Electronic Supplementary Information (ESI)

D-(+)-Glucose-Triggered Metallogel to Metallogel Transition

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Experimental Procedures

Materials and Physical Methods:

All the compounds were synthesized by slight modification of the literature procedures.[1,2] The solvents were distilled and dried by standard procedures prior to their use. Reagents and solvents used in experiment were purchased from Merck Specialities Private Limited and S. D. Fine Chem. Ltd, Mumbai, India and used as received without further purification. DMSO and Ethanol were purchased from Qualikems Fine Chem Pvt. Ltd., Vadodara (India). Methanol was purchased from Avantor performance material India Limited, Thane, Maharashtra (India). Lithium hydroxide were purchased from Spectrochem Pvt. Ltd., Mumbai (India), Hydrazine hydrate (80%), 4-formylphenylboronic acid and 2-formylphenylboronic acid were purchased from Sisco Research Laboratories Pvt. Ltd. Mumbai (India). D-(+)-glucose is purchased from Alfa Aesar.

UV-vis study was done on UV2600 Schimazdu spectrophotometer. ^{1}H NMR spectra were obtained on a Bruker AVANCE III 400 Ascend Bruker Bio Spin International AG spectrometer. Electrospray ionization mass (ESI-MS) spectra were recorded on a Waters (Micro mass MS Technologies) Q-tof Premier and FE-SEM images were captured by JOEL-7610 F Plus. Powder XRD data was collected on Rigaku Smart Lab between angle $2\theta = 5$–80°. CD spectra were recorded on a JASCO instrument, Model J-815-150S. Experiments were performed by purging dry N_2 gas continuously at 15 L min^{-1} during data acquisition. Data were collected in a quartz cuvette with a path length of 1 mm between 200 and 400 nm.

Rheological Study:

Measurements were performed using Rheometer MCR 102 (Anton Paar) equipped with stainless steel parallel plates (20 mm diameter, 1.0 mm gap). Experiments were carried out on freshly prepared **MG-Li** and **MG-GL** metallogel (2% w/v). Linear viscoelastic regions of the metallogel samples were determined by measuring the storage modulus, G' (associated with energy storage) and the loss modulus, G" (associated with the loss of energy) as a function of stress amplitude at constant angular frequency 10 rad/sec. Dynamic oscillatory frequency sweep was conducted at 25 °C (20 min and from 0.1 to 100 rad/sec.) at a constant shear strain of 0.5%. Dynamic temperature ramp experiment was conducted within the temperature range of 25 to 130 °C at a constant frequency of 10 rad/sec and strain of 0.5%.

Conductance Study:

Electrochemical impedance measurements (EIS) were carried out on a CH instruments CHI604E Electrochemical Workstation within the frequency range 10^6 Hz to 10 Hz at a small perturbation voltage of 10 mV. All impedance measurements were conducted at room temperature. The electrochemical measurements were performed in a cylindrical electrochemical cell with three electrodes system, *viz* Ag/AgCl reference electrode, platinum wire counter electrode and glassy carbon working electrode as shown in **figure S1**. The Nyquist plots were fitted with a suitable electrical circuit model with the help of an inbuilt software provided by CH instruments.

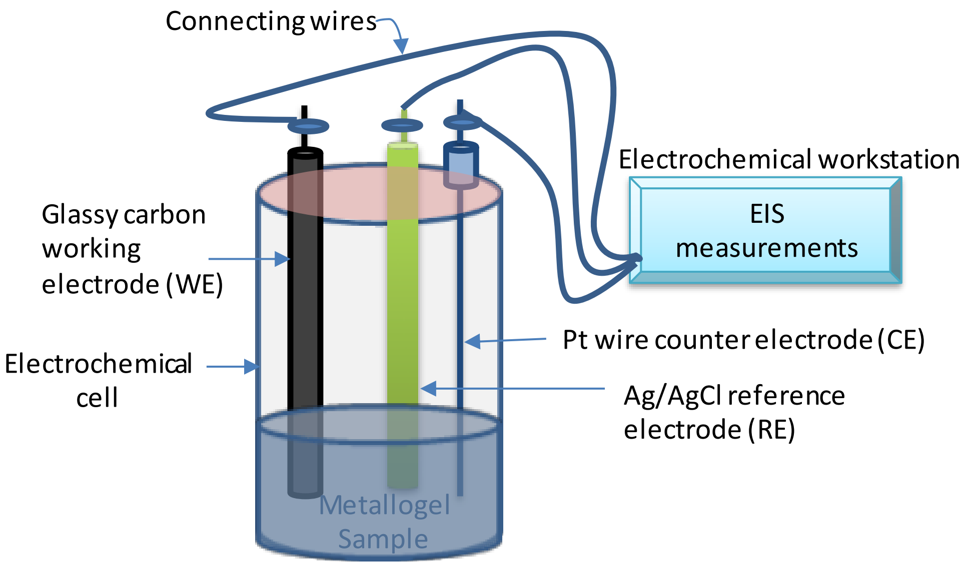


Figure S1. Diagram for complete Electrochemical impedance spectroscopic (EIS) measurements setup

Synthesis and Characterization:

(((1E,1'E)- (((2R,3R)-2,3-dihydroxysuccinyl) *bis*(hydrazin-2-yl-1-ylidene)) *bis*(methaneylylidene)) *bis* (4,1-phenylene)) diboronic acid (*p*-H_6BAL):

