C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.69 (6H, s, CH_3), 0.88 (d, 6H, J = 1.6 Hz, CH_3), 0.90 (d, 6H, J = 1.6 Hz, CH_3), 0.93-0.94 (d, 6H, J = 6.4 Hz, CH_3), 1.00-2.04 (m, 72H, cholesterol), 3.10 (t, 2H, J = 1.2 Hz, CH_2), 3.70 (d, 2H, J = 2.8 Hz, CH_2), 4.03-4.05 (m, 1H, CH), 4.73-4.75 (m, 1H, CH), 5.26-5.40 (m, 2H, =CH), 7.86-7.89 (t, 1H, J = 7.6 Hz, Ar H), 8.01-8.08 (d, 1H, J = 7.6 Hz, Ar H), 8.43-8.45 (d, 1H, J = 7.6 Hz, Ar H), 8.59-8.61 (d, 1H, J = 8.4 Hz, Ar H), 8.67-8.69 (d, 1H, J = 6.8 Hz, Ar H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 11.88, 18.73, 18.35, 21.06, 22.57, 22.84, 23.89, 24.29, 29.48, 31.86, 35.83, 36.22, 36.54, 36.94, 37.01, 38.47, 38.47, 38.61, 39.69, 39.79, 42.33, 49.99, 56.22, 56.72, 74.27, 74.77, 121.88, 122.48, 122.59, 122.76, 128.15, 129.01, 130.62, 131.20, 131.51, 132.33, 133.54, 139.83, 156.40, 164.07, 172.31. HRMS calc. for $C_{76}H_{111}BrN_4NaO_7$ ($M+Na^+$): 1293.7534, 1295.7513; found: 1293.7427, 1295.7401.

2. Gelation properties:

Table S1 The gelation situation of **1** (2.5% wt/v) in different solvent.

Solvent	**H-C**	**S**
Ethyl acetate	G	G
benzene	G	G
Xylene	G	G
toluene	G	G
cyclohexane	G	G
ethanol	P	G
isopropanol	G	G

H-C: heating (> 85 ºC) until the solid was dissolved and then cooling to room temperature. **S**: sonication at room temperature for 1 min after **H-C**. All the gelation process need less than ten minutes at room temperature; G: gel, P: precipitate from sol.

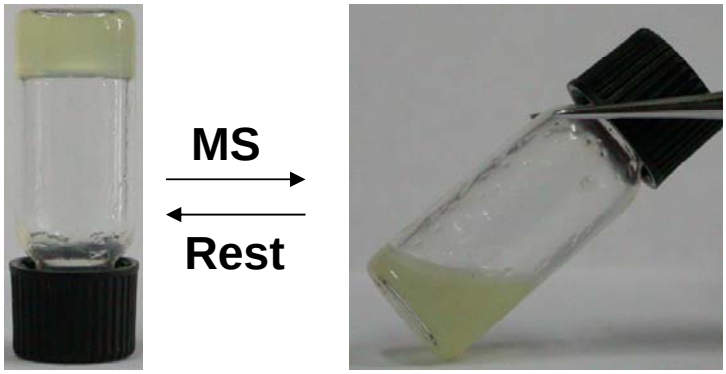


Fig. S1 Photographs of the gel's thixotropic response in isopropanol.

