Electronic Supporting Information

Heat triggered molecular restructuring responses the triple gel-gel-gel transformations in a Li^+-integrated metallogel

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Materials and Physical Methods:

Methanol was acquired from Avantor performance material India Ltd., Thane, Maharashtra (India). Concentrated H_2SO_4, DMSO, Ethanol were obtained from Qualikems Fine Chem Pvt. Ltd., Vadodara (India). All solvents were properly distilled and dried using protocol prior to use. Lithium hydroxide and Hydrazine hydrate (80%) were procured from Spectrochem Private Limited. and Sisco Research Laboratories Pvt. Ltd. (Mumbai, India). 4-(Diethylamino)salicylaldehyde was acquired from TCI Chemicals (India). Chennai (India). All the reagents were used as-received without further purification.

FT-IR data were acquired using spectrum two PerkinElmer ATR FT-IR spectrometer. Fourier Transform Nuclear Magnetic Resonance spectrometer (Model AVNACE NEO500 Ascend Bruker BioSpin International AG, Switzerland) was used to procure ^{1}H NMR spectra. UV-vis study was done on UV2600 Schimazdu spectrophotometer. PXRD data was obtained from Empyrean Malvern Panalytical instrument (Cu-Kα radiation) between angle 2θ = 5-80°. ESI-MS spectral analysis was carried out on Waters (Micro mass MS Technologies) Q-Tof Premier instrument and FE-SEM images were procured using JEOL-7610 F Plus. JASCO instrument (Model J-815-150S) was used to acquire CD spectra. Dry N_2 gas was purged (15 L.min^{-1}) throughout the entire experiment. Quartz cuvette (l= 1 mm) was chosen for CD data acquisition (data recorded in the range of 200-400 nm). CH Instrument electrochemical workstation (model No. CHI604E) was employed to conduct Electrochemical impedance studies

Rheological Study:

Freshly prepared metallogels **Y-TLG** (1% w/v) and **R-TLG** were subjected to rheological measurements and experiments were conducted on a Rheometer MCR 102 (Anton Paar) with the help of stainless steel parallel plates (1.0 mm gap was maintained between 25 mm diameter plates). Linear viscoelastic regions (LVE) of the metallogels were obtained in dynamic amplitude sweep experiments at constant angular frequency 10 rad.sec^{-1}. Further, dynamic oscillatory frequency sweep was conducted between 0.1-100 rad.sec^{-1} frequency range at constant 0.1% shear strain. Amplitude and frequency sweep experiments were conducted at 25°C for all the metallogels. Dynamic temperature ramp experiments were conducted within 25°C-100°C. Throughout the experiments, a constant 10 rad.sec^{-1} frequency and 0.1% strain were maintained.

Conductance Study:

Metallogels used in this experiment were synthesized *via* sonication and two different heat-cool methods which produced weak and strong gels, respectively. These freshly formulated metallogel samples and **H_4TL**/LiOH solution were subjected to electrochemical impedance measurements (EIS). Experiments were carried out on an Electrochemical Workstation (model CHI604E) within the 10^6-1 Hz frequency range at 0.01 V of minimal perturbation voltage. All impedance analysis were acquired at room temperature. Three electrodes set up *viz.,* Ag/AgCl reference electrode, platinum wire counter electrode and glassy carbon working electrode were used in a cylindrical electrochemical cell. The Nyquist plots obtained for metallogels were then fitted with suitable electrical circuit models with an inbuilt software provided by CHI604E instrument.

Confocal Laser Scanning Microscopy (CLSM)

Confocal microscopic imaging for the freshly prepared **S-TLG**, **Y-TLG**, **R-TLG** metallogels and **HY** molecule were recorded on a OLYMPUS (model- IX-83). For **S-TLG**, 40 μL gel was pipetted out and was drop-casted on a thoroughly clean coverslip. For **S-TLG** and **Y-TLG**, the initial **H_4TL**/LiOH solution was heated at first at 65 ^oC and then at 95 ^oC, respectively. 40 μL aliquots of the heated solutions were then drop-casted on the coverslip and kept for 1 min. to form the metallogels. Further, HY/Li^+ solution (provided similar gelation condition) was drop-casted in a similar way. The images were recorded thereafter in the gel phase. For all the three metallogels, excitation wavelength of 405 nm and detection wavelength regions of 450-510 nm and 520-590 nm were employed.

Synthesis and Characterization:

Synthesis of Gelator H_4TL:

Preparation of the precursor L-taratric dihydrazide is mentioned in previous literature.[1-3] Briefly, in a round bottom flask containing methanolic solution (50 mL) of L-tartaric acid (2.00 g, 13.3 mmol) conc. H_2SO_4 (catalytic) was charged and reflux condition was maintained for the next 15 hours. Reaction produced Dimethyl-L-tartarate as a clear oil with fruity smell and the solution was concentrated using laboratory rotatory evaporator. The resultant was then used directly for next step. Hydrazine hydrate (1.60 g, 32.00 mmol) was added drop wise to the methanolic solution of as obtained methyl L-tartarate with stirring. The resultant solution was then refluxed for 6-8 hours and further kept to cool down. Afterwards, white crystals of L-tartaric dihydrazide were obtained which were separated by filtration, washed several times with adequate amount of diethylether and dried under vacuum.

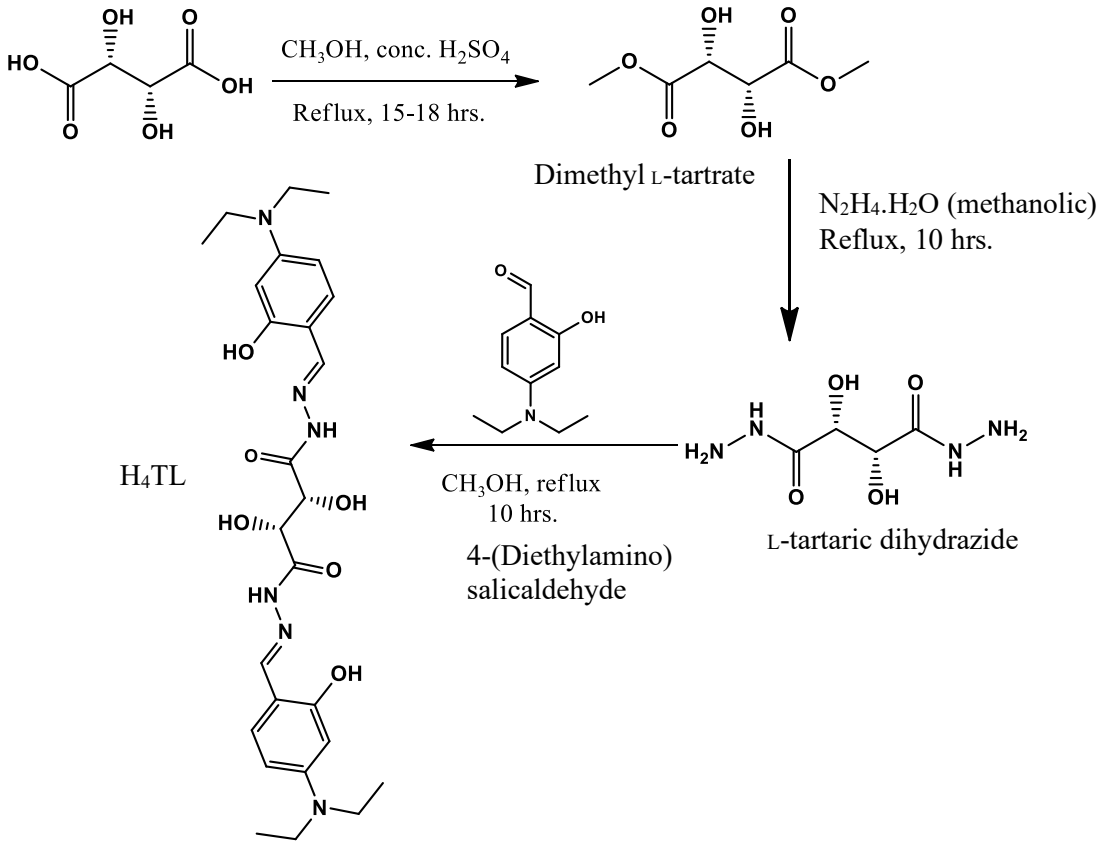
Methanolic solution of 4-(Diethylamino) salicylaldehyde (1.082 g, 5.6 mmol) was added dropwise to lukewarm aqueous solution of L-tartaric dihydrazide (0.500 g, 2.8 mmol) and stirred for 10-15 min. Further, the resulting suspension was refluxed for 7-8 hours at 55^{o}C. This afforded pale beige-coloured solid compound and consecutively washed with methanol, diethyl ether, Dichloromethane and water. A quick wash with chloroform was served and dried in vacuum afterwards. Yield 1.064 g (72%). ^{1}H NMR (400 MHz, DMSO, ppm): 1.12 (t, 12H, CH), 3.45 (8H, CH), 4.51 (d, 2H, chiral -CH), 5.95 (s, 2H, -OH), 6.1-6.38 (4H, Ar-H), 7.2 (s, 2H, Ar-H), 8.45 (s, 2H, =CH), 11.28 (s, 2H, -NH), 12.02 (s, 2H, -OH); ESI-MS $[M+H]^+$, 529.27 (529.27).