Catalytic amount of conc. sulphuric acid was added to a stirring solution of L-tartaric acid (1.00 g, 6.60 mmol) in methanol (30 mL). The solution was refluxed for 15 hours with mild heating (60 ºC), the reaction produced methyl tartarate as a clear oil with fruit like smell. Hydrazine hydrate (0.80 g, 16.00 mmol) was added drop wise to methanolic solution of as obtained methyl tartarate with continuous stirring at room temperature and the resulting solution was refluxed for 5 hours. Upon slow cooling, the reaction mixture afforded the white crystals of L-tartaric dihydrazide which were separated by filtration, washed with diethylether and dried under vacuum. Further, the ethanolic solution of 4-formylphenylboronic acid (0.339 g, 2.262 mmol) was added dropwise to suspension of L-tartaric dihydrazide (0.500 g, 1.131 mmol) in ethanol and stirred for 10-15 min at room temperature. Further, the resulting suspension was refluxed for 6 hours at 80°C to complete the reaction. It afforded white colored solid compound which was washed with ethanol, water and quick wash with methanol and dried in vacuum. Yield 0.580 g (69%). Anal. Calc. for Anal. Calc. for $C_{18}H_{20}B_2N_4O_8$: C, 48.85; H, 4.56; N, 12.67. Found C, 48.76; H, 4.59; N, 12.71. ^{1}H NMR (DMSO-d_6, 400 MHz, δ_H, ppm) 4.57 (d, 2H,CH), 6.03 – 5.91 (s, 2H, OH), 7.75 -7.64 (d, 4H, Ar), 7.94 - 7.84(d, 4H, Ar), 8.20 (br. s, 4H, $B(OH)_2$), 8.60 (s, 2H, =CH) and 11.28 (s, 2H,-NH). ESI-MS: $[M]^+$, 443.20 (*calcd*. 443.20).

(((1E,1'E)- (((2R,3R)-2,3-dihydroxysuccinyl) *bis*(hydrazin-2-yl-1-ylidene)) *bis*(methaneylylidene)) *bis* (2,1-phenylene)) diboronic acid (*o*-H_6BAL):

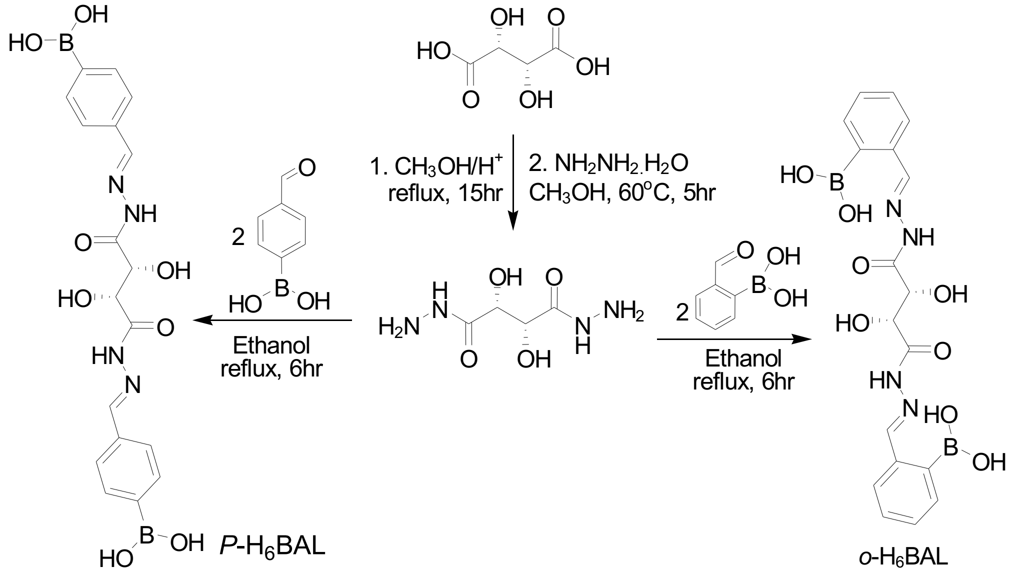
Ethanolic solution of 2-formylphenylboronic acid (0.339 g, 2.262 mmol) was added dropwise to suspension of L-tartaric dihydride (0.500 g, 1.131 mmol) in ethanol and stirred for 10-15 min at room temperature. Further, the resulting suspension was refluxed for 5-6 hours at 80°C to complete the reaction. It afforded white colored solid compound which was washed with ethanol, water and quick wash with methanol and dried in vacuum. Yield 0.560g (66%). Anal. Calc. for $C_{18}H_{20}B_2N_4O_8$: C, 48.91; H, 4.56; N, 12.68. Found C, 48.82; H, 4.62; N, 12.64. ^{1}H NMR (400 MHz, DMSO-*d*$_6$, δ_H, ppm): 12.28 (s, 2H, -NH), 8.62 (s, 4H, $B(OH)_2$) 8.20 (s, 2H, =CH), 7.39 (d, 2H, Ar), 7.06 (t, 2H, Ar), 6.54 (d, 2H, Ar), 6.46 (t, 2H, Ar), 4.32 (s, 2H,-CH). ESI-MS: $[M]^+$, 443.20 (*calcd*. 443.20).