3. Morphological study:

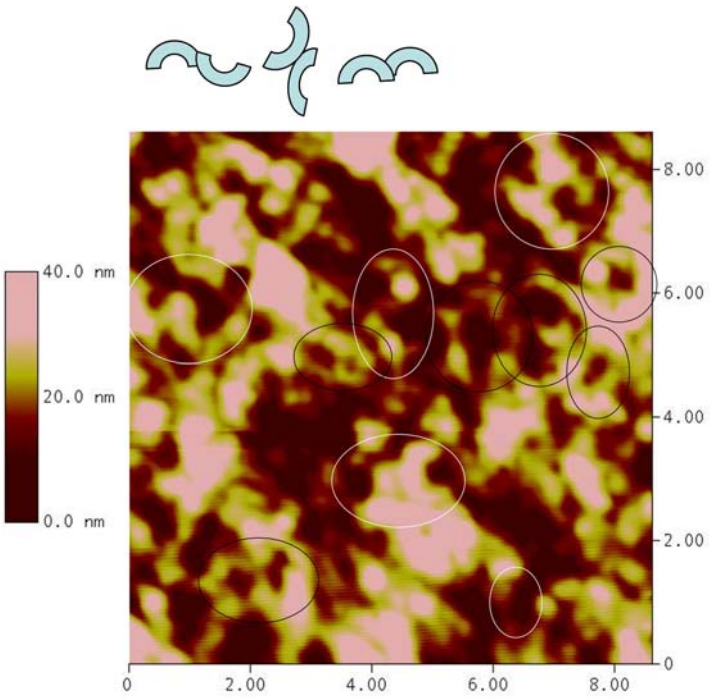


Fig. S2 AFM images of sol-like state of **1** in toluene (0.57 wt%) with some viscosity, helical bias existed.

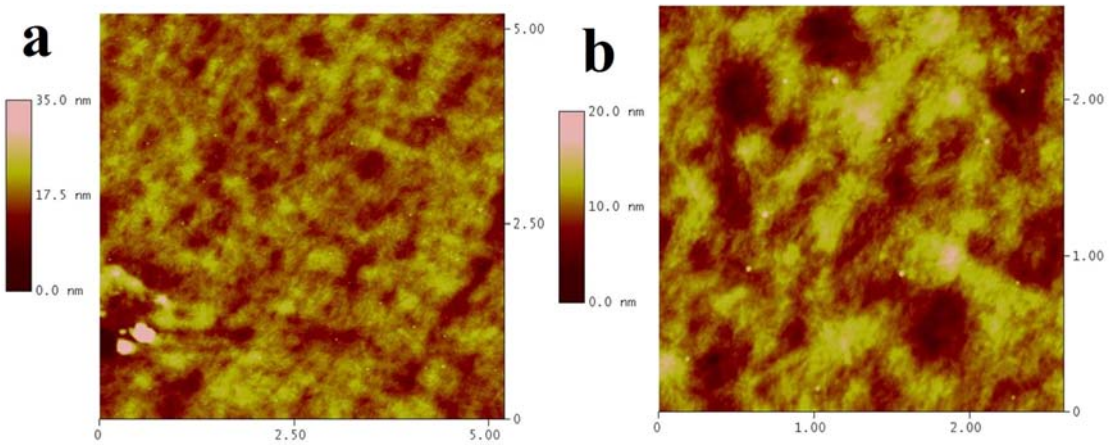


Fig. S3 AFM images of **1** gel (0.86 wt%) in toluene when treated with ultrasound for 30 s; b) was the magnified picture of a).

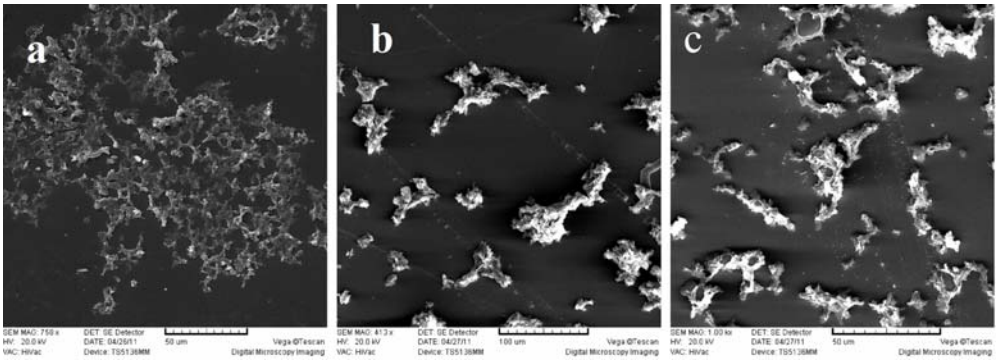


Fig. S4 SEM images of **1** gel in isopropanol; a) T-gel (1.63 wt%); b) broken gel; c) self-healing gel after 8 hours, the scale bars for a, b and c are 50, 100 and 50 μm, respectively.