Separate synthesis of HY:

HY was prepared by slightly modifying earlier reported synthesis procedure.[4] To a Methanolic solution of hydrazine hydrate (100 mg, 2.05 mmol), 4-(Diethylamino) salicaldehyde (795 mg, 4.10 mmol, dissolved in minimum quantity of methanol) was added dropwise. Thereafter, the mixture was refluxed for next 8 hours affording yellow coloured precipitate. The precipitate was washed with methanol (x3) and dried in vacuum. ^{1}H NMR (500 MHz, DMSO, ppm): 1.07-1.12 (t, 12H, CH), 3.45 (q, 8H, in solvent proximity), 4.51 (d, 2H, -CH), 6.0-7.1 (6H, Ar-H), 8.51 (s, 2H, =CH), 11.47 (s, 2H), ESI-MS $[M+H]^+$: 383.2, *calc.* 383.2.

Synthesis of metallogels S-TLG and Y-TLG:

H_4TL (10 mg, 0.019 mol) was dissolved in DMSO (0.20 mL) in a small 10 mL glass vial leading to clear pale-yellow solution. The fresh LiOH.H_2O solution (0.002 g, 0.038 mol) in DMSO (0.8 mL) was added drop wise to the solution of gelator and was then subjected to brief sonication. The ultrasound resulted in a weak faint yellow coloured metallogel (**S-TLG**). The **S-TLG** was then heated to 65 ^{o}C to convert it into solution and kept for cooling to room temperature. The yellow coloured metallogel **Y-TLG** was formed upon cooling and gel phase formation was preliminarily checked by inverted vial method.



Scheme S1: Synthetic procedure followed to synthesize gelator **H_4TL**.

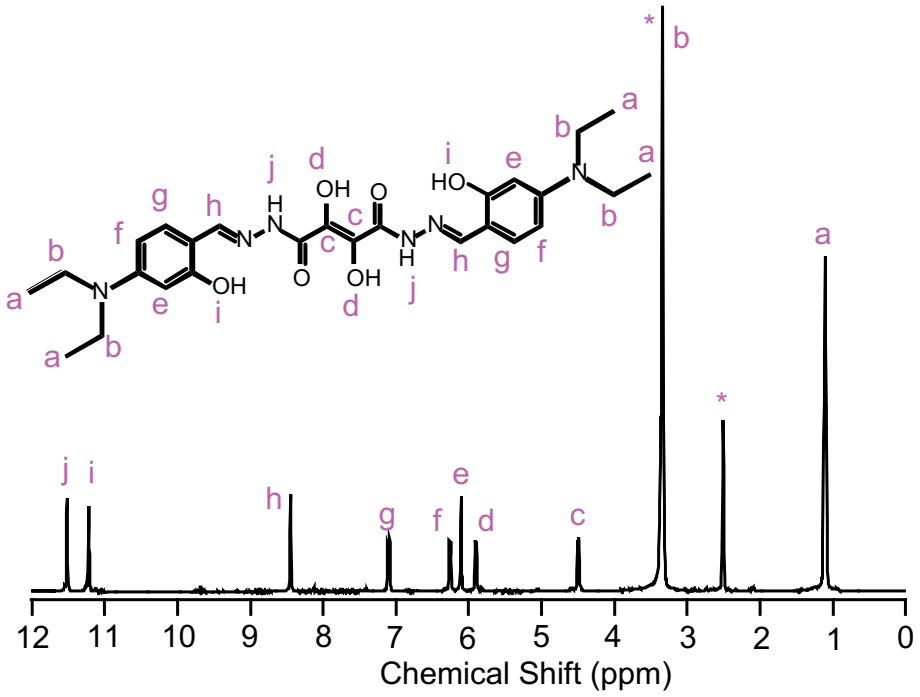


Figure S1: ^{1}H NMR spectra of **H_4TL** performed in dmso-d_6.

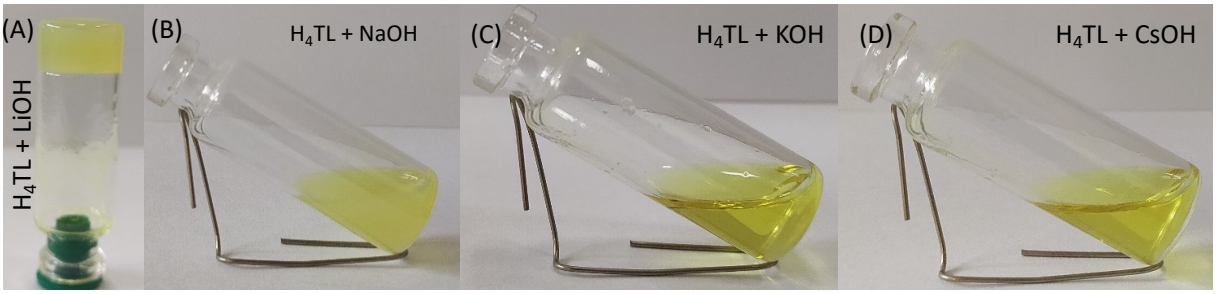


Figure S2: Response of **H_4TL** with respect to (A) LiOH, (B) NaOH, (C) KOH and (D) CsOH under similar conditions.

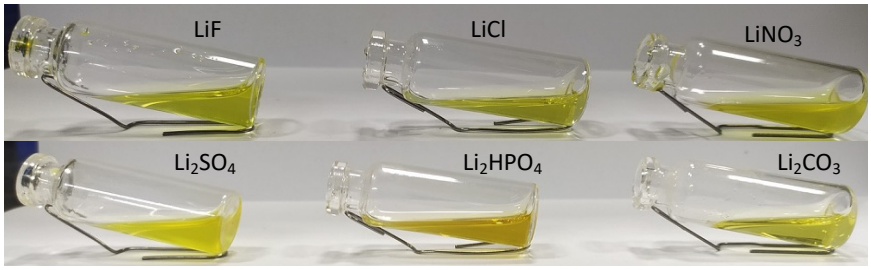


Figure S3: Response of **H_4TL** with respect to various Li^+-salts under similar conditions to gelation.

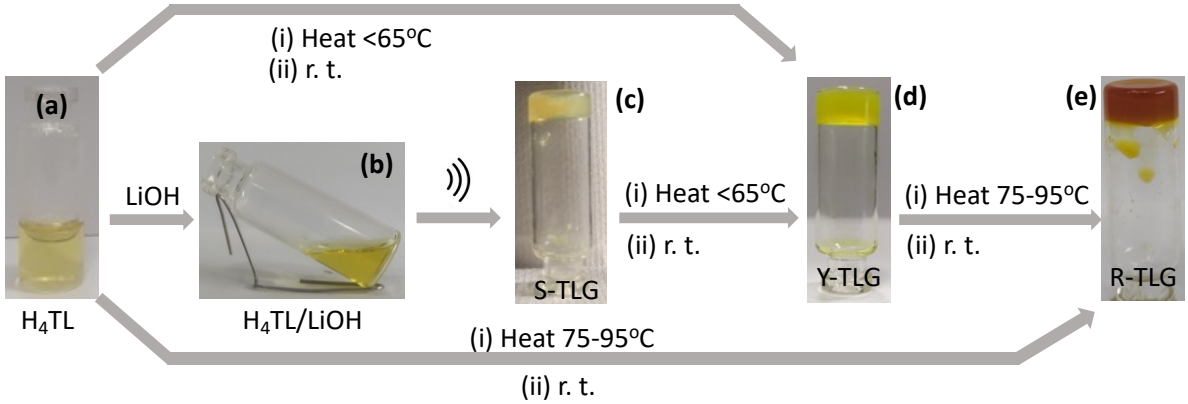


Figure S4: Steps involved in (a-b) **S-TLG**, (c-d) **Y-TLG** and (e-f) **R-TLG** formation.