Synthesis of metallogel (MG-Li):

p-**H_6BAL** (0.020 g, 0.0045 mol) was dissolved in DMSO (0.3 mL) in round bottom flask at constant stirring which lead to clear solution. The freshly prepared $LiOH.H_2O$ solution (0.0011 g, 0.0271 mol) in DMSO (0.7mL) was added drop wise to above stirring mixture and obtained a clear solution. The solution was transferred into vial and kept the undisturbed position for 15 min. The white color metallogel formation was confirmed by inverted vial method. Anal. Calc. for $[(C_{18}H_{14}B_2N_4O_8Li_6)].CH_3OH$: C, 44.69; H, 3.55; N, 10.98. Found C, 44.51; H, 3.67; N, 10.94. ESI-MS: $[C_{18}H_{15}B_2N_4O_8Li_6CH_3OH]^+$, 511.30 (*calcd*. 511.30).

Metallogel to metallogel (MG-GL) transition:

D-(+)- glucose (0.016 g ,0.0090 mol) dissolved in DMSO (0.01 mL) was added to above **MG-L** metallogel, in turn, the white colored metallogel completely converted into red color metallogel (**MG-GL**) within 3 hours. Anal. Calc. for $C_{30}H_{31}B_2N_4O_{16}Li_3$: C, 48.30; H, 4.19; N, 7.51. Found C, 48.23; H, 4.27; N, 7.54. ESI-MS: $[C_{30}H_{32}B_2N_4O_{16}Li_3]^+$, 747.2 (*calcd*. 747.2).



Scheme S1. Synthetic route adopted for the synthesis of ***p*-H_6BAL** and ***o*-H_6BAL**.

Table S1. Gelation tests with respect to isomers, LiOH and solvents

S. N.	**Solvent**	***p*-H_6BAL+LiOH**	***o*-H_6BAL+LiOH**
1.	Water	S	S
2.	Acetonitrile	S	S
3.	Methanol	S	S
4.	Ethanol	S	S
5.	DMF	S	S
6.	DMSO	**G**	S
7.	Acetone	S	S
8.	Chloroform	S	S
9.	DCM	S	S
10.	THF	S	S

Where, S= solution, G= gel

Table S2: Gel or sol formation of ***p*-H_6BAL** (1) with different alkali bases

Solvent	**1 + LiOH**	**1 + NaOH**	**1 + KOH**	**1 + CsOH**
DMSO	G	GP	GP	S

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

Table S3: Gelation time of ***p*-H$_6$BAL** (1) at different %w/v with LiOH

S.N.	% w/v	Nature	Gelation time
1	0.5	Sol	N/A
2	1	Sol	N/A
3	1.5	Gelatinous sol	72 hr
4	2	Gel	5 min

Table S4: Gel or sol formation of ***p*-H$_6$BAL** with varying amounts of LiOH

p-H$_6$BAL	LiOH (Equivalents)	MG-Li
20 mg	4	Solution
20 mg	6	Gel
20 mg	8	Gel (less transparent)

Table S5: Gel properties of **MG-Li** upon addition of lower and higher amounts of D-(+)- Glucose

MG-Li	D-(+)- Glucose (Equivalents)	MG-GL
MG-Li	1	No effect
MG-Li	2	Gel (Red color)
MG-Li	6	Solution (Dark red color)

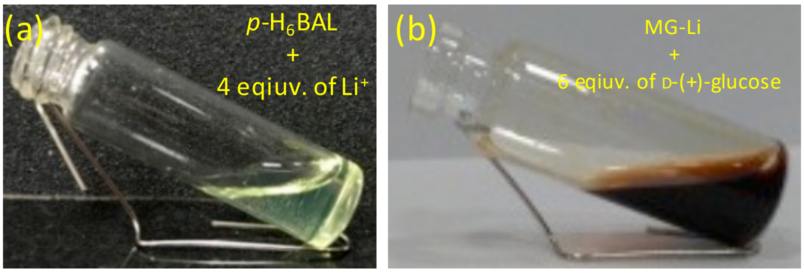


Figure S2: Gel properties upon addition of (a) 4 equiv. of LiOH to ***p*-H$_6$BAL** (b) 6 equiv. of D-(+)- Glucose to **MG-Li**

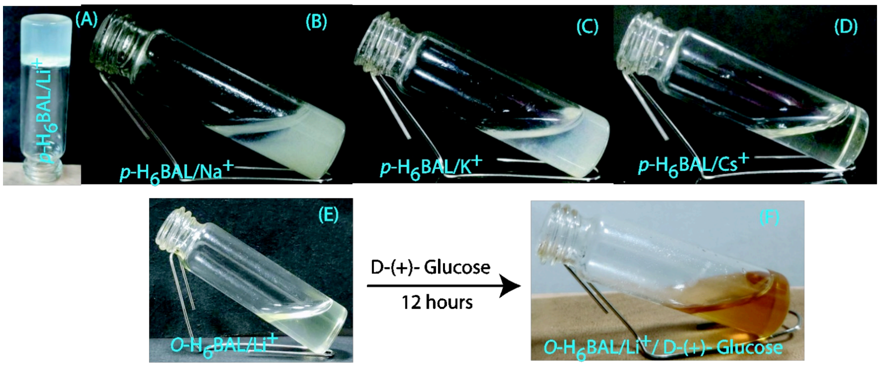


Figure S3. Picture represents the gelation ability of ***p*-H$_6$BAL** with (A) LiOH, (B) NaOH, (C) KOH, (D) CsOH, (E) ***o*-H$_6$BAL** with LiOH and (F) ***o*-H$_6$BAL**/Li$^+$ adduct in presence of D-(+)-glucose.

