Electronic Supplementary Information

D-(+)-glucose triggered selective hydrometallogelation in a C_3-symmetric gelator

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Materials and Physical Methods:

Methanol was purchased from Avantor performance material India Limited, Maharashtra (India). DMSO, Ethanol was obtained from Qualikems Fine Chem Pvt. Ltd., Vadodara (India). Glacial acetic acid was obtained from Sigma Aldrich. Lithium hydroxide was purchased from Spectrochem Pvt. Ltd., Mumbai (India). Hydrazine hydrate (80%) and Trimethyl-1,3,5-benzenetricarboxylate were purchased from Sigma Aldrich. 4-formylphenylbrnicacid was acquired from TCI Chemicals (India) Pvt. Ltd. Chennai (India). All the reagents were used exempting any further purification.

^{1}H NMR spectra were obtained on a Bruker AVANCE III 500 Ascend Bruker Bio Spin International AG spectrometer. UV-vis study was done on UV2600 Schimazdu spectrophotometer. All the CD spectra were obtained from JASCO instrument (Model J-815-150S) and during experiment Dry N_2 gas purging was mandatory (15 L.min-1). The selection for CD data acquisition involved opting for a quartz cuvette with a length of 1 mm, and the data was recorded within the 200-400 nm range. 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. Electrochemical impedance studies were performed on a CH Instrument electrochemical workstation, model No. CHI604E.

Rheological Study:

Freshly prepared metallogels (G1, MBLG-2, MBLG-4, MBLG-5) were subjected to rheological measurements and experiments were performed using Rheometer MCR 102 (Anton Paar) equipped with stainless steel parallel plates (20 mm diameter, 1.0 mm gap). 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. Further, dynamic oscillatory frequency sweep was conducted from 0.1 to 100 rad/sec at 25 °C at a constant shear strain of 0.1%. Dynamic temperature ramp experiment was conducted within the temperature range of 25 °C to 100 °C at a constant frequency of 10 rad/sec and strain of 0.1%.

Conductance Study:

The freshly prepared metallogel samples were analysed through electrochemical impedance spectroscopic measurements (EIS). The experiments took place on a CH Instruments CHI604E Electrochemical Workstation, covering a frequency range from 10^6 Hz to 1 Hz, with a minimal perturbation voltage of 0.01 V. All impedance measurements were conducted at room temperature. Electrochemical measurements were performed using a cylindrical electrochemical cell that was constructed in-house. This cell comprised two stainless steel disc electrodes positioned at a constant separation distance. The Nyquist plots obtained during the experiments were analyzed by fitting them with an appropriate equivalent electrical circuit using the built-in software from CH instruments. The conductivity (σ) of the metallogels was determined using the formula-

$$\sigma = \frac{1}{R} \cdot \frac{d}{A}$$

Where, R represents the resistance of the metallohydrogel, d is the distance between the electrodes, and A is the electrode area.

Stability tests were performed over a 3-hour period at both low frequency (1 Hz) and high frequency (10^5 Hz). The experimental setup included three electrodes: an Ag/AgCl reference electrode, a platinum wire counter electrode, and a glassy carbon working electrode, all arranged in a cylindrical electrochemical cell.

Synthesis and Characterization:

Synthesis of MB:

The precursor 1,3,5-benzenetricarboxylic hydrazide was obtained by using a modified literature procedure.[1-2] Trimethyl 1,3,5- benzenetricarboxylate (1.00 g, 6.60 mmol) and Hydrazine hydrate (1.2 g, 24 mmol) were mixed with methanolic solution (30 mL) in a round bottom flask. The reaction mixture was kept at continuous stirring and reflux condition for the next 12 hours. Afterwards, white precipitate of 1,3,5- benzenetricarboxylic hydrazide was obtained which was separated by filtration, washed several times with adequate amount of methanol, diethylether and dried under vacuum.