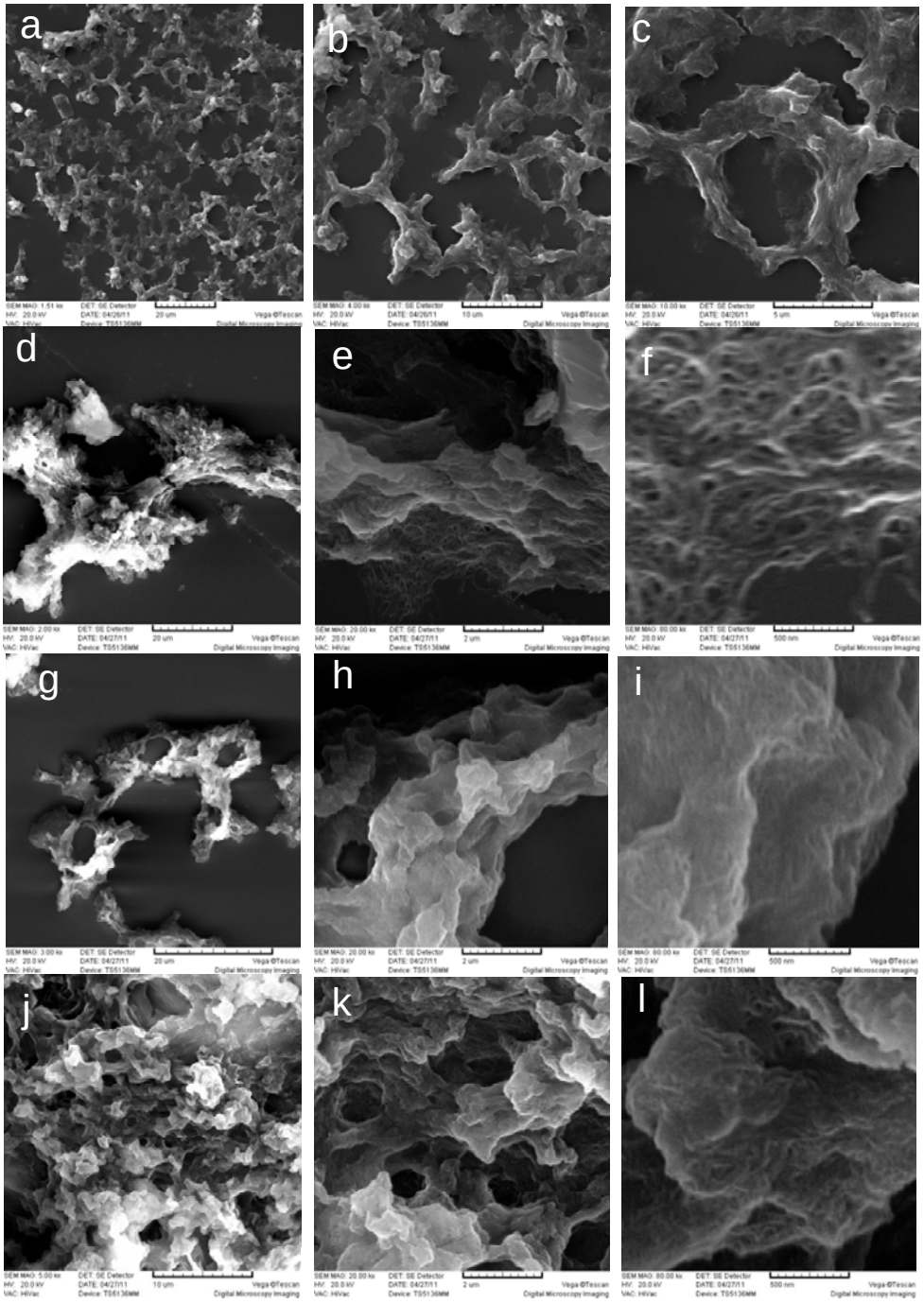


Fig. S5 SEM images of **1** gel (1.63 wt%) in isopropanol; a) T-gel, b and c) the magnification images of a; d) broken gel, e and f) the magnification images of d; g) self-healing gel, h and i) the magnification image of g; j) S-gel for 2 min, k and l) the magnification image of j. Scale bars for a-j are 20, 5, 1, 20, 2, 0.5, 20, 2, 0.5, 10, 2, 0.5 μm, respectively.