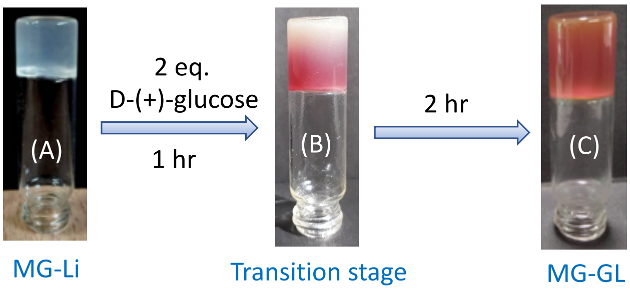


Figure S4. Pictures represent the metallogel to metallogel transition from **MG-Li** (white gel) to **MG-GL** (red gel) in presence of 2 equivalents of D-(+)-glucose.

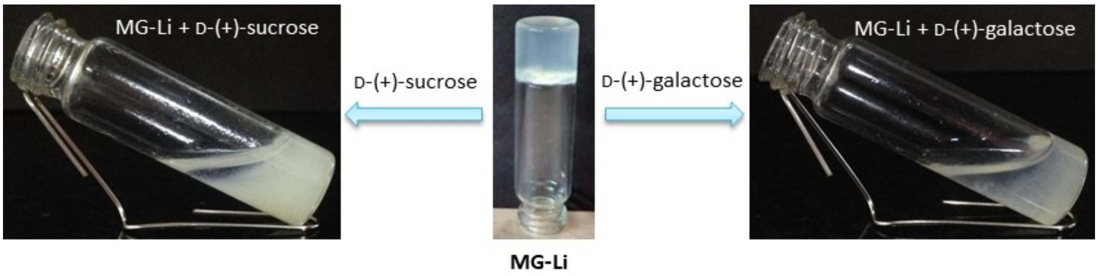
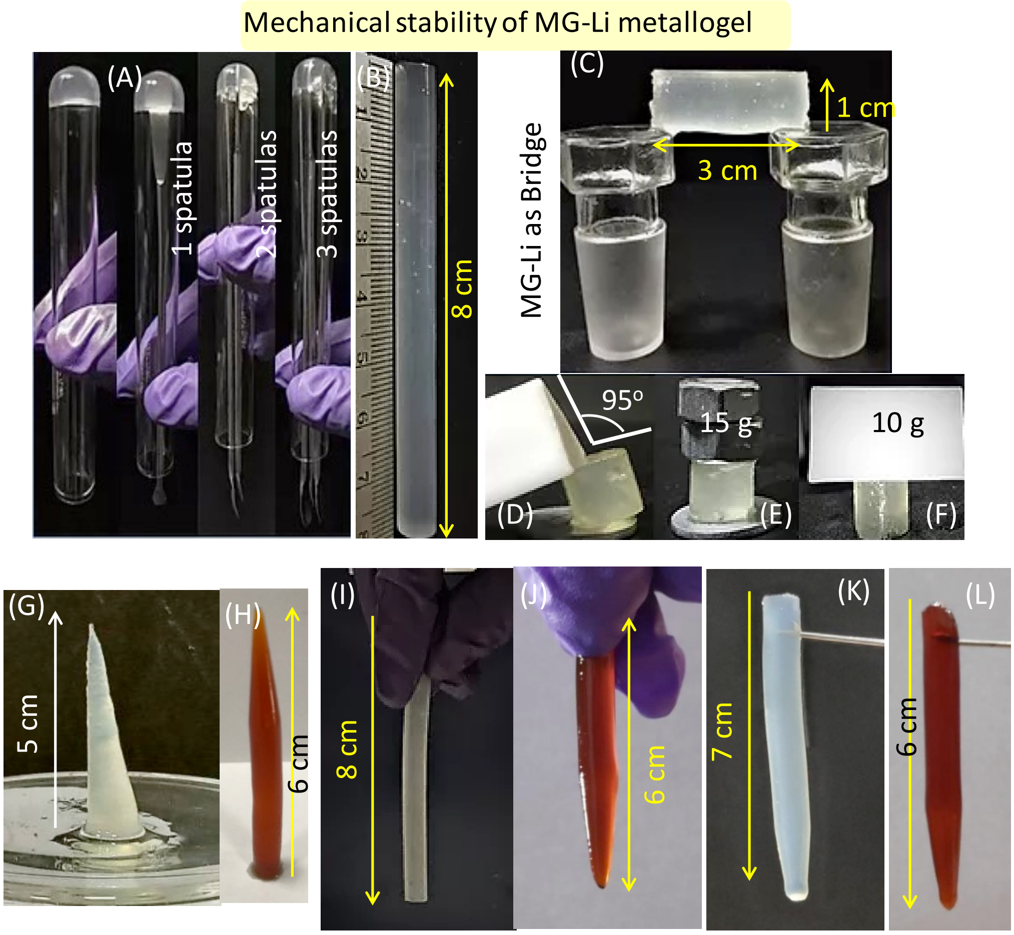


Figure S5: Pictures showing sol formation upon addition of D-(+)-sucrose (left) and D-(+)-galactose (right) to **MG-Li**.