Table S1. Gelation tests with respect to alkali bases.

Solvent	**H_4TL + LiOH**	**H_4TL + NaOH**	**H_4TL + KOH**	**H_4TL + CsOH**
DMSO	G	GP	S	S

Where, S= solution, G= gel, GP= gelatinous precipitate

Table S2. Gelation tests with respect to LiOH and solvent

S. No.	**Solvent**	**Solubility of H_4TL**	**Gelation Property (H_4TL + LiOH)**
1.	DMSO	S	G
2.	DMSO-water	S	P
3.	DMF	S	GP
4.	Acetone	NS	P

5.	Acetonitrile	NS	P
6.	Water	NS	P
7.	Methanol	PS	GSP
8.	Ethanol	NS	P
9.	Chloroform	PS	P
10.	DCM	NS	P

Where, S= solution, G= gel, NS= not soluble, PS= partially soluble, GP= gelatinous precipitate, GSP= Gelatinous suspension.

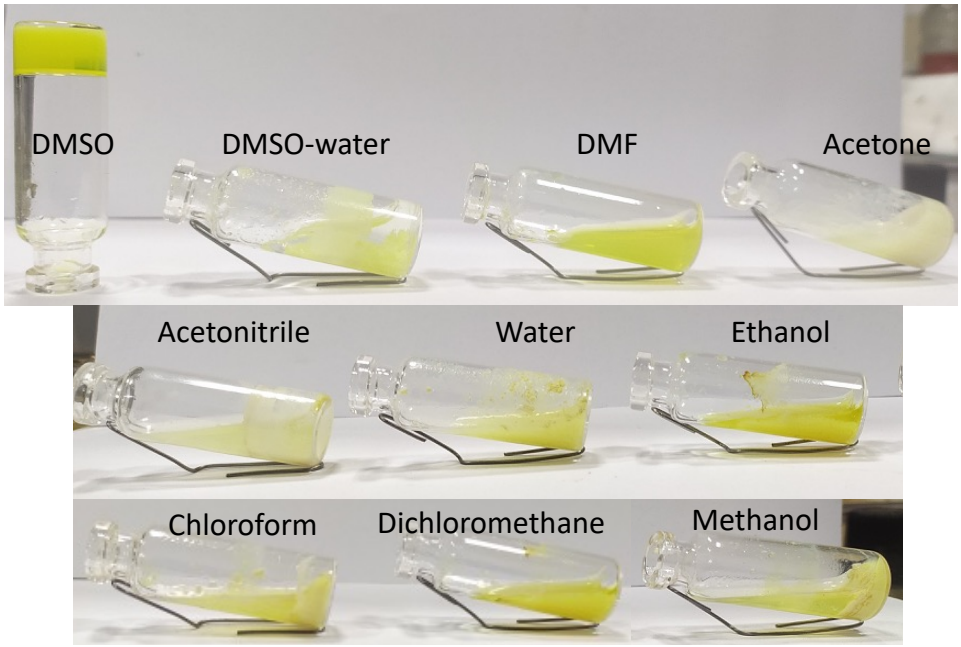


Figure S5. Gelation tests with respect to LiOH in presence of different solvents, as depicted in Table S2.

Table S3: Effect of initial weight percentage of **H_4TL** with 4 equivalent of LiOH over gelation time.

S. No.	**H_4TL (% w/v)**	**Nature of mixture**
1.	0.5	Sol
2.	0.6	Sol
3.	0.7	Sol
4.	0.8	Partial gelatinous sol
5	0.9	Partial gelatinous sol
6.	1*	Self-standing Gel (within 2 minutes)
7.	2	Gel

*= Minimum gelation concentration determined.

Table S4: Gelation ability of **H_4TL** with increasing equivalence of LiOH.

S. No.	H_4TL (mg)	LiOH (equivalent)	Result (H_4TL + LiOH)
1.	10*	1	Sol
2.	10	2	Weak Gel
3.	10	3	Weak Gel
4.	10	4	Gel
5.	10	6	Gelatinous suspension

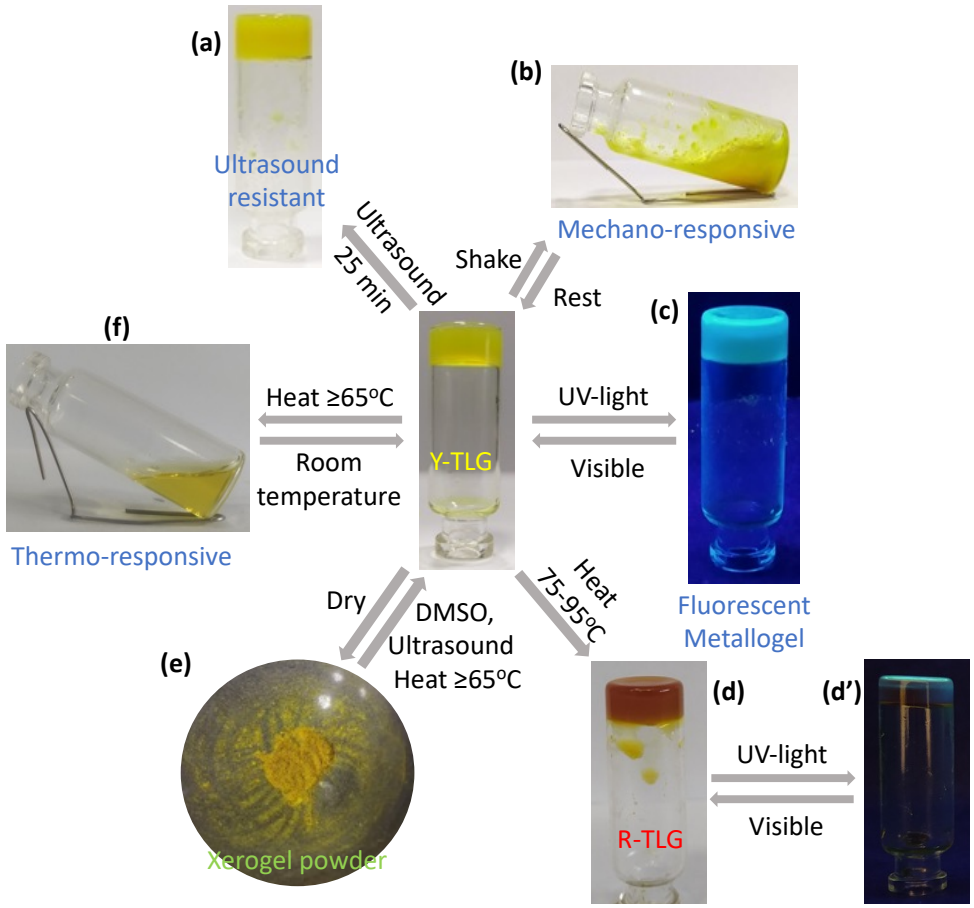


Figure S6: Metallogel (**Y-TLG**) was found to be (a) ultrasound resistant and (b) mechanoresponsive, (c) response under UV-light, (d) Thermal response of metallogel in the heating range of 65-95°C, (d') **R-TLG** under UV light (e) reswelling behaviour of metallogel, (f) thermo-responsive behaviour of metallogel upon heating nearly up to 65°C.