4. Viscoelasticity study of the gels in toluene

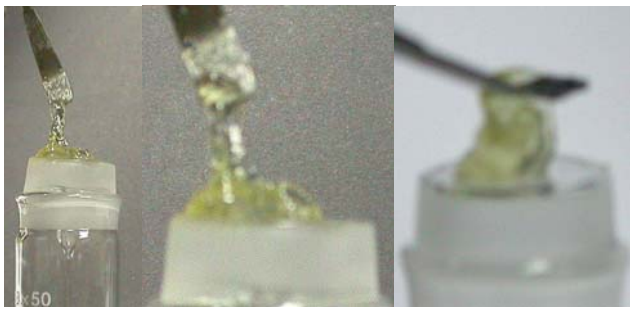


Fig. S6 Pictures of the **1** gel in toluene, indicating the good gel state of **1** when a small strain was imposed.

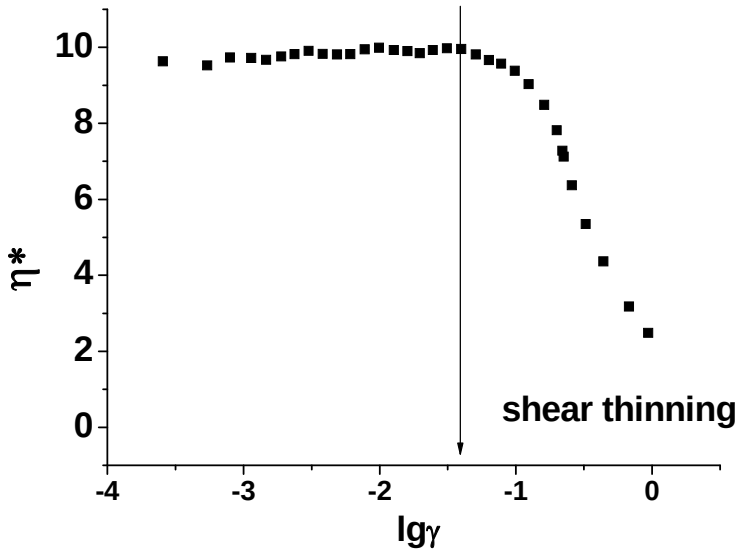


Fig. S7 Amplitude sweep rheometry data (complex viscosity vs. shear strain) for **1** gel in toluene (0.86 wt%) at 25°C (angular frequency: 6.283 rad/s, f = 1.0 Hz, strain: 0.0001-1). The results indicated that shearing thinning phenomena happened when the shear strain > 0.04.

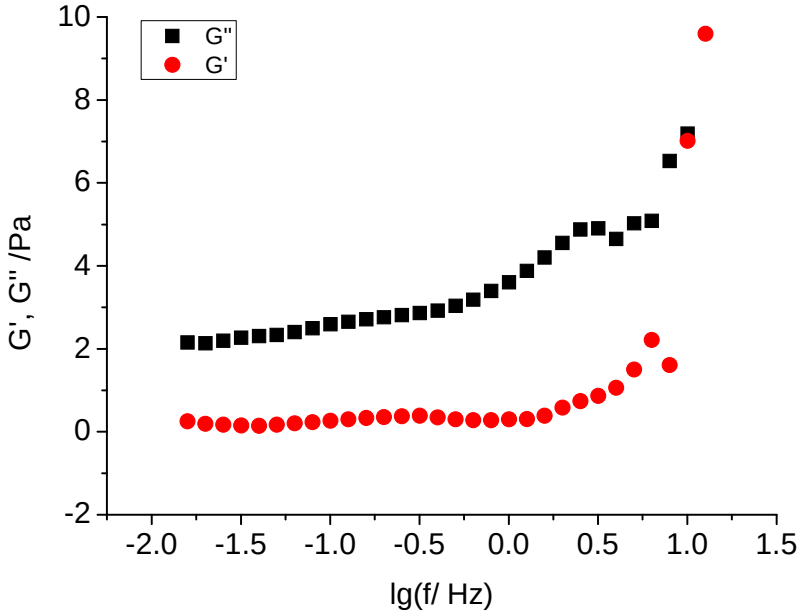


Fig. S8 The frequency sweep data of broken gel of **1** for the second cycle; angular frequency from 0.1-100 rad s^{-1}; keep a shear strain at 500% to destroy the gel state, deformation happened, and $G'' > G'$, indicating destroyed ring structure and the flowing state.