Methanolic solution of 4-formylphenylboronicacid (1.082 g, 5.6 mmol) was added dropwise to lukewarm methanolic solution of 1,3,5- benzenetricarboxylic hydrazide (0.500 g, 2.8 mmol) and stirred for 10-15 min. Further, the resulting suspension was then treated with catalytic amount of Glacial acetic acid and the resulting clear solution mixture was refluxed for 2 days at 80^{o}C. Further, the solution was cooled to room temperature with continuous stirring

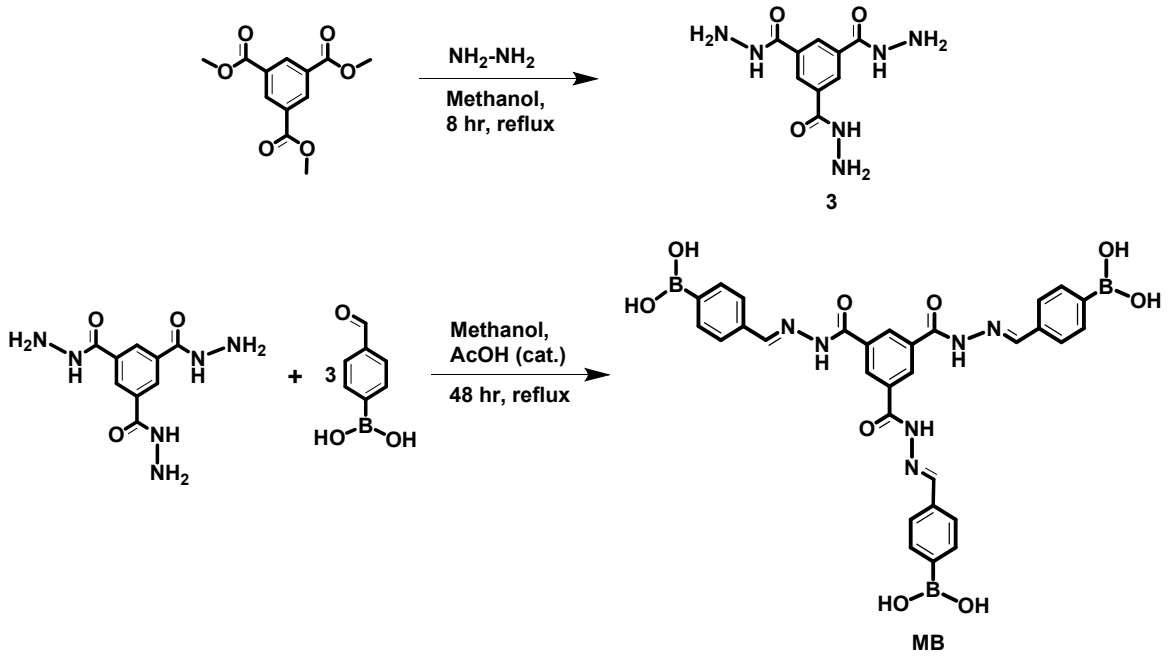
for 12 hours which afforded white coloured solid compound. The product was quickly washed with cold methanol and dried in vacuum afterwards. Yield 1.064 g (72%). ^{1}H NMR (500 MHz, DMSO-d_6, ppm): 7.75 (d, 6H, Ar-H_b), 7.90 (d, 6H, Ar-H_d), 8.19 (s, 6H for B-$(OH)_2$), 8.53 (s, 3H for Ar-H_a), 8.67 (s, 3H, aldimine =CH) and 12.32 (s, 3H, -NH). ESI-MS *m/z*: $[C_{30}H_{27}B_3N_6O_9+Na]^+$, 671.2. (*calcd.* 671.2).