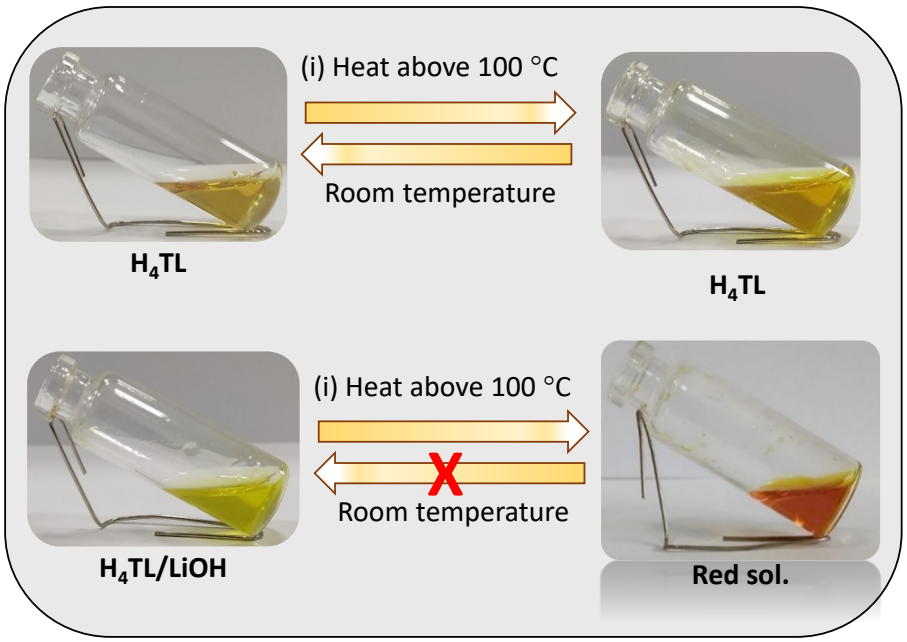


Figure S7: (A) No visible colour change upon heating the gelator **H_4TL** without LiOH even above 100°C while (B) Drastic irreversible colour change from yellow to red of **H_4TL**/LiOH solution, conferring essential role of basic medium in colour change.

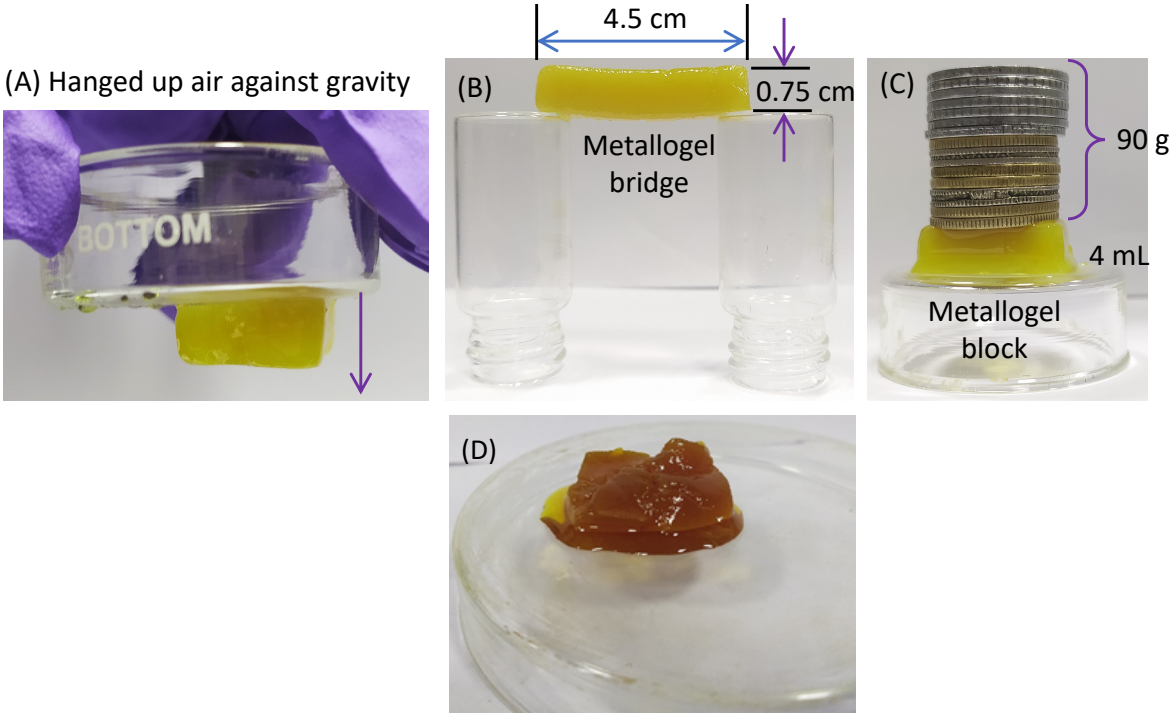


Figure S8: Pictures of freshly formulated **Y-TLG** (1% w/v) as (A) a free-standing metallogel block against gravity presenting the partial adhesive property of metallogel, (B) Metallogel can be converted in to 4.5 cm x 0.75cm block which was able to maintain a bridge like shape supported by two glass vials, and (C) A 4 ml **Y-TLG** block can bear up to 90 g load without its shape deformation, (D) **R-TLG** could not show self-standing ability.

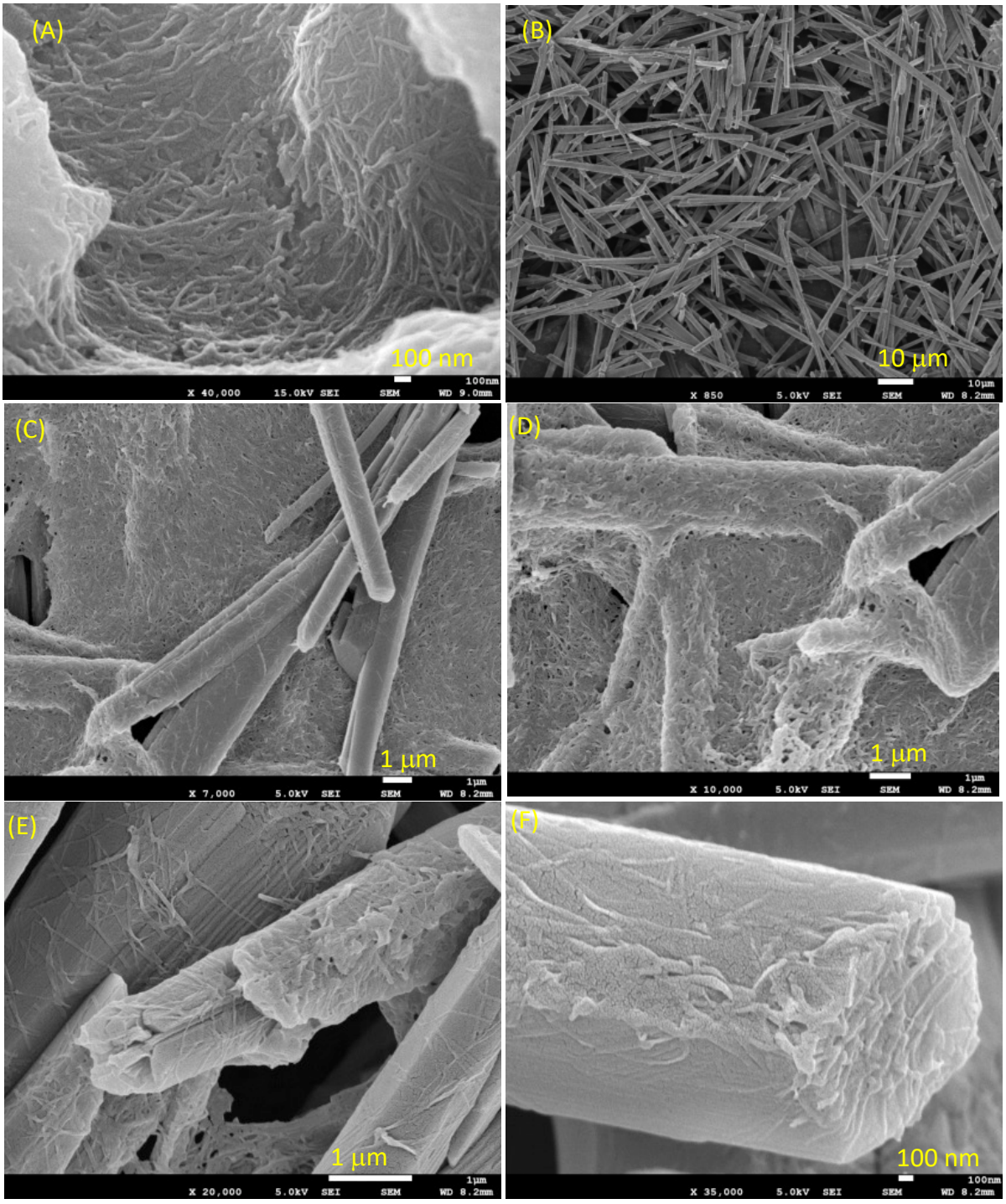


Figure S9: FE-SEM images of dried (A) **S-TLG** and (B-F) **Y-TLG** metallogels at three different magnifications.