Molded in cone shape

Hanged up in air

Figure S6: Properties of **MG-Li** (A) Bottom-up spatula load holding, (B) Molded in fine cylindrical shape up to 8 cm length, (C) gel bridge, (D-F) Load bearing, (G-H) **MG-Li** (white) and **MG-GL** (red) molded in cone shape. (I-L) the molded **MG-Li** (White) and **MG-GL** (Red) suspended in air with the help of fingers and pin.

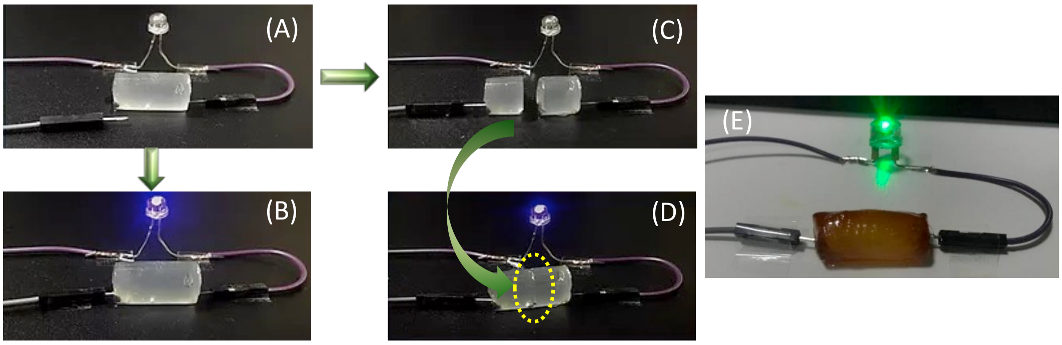


Figure S7: LED Lightening experiment to demonstrate conductance propeties: (A-B) Off-On phenomenon before and after connecting the wire to the **MG-Li gel** block, (C-D) lightening of LED after attaching the gel block, (E) Lightening the LED upon completion of electrical circuit through **MG-GL** gel block.

Note: Metallogels were used to complete an electrical circuit consisting of an LED and a DC voltage source. When the circuit was completed through metallogel piece the LED turned ON and when metallogel was cut into two pieces or wire was detached from the gel, the LED turned OFF.

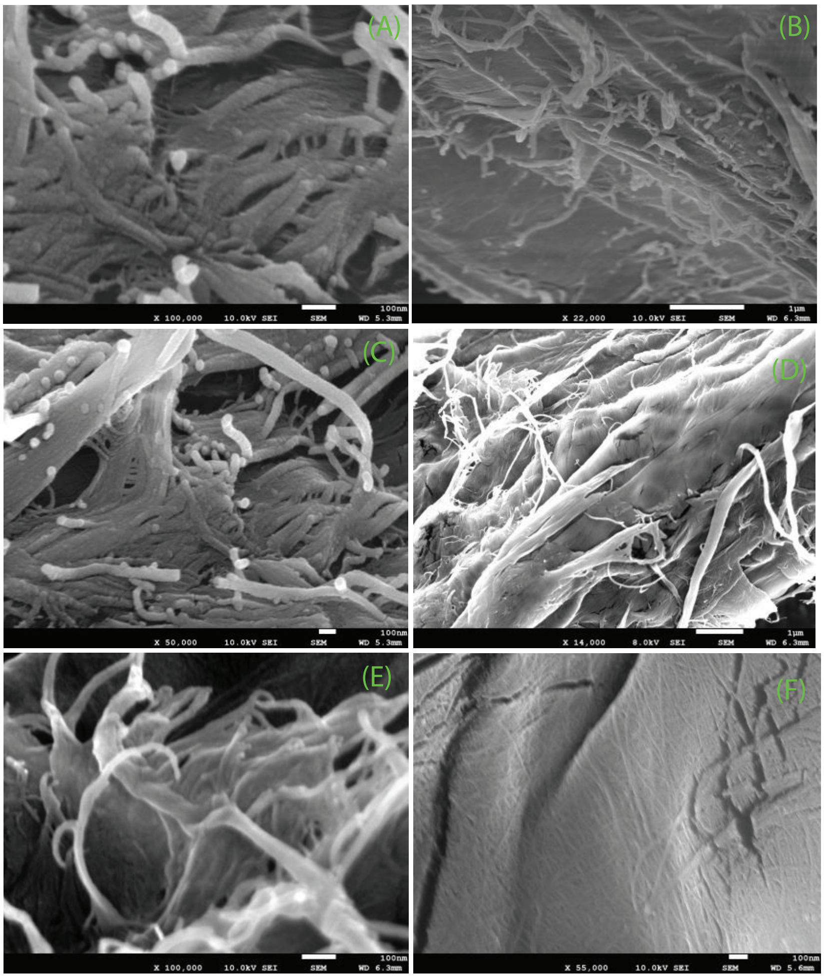


Figure S8: FE-SEM images (A–C) of **MG-Li** with average fibres diameter ~50 nm, and (D-F) showed **MG-GL** with average fibres diameter of ~20 nm.