Synthesis of metallogel (MBLG):

The pro-gelator **MB** (20 mg, 0.031 mol) was suspended in 0.5 mL water in a glass vial followed by addition of aqueous LiOH (7.7 mg, 0.185 mol) led to clear solution upon applying sonication. The freshly prepared D-(+)-glucose solution (0.008 g, 0.046 mol, 0.5 mL) in water was added drop wise to the LiOH treated solution of MB gelator and then left as it is at room temperature for 5 minutes to obtain a transparent, robust hydrogel (**MBLG**).

Notably, metallogel (**MBLG-2)** can also be obtained without application of the ultrasound but it takes 4 hours to form robust gel. Similarly, **MBLG-4**, **MBLG-5** were also synthesized in similar fashion.

It is noteworthy that in DMSO, addition of LiOH yielded translucent yellow gel (**G1**) upon a brief sonication (Figure S6, S12 and Table S1, S3, ESI†). However, in a striking contrast to the **MBLG** hydrogel, D-(+)-glucose addition to **G1** resulted in destruction of gel phase (Table S3 ESI†). This indicates the prominent role of solvents in the gelator self-assembly.[3] Moreover, upon visual observation **G1** exhibited comparatively inferior mechanical properties than the **MBLG** (Table S4, ESI†). Hence, we carried all our further investigations using the more mechanically robust gel **MBLG** considering the benefits in device design.



Scheme S1: Synthetic scheme adapted to obtain **MB.**

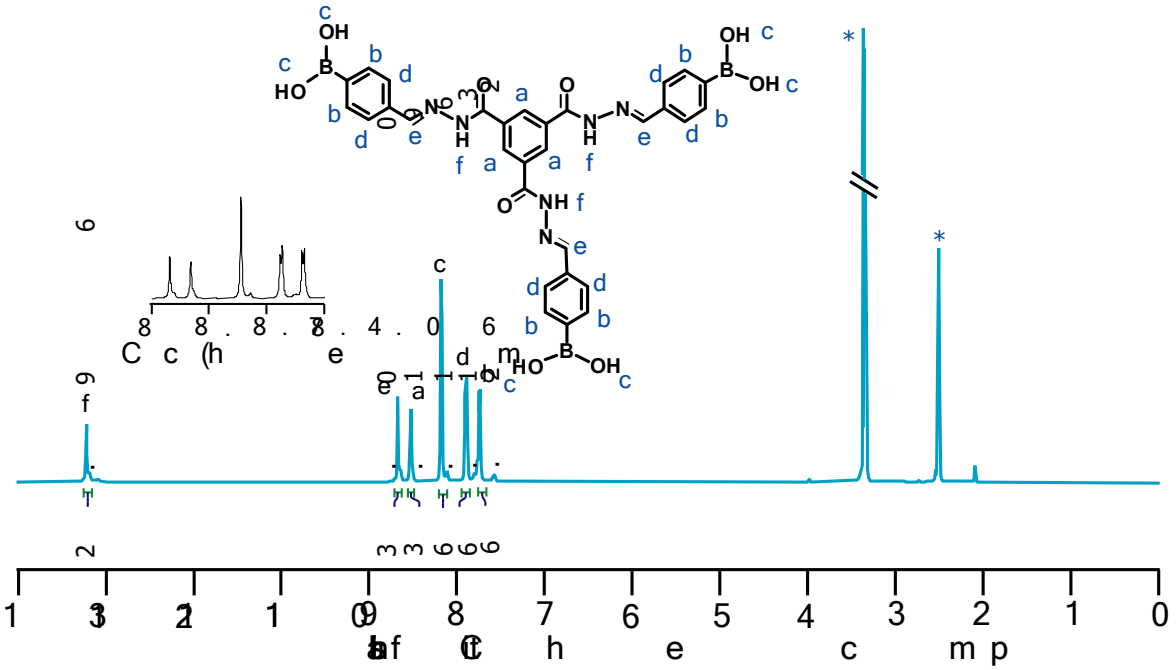


Figure S1: ^{1}H NMR (500 MHz, DMSO-$\mathbf{d_6}$) spectrum of **MB**.