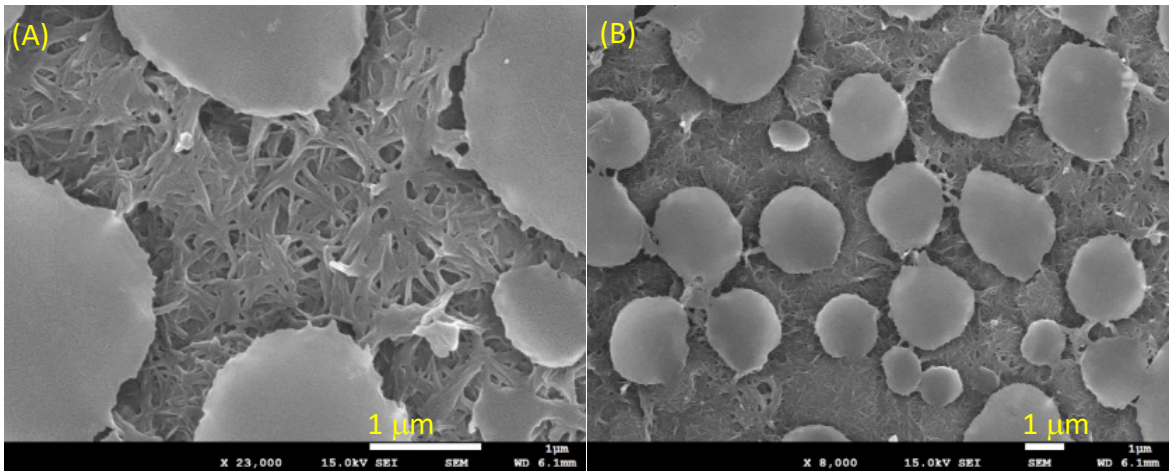


Figure S10: FE-SEM images of dried **R-TLG** metallogel at two different magnifications displaying comparatively thicker fibres along with lumping of fibres during heat cool cycle of 25°-95°-25°C.

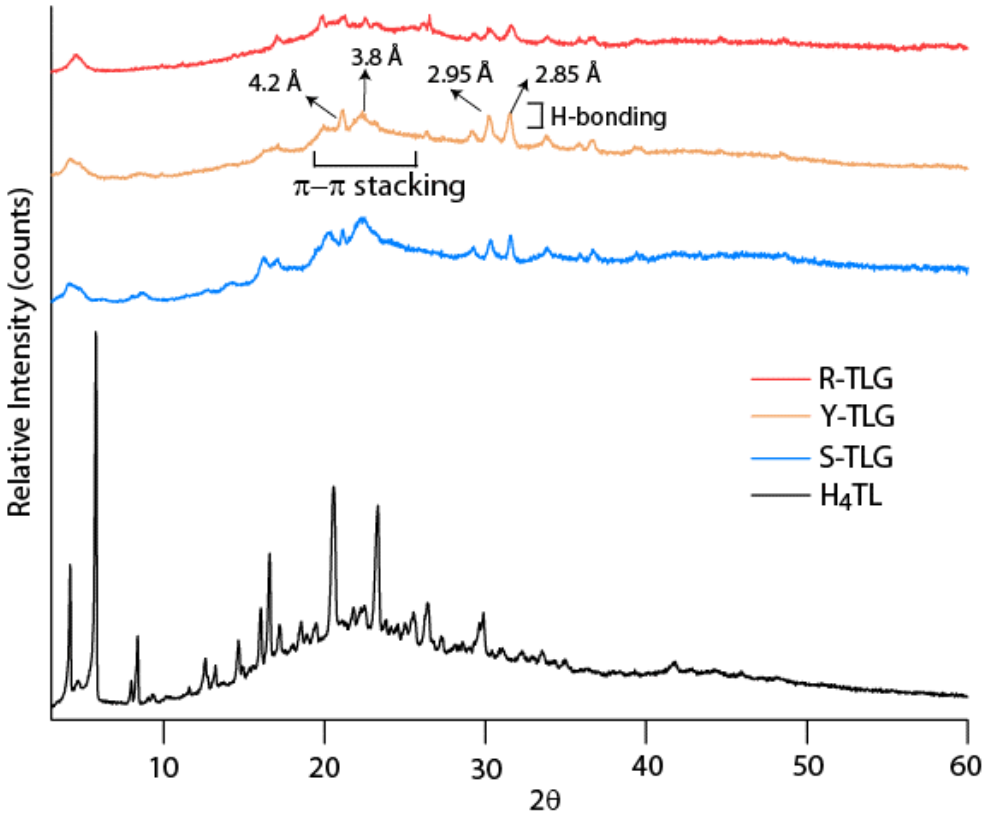


Figure S11: A comparative PXRD patterns of **H_4TL** (red line), **S-TLG** (blue line), **Y-TLG** (orange line) and **R-TLG** (red line) xerogels.

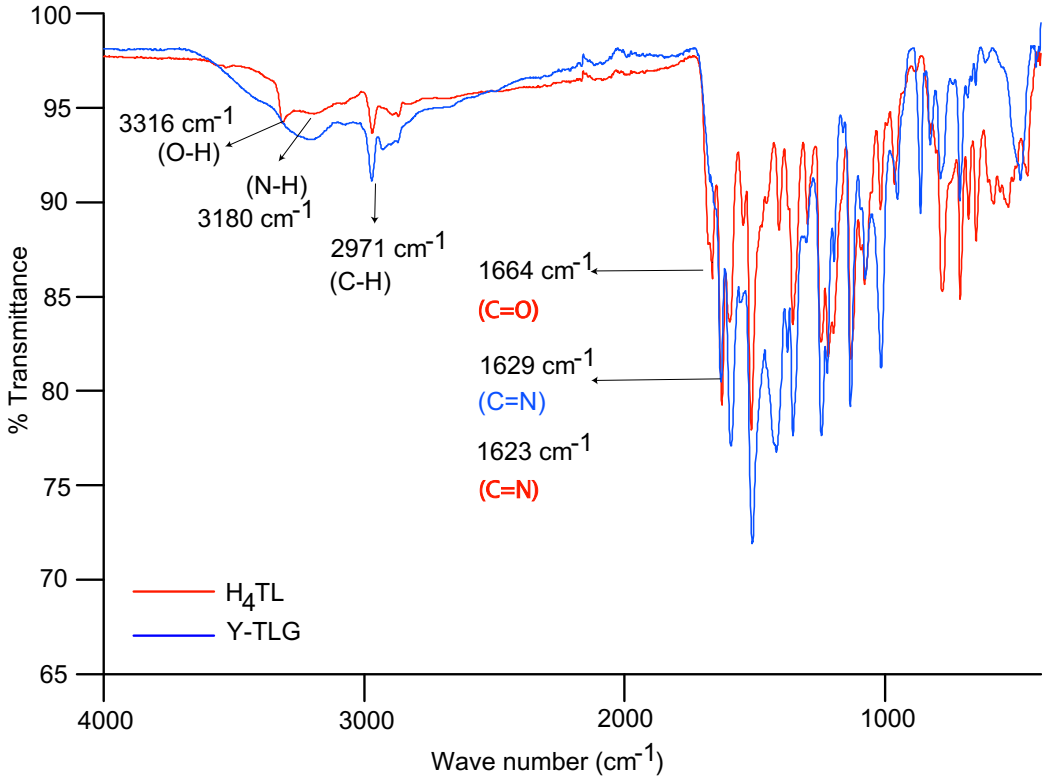


Figure S12: A comparative FTIR spectra of **H_4TL** (red line) and **Y-TLG** xerogel (blue line).
Note: Y-TLG and **R-TLG** exhibit similar spectra pattern and hence not shown separately.