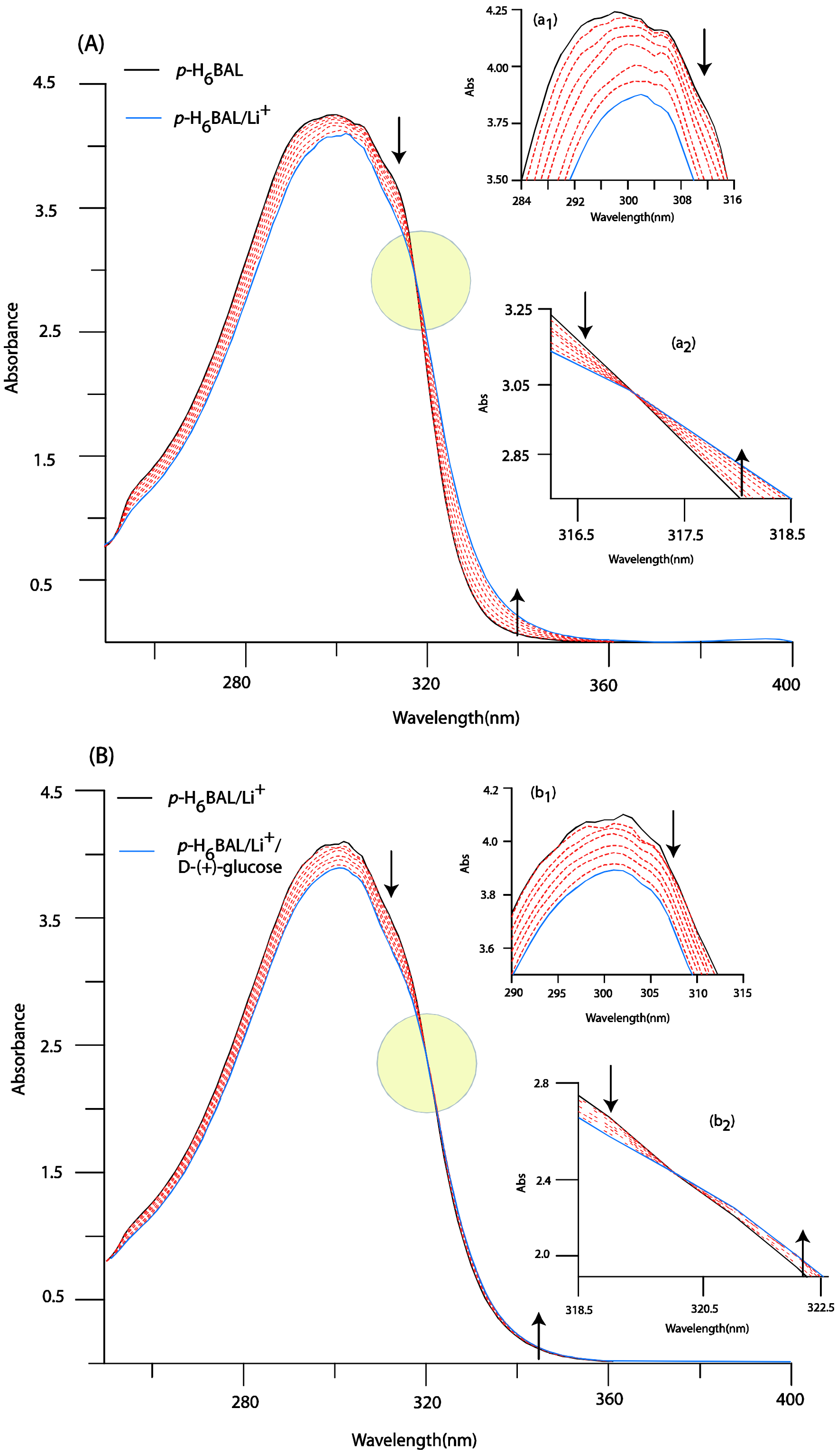


Figure S9: UV-vis titration of *p*-H$_6$BAL (1x10^{-4} M, DMSO) with (A) LiOH (1x10^{-2} M, DMSO) and (B) *p*-H$_6$BAL/Li$^+$ with D-(+)-glucose (1x10^{-2} M, DMSO). Insets (a$_1$), (b$_1$) the magnified view of the peaks and (a$_2$), (b$_2$) show the clear isosbestic point in each case.

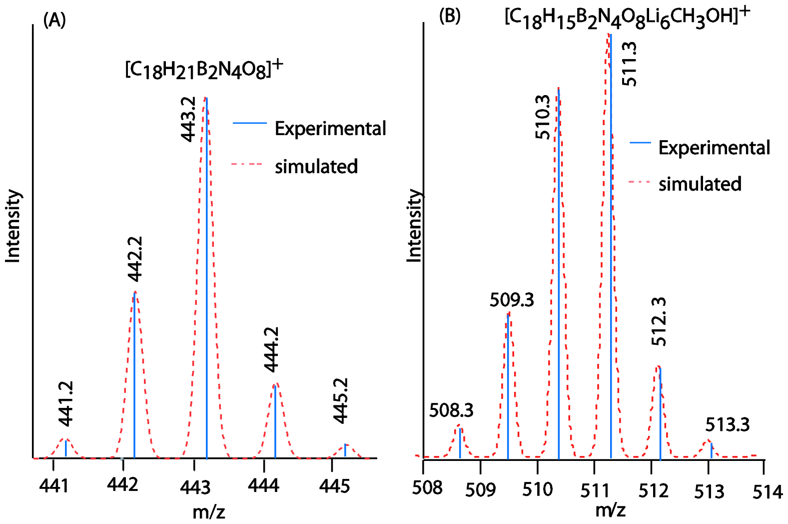


Figure S10: ESI-MS spectra: Isotopic abundance pattern for (A) ***p*-H$_6$BAL**, (B) diluted **MG-Li** and (C) diluted **MG-GL.** The simulated (red dotted line) and experimental (blue line) matches nicely with each other.