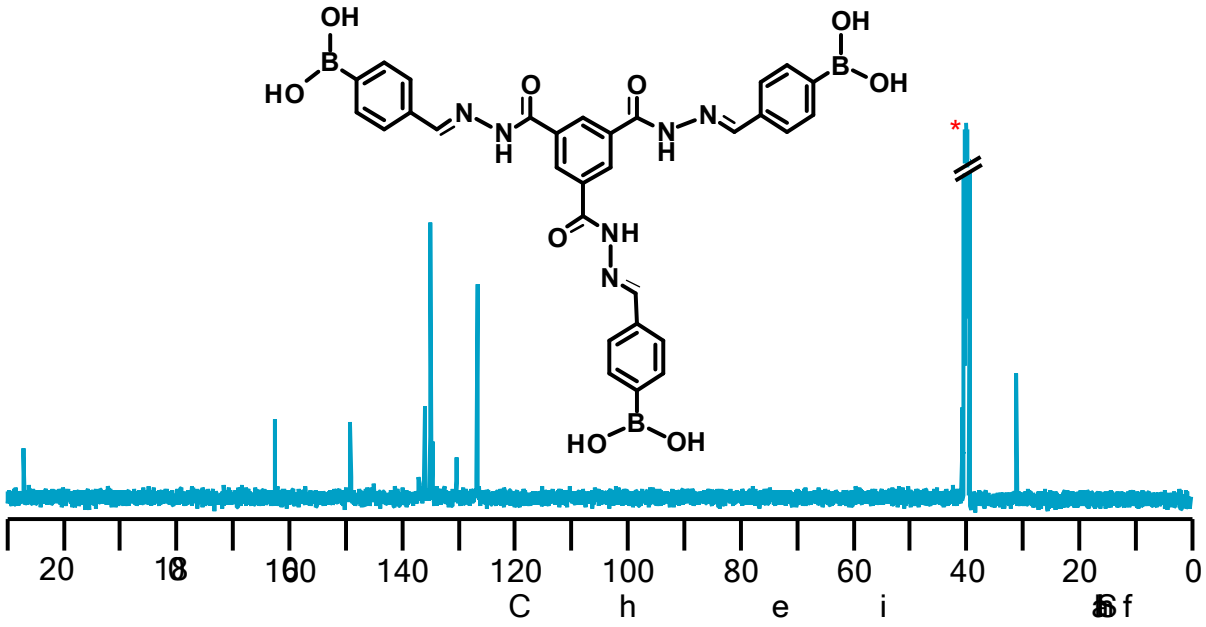


Figure S2: ^{13}C NMR (500 MHz, DMSO-$\mathbf{d_6}$) spectrum of **MB**.