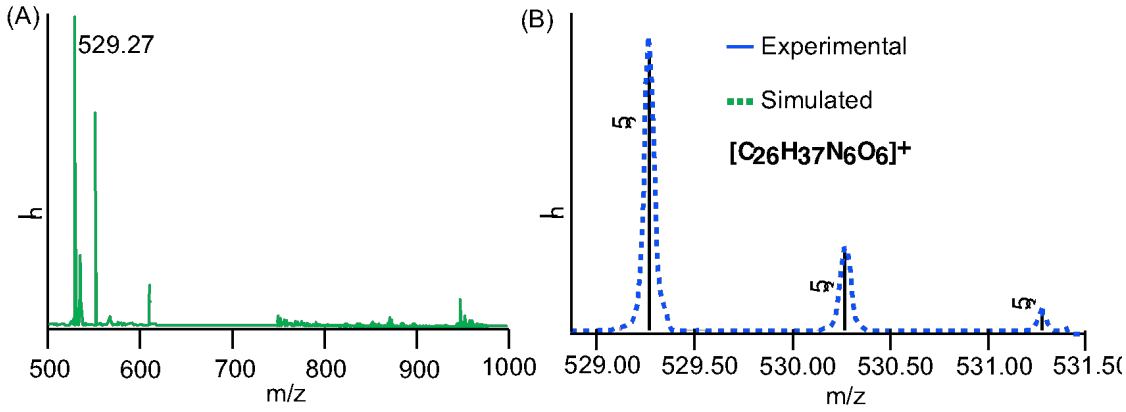


Figure S13: (A) ESI-MS spectra of gelator **H_4TL** and (B) isotopic abundance pattern for *m/z* 529.7 for $[C_{26}H_{37}N_6O_6]^+$ matches nicely with simulated pattern.

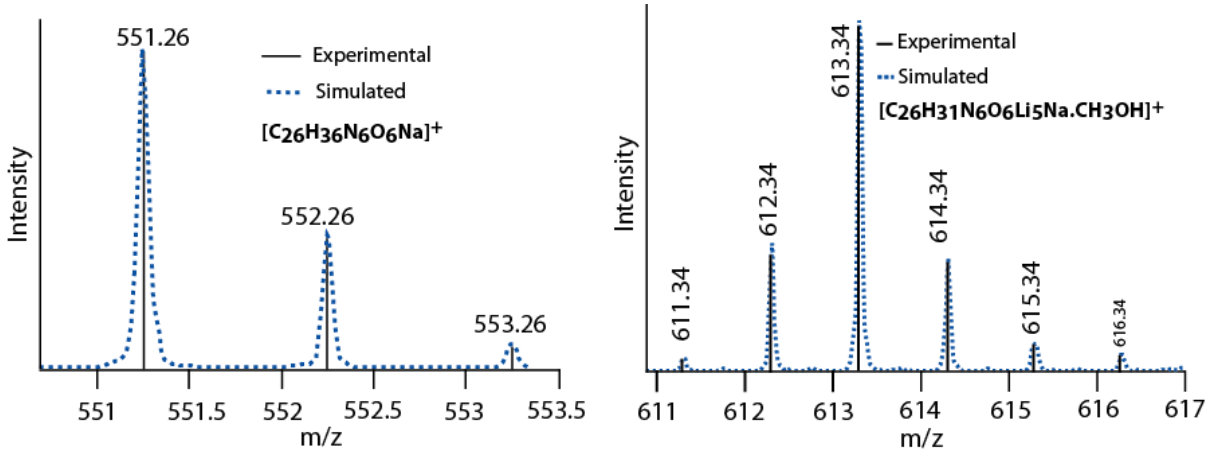


Figure S14: ESI-MS spectra: Isotopic abundance pattern for **Y-TLG**; *m/z* (left) 551.26 for $[C_{26}H_{36}N_6O_6Na]^+$ and (right) 613.34 for $[C_{26}H_{31}N_6O_6Li_5Na.CH_3OH]$. The experimental pattern (black) matches with simulated (blue dotted line) pattern.

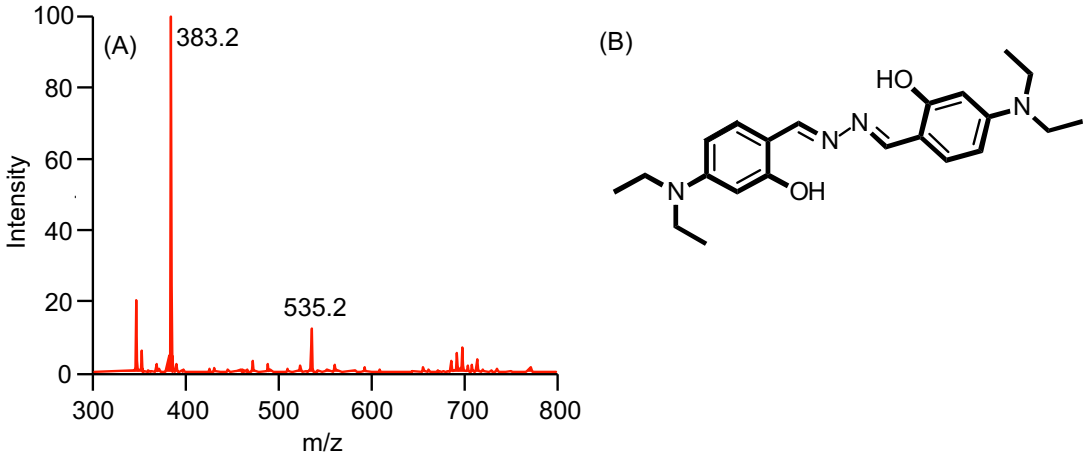


Figure S15: (A) ESI-MS study of the high temperature (110 °C) treated **R-Sol**, showing base peak at *m/z* 383.2, (B) corresponding **HY** molecule, formed *via in situ* gelator dissipation and restructuring.

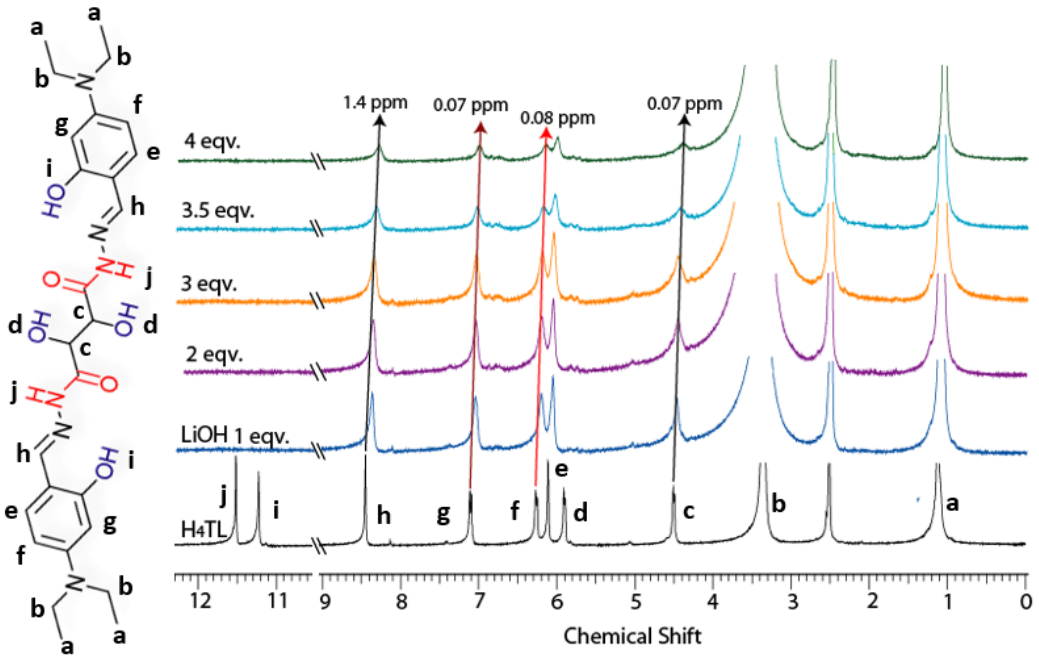


Figure S16: ^{1}H NMR titration spectra of **H_4TL** with 4 equiv. of LiOH (d_6-DMSO).