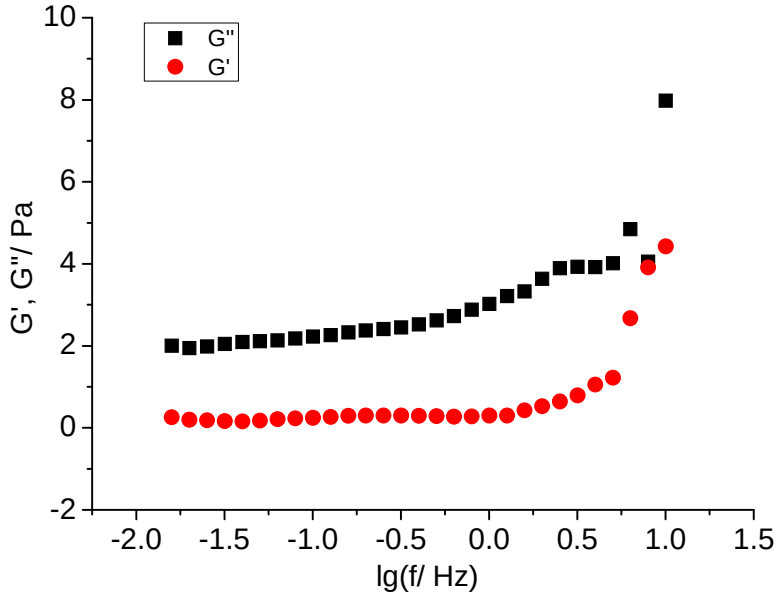


Fig. S9 The frequency sweep data of the broken gel for the third cycle; angular frequency from 0.1-100 rad s^{-1}.

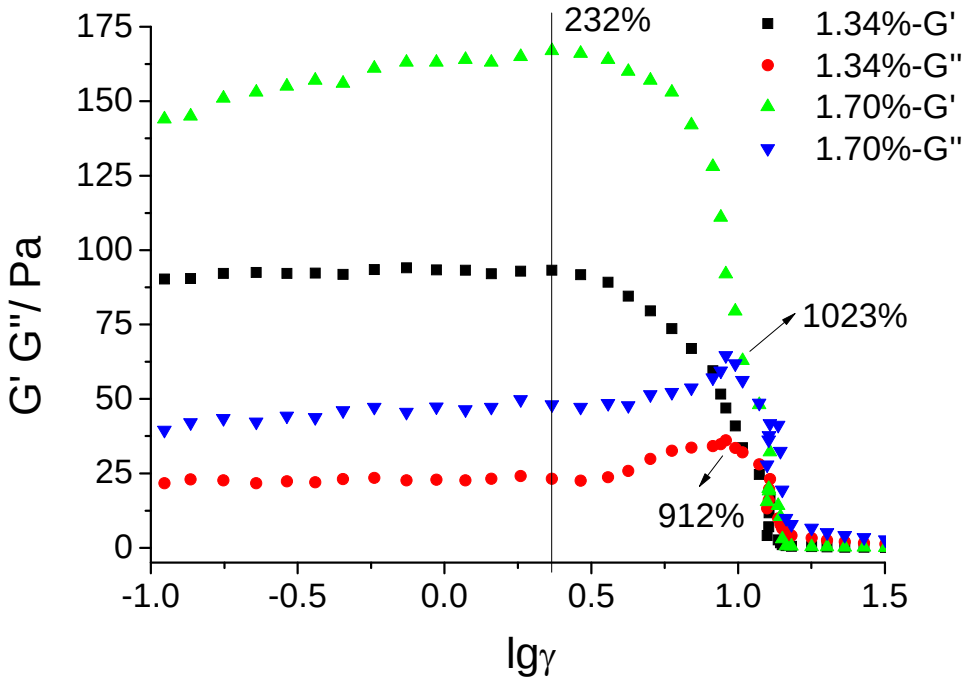


Fig. S10 Amplitude sweep rheometry data (storage modulus $G^{'}$ and loss modulus $G^{''}$ vs. shear strain γ) for the gel **1** in toluene with a concentration of 1.34 wt% and 1.70 wt% at 25°C (angular frequency: 6.283 rad s^{-1}), respectively.