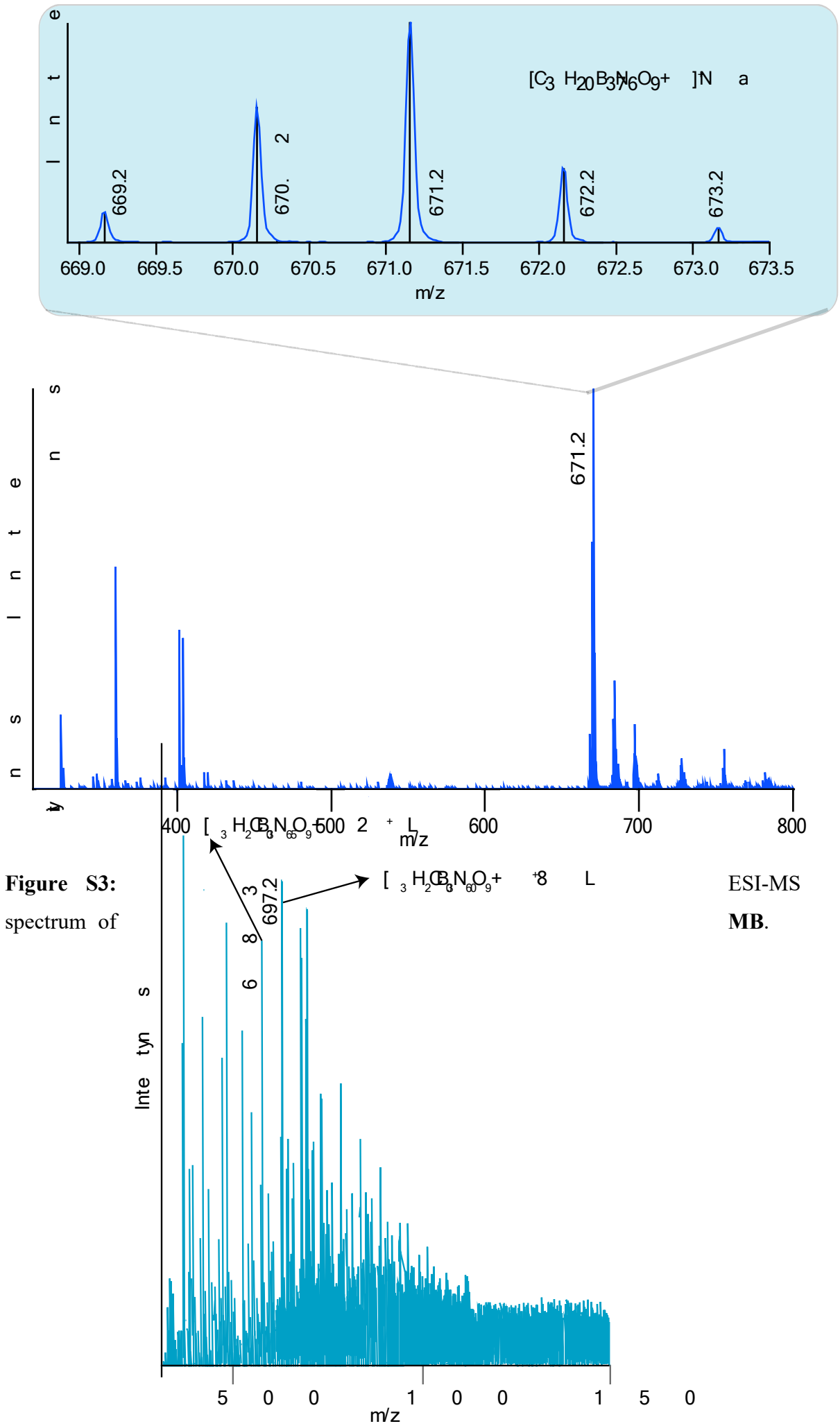


Figure S3: ESI-MS spectrum of **MB**.

Figure S4: ESI-MS spectrum of **MB/LiOH**.