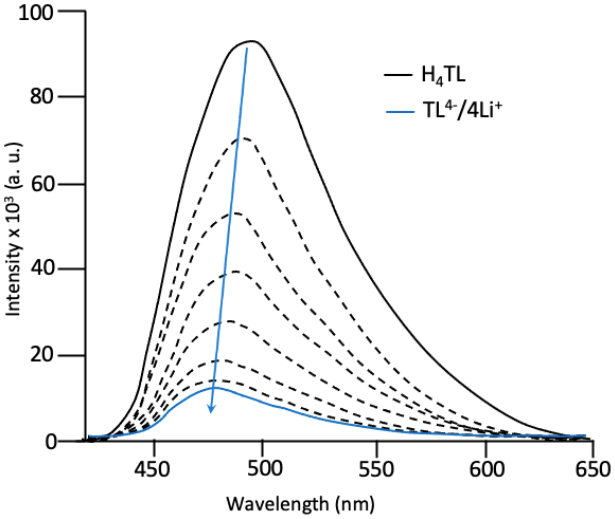


Figure S17: Fluorescence titration experiment of **H_4TL** (10^{-3}M, DMSO, λ_{ex}= 405 nm) with 4 equivalent of LiOH (10^{-1}M, DMSO).

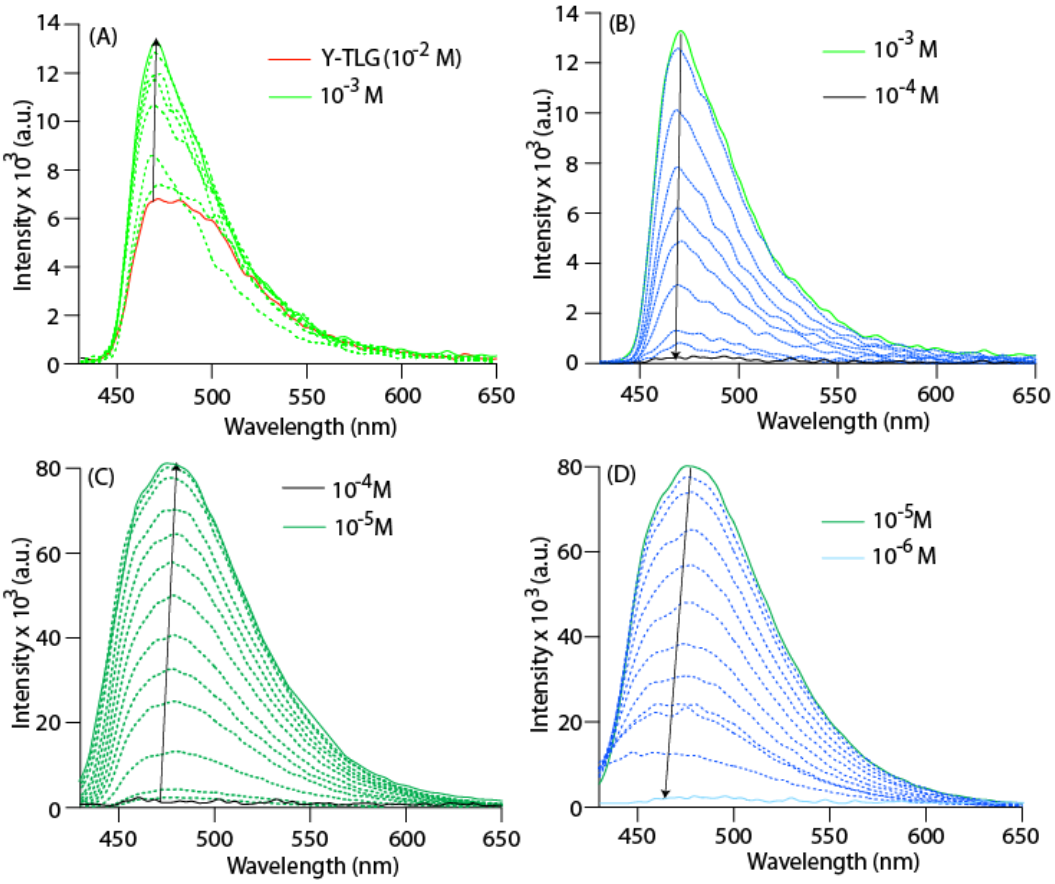


Figure S18: (A-D) Fluorescence dilution experiment (10^{-2}-10^{-6}M) performed over **Y-TLG** (1x10^{-2} M).

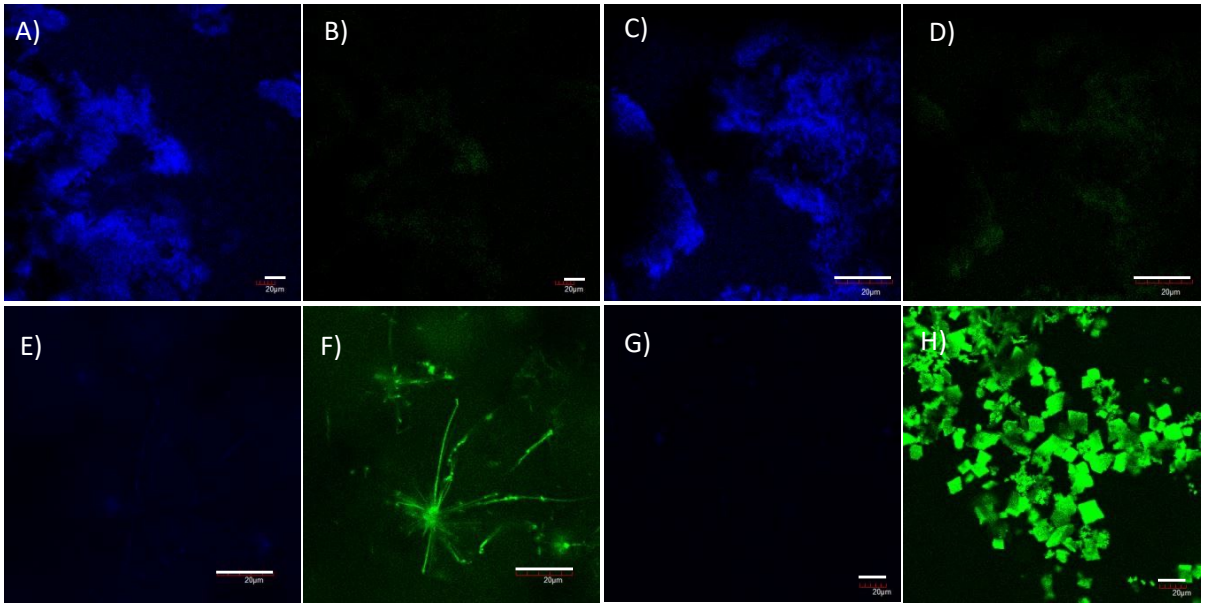


Figure S19. Confocal Laser scanning microscopic (CLSM) images obtained for (A, B) **S-TLG**, (C, D) **Y-TLG,** (E, F) **R-TLG**, (G, H) separately synthesized **HY**/Li^+ for two emission channels (430-500 nm and 510-590 nm, λ_{ex} = 405 nm), scale bar= 20 μm.