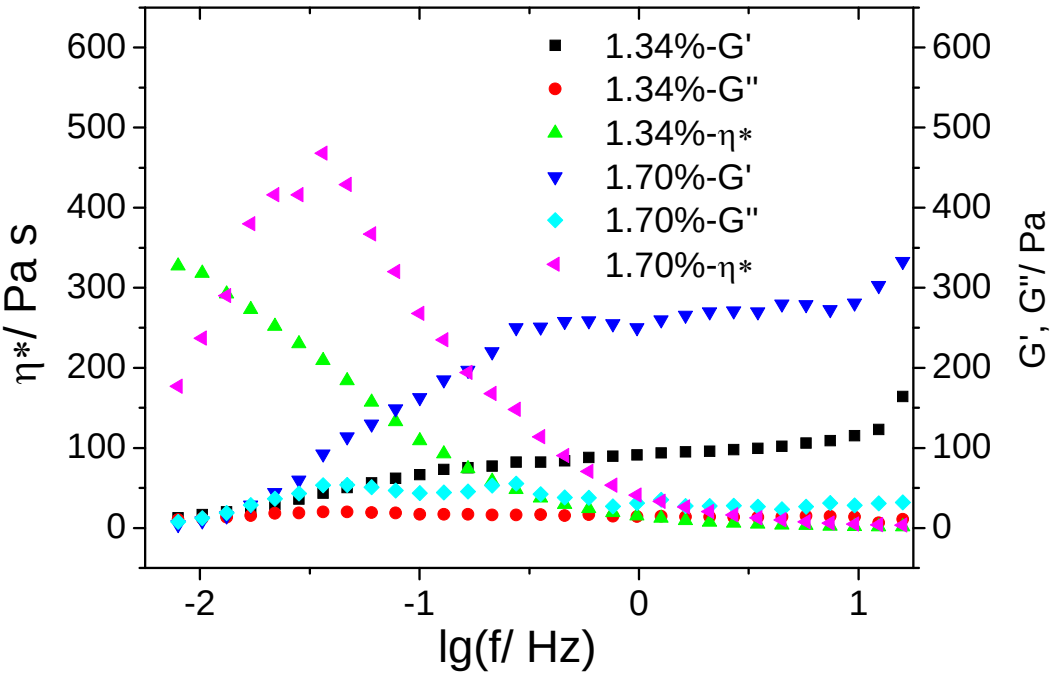


Fig. S11 Dynamic frequency sweep rheometry data for gel **1** in toluene with a concentration of 1.34 wt% and 1.70 wt% at 25°C, respectively (angular frequency from 0.05-100 rad s^{-1}, strain kept at 1% without deformation, $G^{'} > G^{''}$).