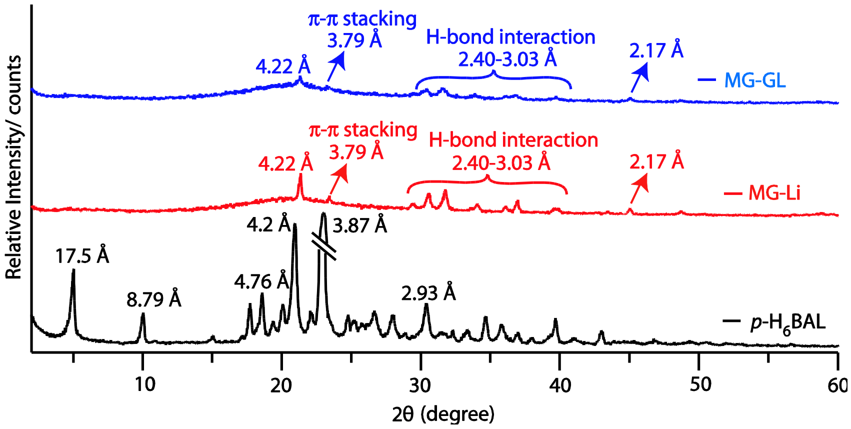


Figure S11: PXRD spectra of ***p*-H$_6$BAL** (black line), **MG-Li** (red line), **MG-GL** (blue line). The ***p*-H$_6$BAL** shows intense peaks at 2θ = 5.04°, 10.04°, 18.6°, 20.96°, 22.92° and 30.38° which indicates the crystalline nature of *p*-H$_6$BAL. Further, upon addition of LiOH to ***p*-H$_6$BAL** *i.e.* **MG-Li**, all intense peaks were disappeared except few small and broad peak at 2*θ* = 20°, 23.48°, 29°-41° which suggested the amorphous nature and presence of π–π stacking as well as H-bonding interactions in metallogel.[3] Further, in the case of xerogel obtained from **MG-GL** shows similar PXRD pattern to **MG-Li** suggests the presence of similar type of molecular packing in **MG-GL**.