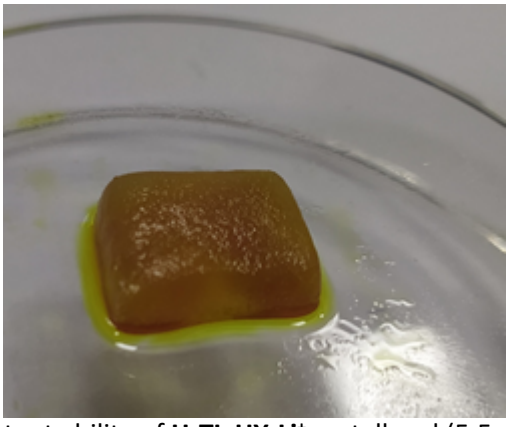


Figure S20: (A) Shape persistent ability of **H_4TL-HY-Li^+** metallogel (5:5; mg).

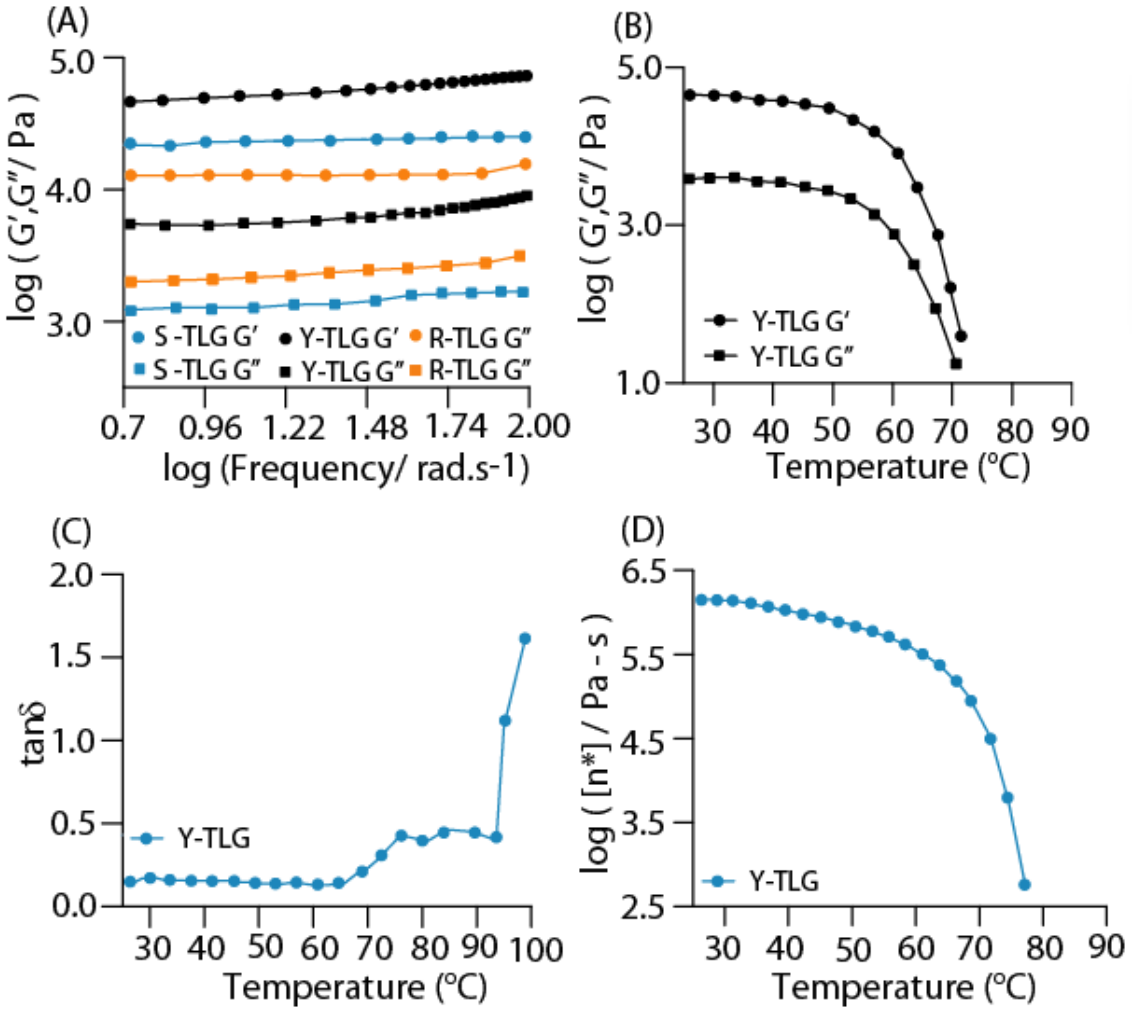


Figure S21: Rheological analysis of freshly formulated **S-TLG**, **Y-TLG, R-TLG** metallogels (1 %, w/v); (A) Dynamic frequency sweep experiment of **S-TLG**, **Y-TLG, R-TLG**. (B) Variation of G"/G' against temperature indicative of the gel to solution transition temperature to be ~65° C, (C) tanδ *vs*. temperature plot of **Y-TLG**, and (D) Variation of complex viscosity (η*) with temperature, altogether illustrating gel-sol transition temperature.

Table S5. G', yield strain and yield stress values obtained from the rheological analysis of **S-TLG**, **Y-TLG** and **R-TLG**.

	S-TLG	**Y-TLG**	**R-TLG**
G' (Pa)	28000	44124	14815
Yield strain (%)	10.12	2.13	7.76
Yield stress (Pa)	180	215	99

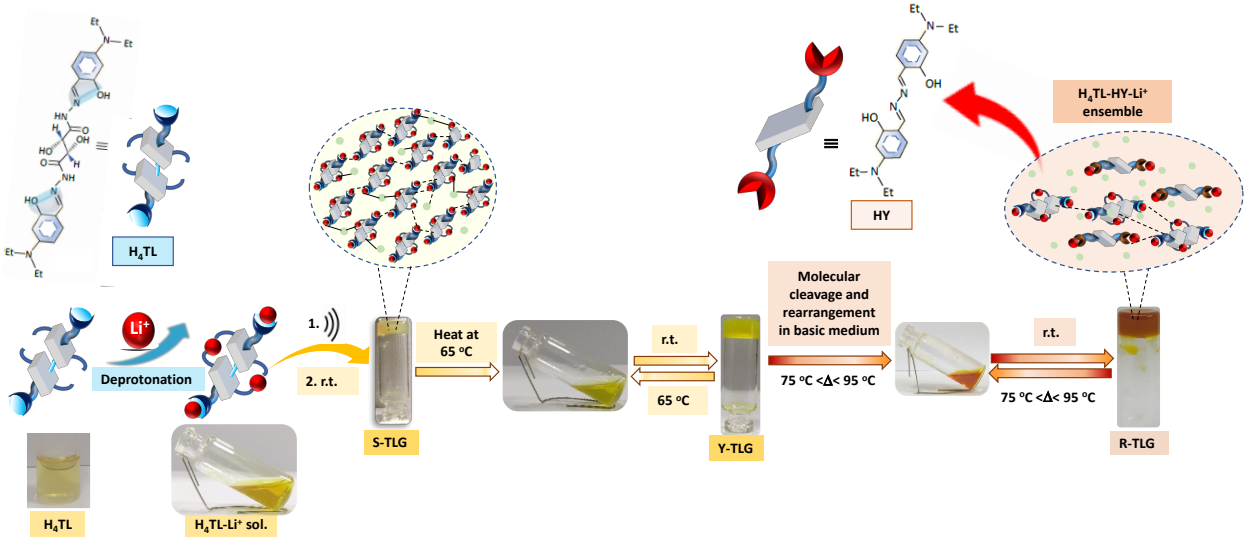


Figure S22: Schematic representation for steps involved during formation of **S-TLG**, **Y-TLG, R-TLG** under the influence of 25 °C, 25-65-25 °C and 25-95-25 °C heat-cool cycles respectively.

Reference:

1. M. K. Dixit, V. K. Pandey and M. Dubey, *Soft Matter*, 2016, 12, 3622.

2. M. Dubey, A. Kumar, R. K. Gupta and D. S. Pandey, *Chem. Commun*., 2014, 50, 8144.

3. C. Mahendar, M. K. Dixit, Y. Kumar and M. Dubey, *J. Mater. Chem. C*, 2020, 8, 11008.

4. F. Gou, J. Cheng, X. Zhang, G. Shen, X. Zhou and H. Xiang, *Eur. J. Inorg. Chem*., 2016, **2016**, 4862-4866.