5. Uv-vis and CD spectra study:

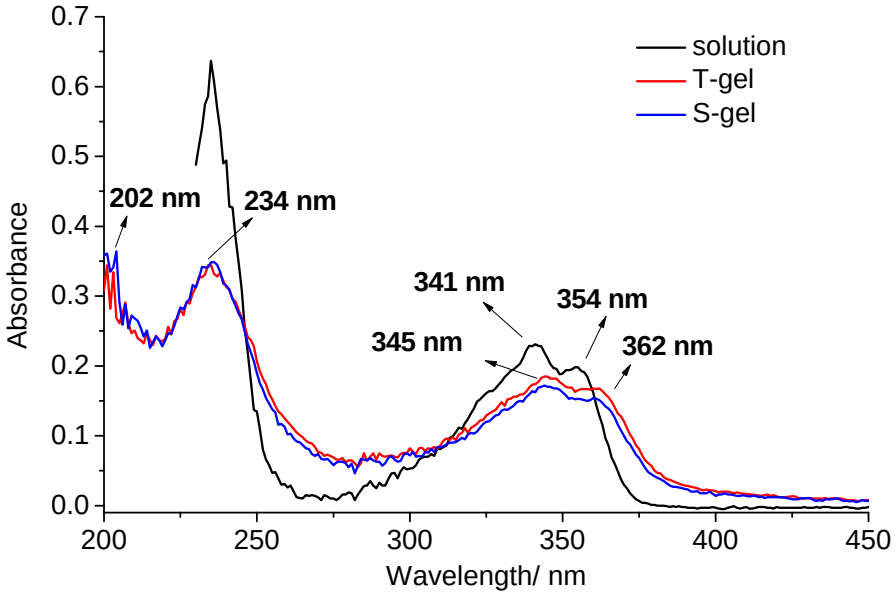


Fig. S12 UV-visible absorption of the solution (1×10^{-4} M) and T/S gel (1.24 wt%) in isopropanol.

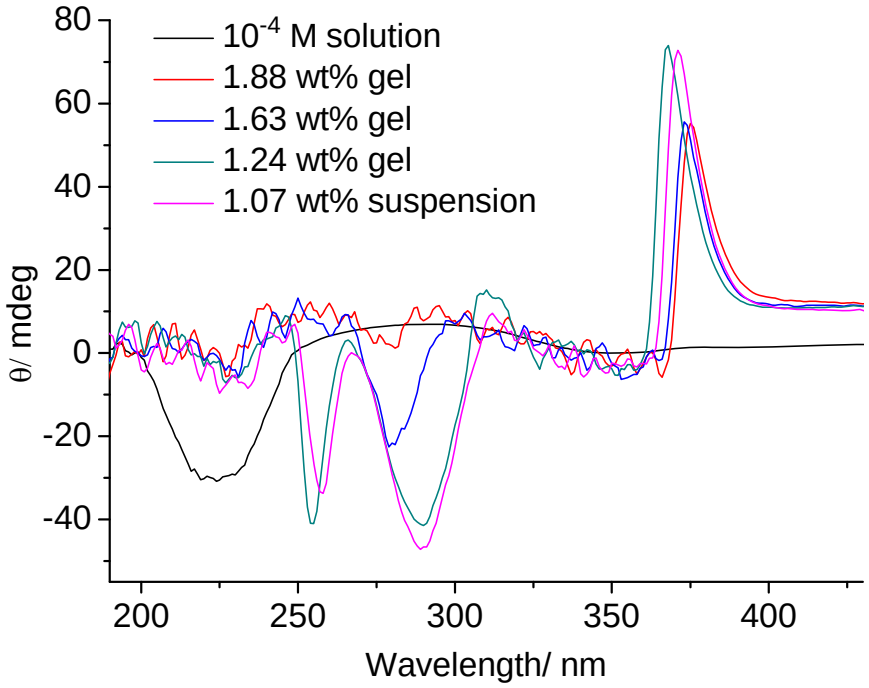


Fig. S13 The CD spectra of **1** in isopropanol with different concentration.

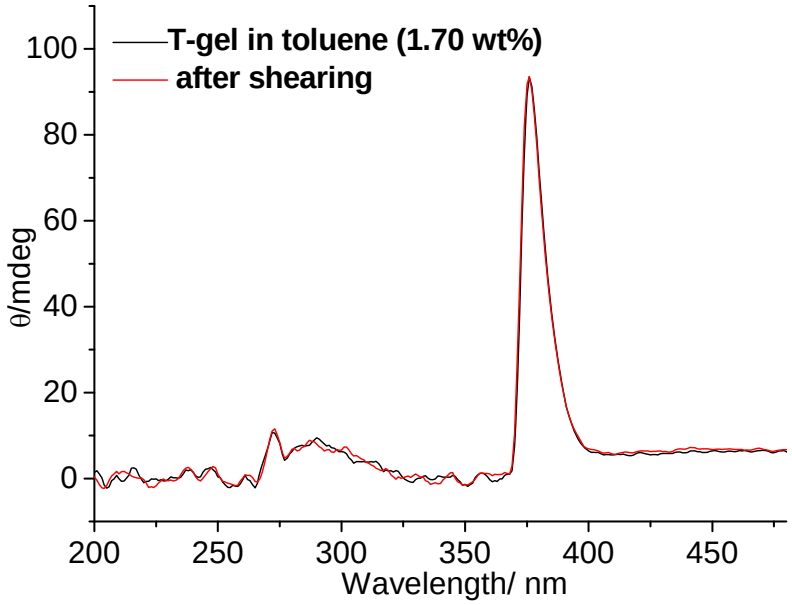


Fig. S14 CD spectra of 1.70 wt% T-gel in toluene after shearing.