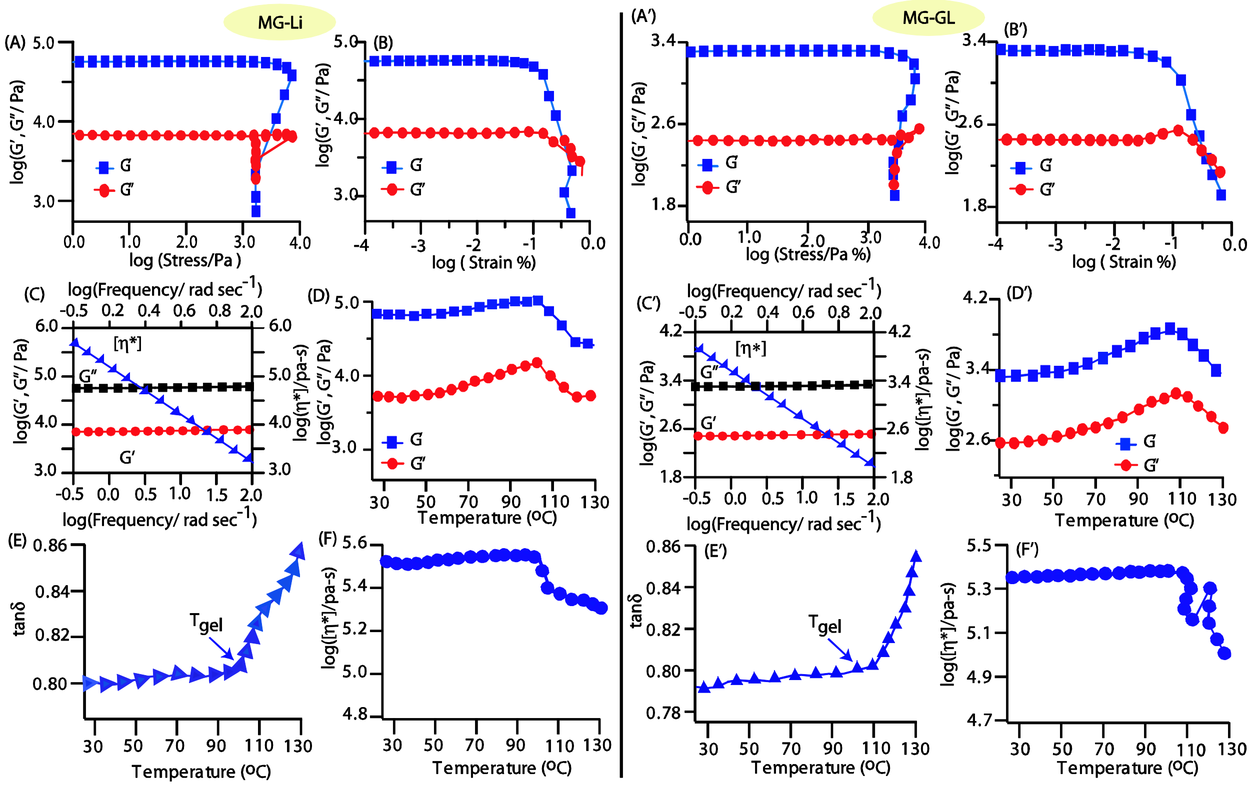


Figure S12: Oscillatory Amplitude sweep of G' and G" at frequency of 10 rad s^{-1} and temperature at 25 ^{0}C for **MG-Li** (A to D) and **MG-GL** (A' and D'). Dynamic frequency sweep (0.1-100 rad s^{-1}, constant shear strain 0.5%) measurement for **MG-Li** (C) and **MG-GL** (C'). Dynamic temperature ramp of G' and G" at a heating rate of 5°C min^{-1}, strain of 0.5 % and frequency of 10 rad s^{-1} for **MG-Li** (D) and **MG-GL** (D'), Dynamic temperature ramp of the loss tangent (tanδ = G"/G') plot at 5 °C min^{-1} with no phase transition temperature (T_{gel}) up to 100 °C for **MG-Li** (E) and **MG-GL** (E') which was further supported by complex viscosity *vs.* temperature plot of **MG-Li** (F) and **MG-GL** (F').

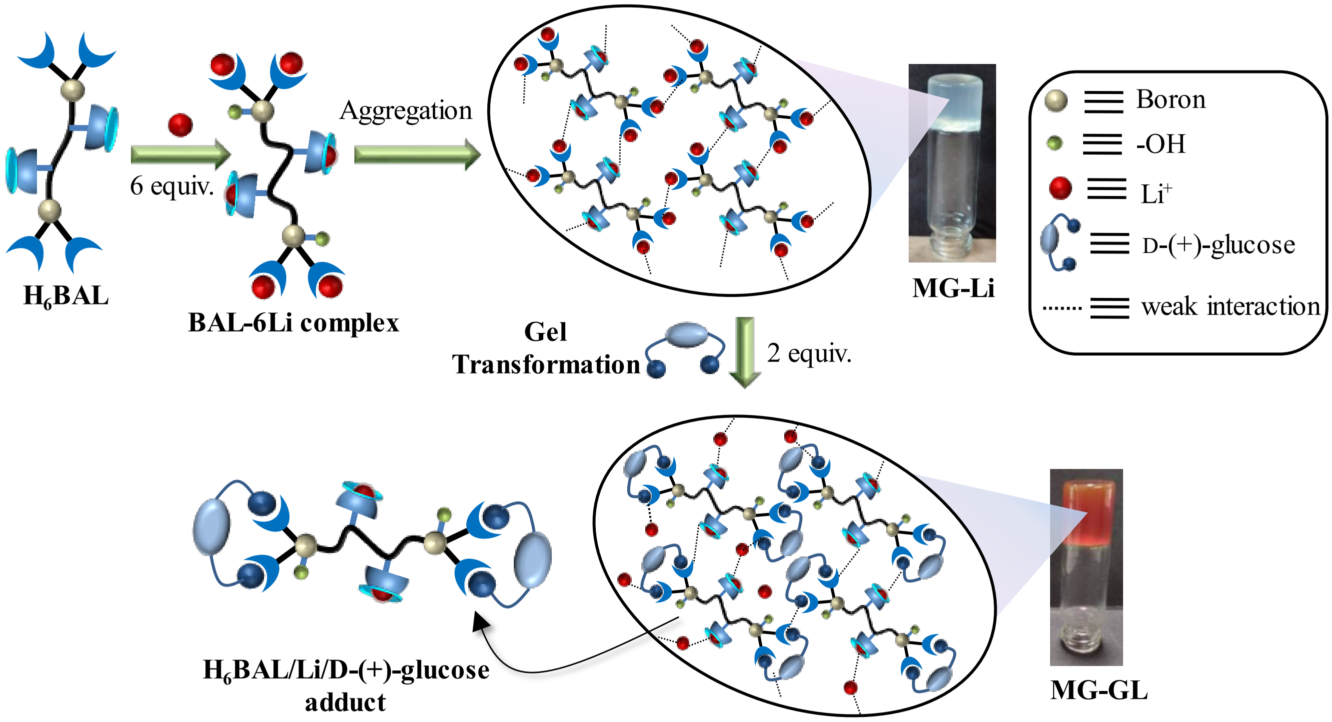


Figure S13: Pictorial presentation for the mechanic steps involved in the metallogel formation and metallogel to metallogel transformation by triggered with D-(+)-glucose.

References

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

[2] M. K. Dixit, V. K. Pandey and M. Dubey, *Soft Matter,* 2016, **12**, 3622.

[3] a) X. Wang, T. He, L. Yang, H. Wu, R. Zhang, Z. Zhang, R. Shen, J. Xiang, Y. Zhang and C. Wei, *Nanoscale,* 2016, **8**, 6479; b) M. K. Dixit, C. Mahendar and M. Dubey, *Chem. Asian J.* 10. 1002/asia.201900559; c) M. K. Dixit and M. Dubey, *Phys. Chem. Chem. Phys.,* 2018, **20**, 23762.