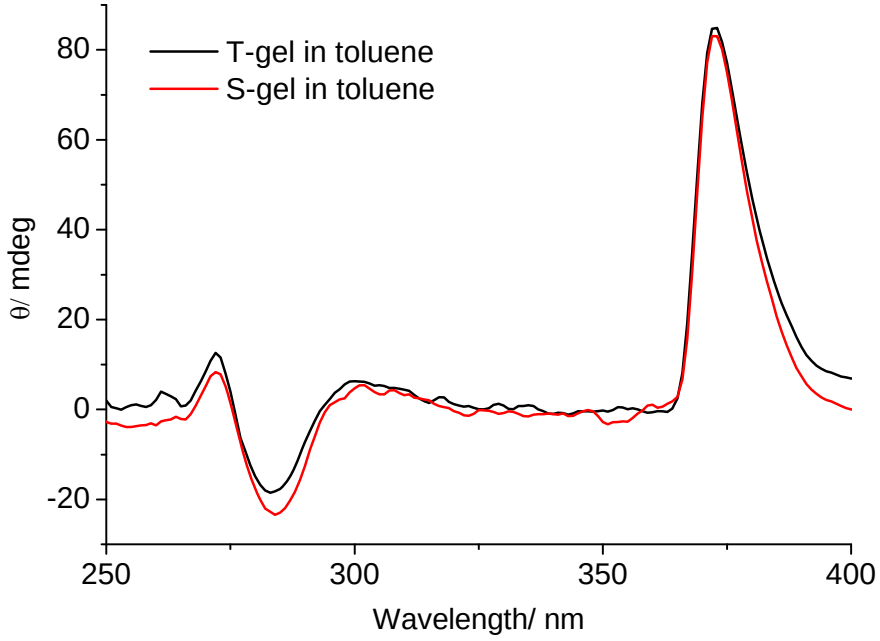


Fig. S15 CD spectra of T-gel of **1** in toluene before and after treated with sonication for 2 min (0.86 wt%).

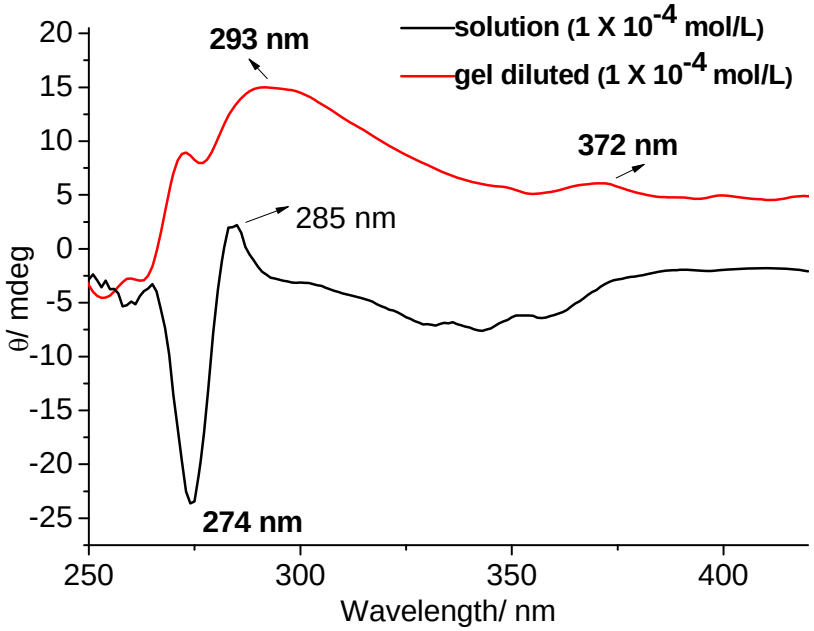


Fig. 16 CD spectra of the samples with the same concentration of solution and sol from diluted gel.

Reference

1. J. H. Qian, X. H. Qian, Y. F. Xu, S. Y. Zhang, *Chem. Commun.* 2008, 35, 4141-4143.