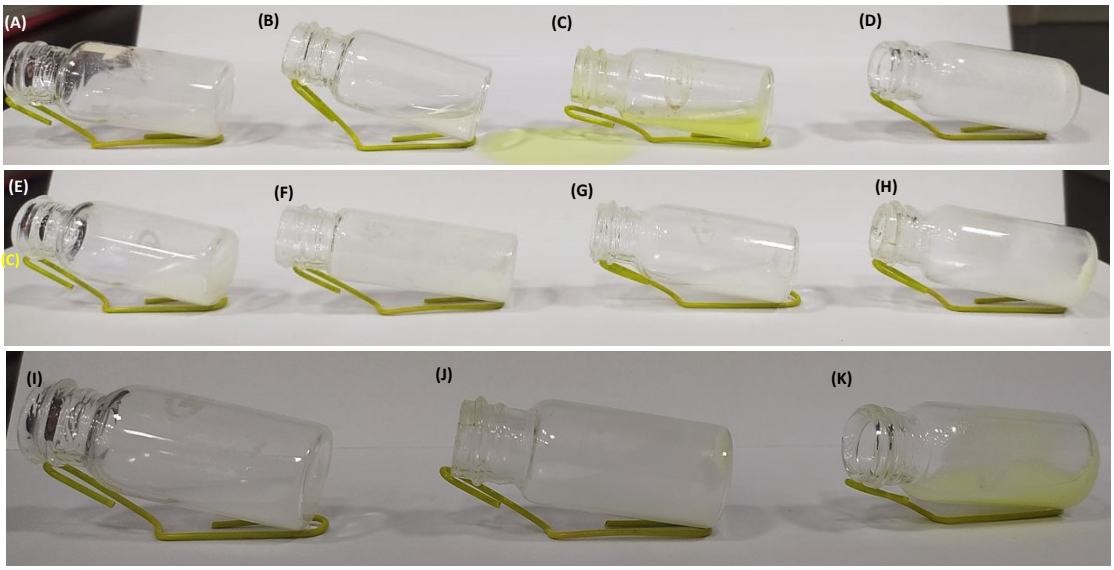


Figure S5: Gelation test of **MB** in presence of LiOH and D-(+)-Glucose in various solvents (A) Acetone, (B) Methanol, (C) Ethanol, (D) Chloroform, (E) DCM, (F) Ammonia solution, (G) Benzene, (H) n-Propanol, (I) n-Butyl alcohol, (J) THF, (K) Toluene.

Table S1: Gelation tests of **MB** (2 wt%) with D-(+)-glucose (1.5 equiv.) in various solvents.

S. No.	**Solvent**	**Solubility of MB**	**Gelation Property (MB + LiOH)**	**Gelation after addition of (D-(+)-glucose)**
1.	Acetone	P	NS	S
2.	Methanol	P	PS	PS
3.	Ethanol	P	PS	PS
4.	Chloroform	P	NS	NS

5.	DCM	P	NS	NS
6.	Ammonia soln.	PS	**S**	**PG**
7.	Benzene	P	NS	NS
8.	n-Propanol	P	NS	NS
9.	n-butyl alcohol	P	NS	NS
10.	THF	P	NS	NS
11	Toluene	P	NS	NS
12.	DMSO	S	**G**	S
13.	DMSO-water	PS	S	**G**
14.	DMF	S	S	S
15.	Water	P	S	**G**

*** P= precipitate, S= solution, PS= partial solution, G= gel**

Table S2: Gelation tests of **MB** (2 wt%) with D-(+)-Glucose (1.5 equiv.) with varying pH values.

pH	MBLG
7	S
8	S
9	S
10	S
11	PG
12	**G**
13	**G**
14	**G**

*** P= precipitate, S= solution, PG partial gel, G= gel**

Table S3: Effect of glucose addition to **MB/LiOH** on the metallogel formation in DMSO and water solvent.

Solvent	MB	LiOH	LiOH + D-(+)-glucose
Water	**2-5 wt%**	**S**	**G**
DMSO	**2-5 wt%**	**G**	**S**

Note: The gel **G1** prepared in DMSO solvent and LiOH, collapses upon treatment with **D-(+)-**glucose. While to prepare **MBLG,** water solvent, LiOH and **D-(+)-** Glucose addition is mandatory condition. *** S= solution, G= gel.**

Table S4: Comparison of mechanical and electronic properties of **G1** (DMSO solvent) and **MBLG** (water solvent).

Material	**log G'**	**Yield strain (%)**	**Yield stress (Pa)**	**$R_1(\Omega)$**	**Conductivity**
G1	3.43	15	136	13000	2.83×10^{-4} S/cm
MBLG-5	4.3	51	5910	41.39	2.67×10^{-2} S/cm

***Note:** The striking change in the properties exemplify the importance of presence of co-gelator D-(+)-glucose and solvent in gel formation.

Table S5. Obtained various parameter values from fitted electrical circuit model along with % error for **MBLG-2, MBLG-4, MBLG-5** and excess LiOH included **MBLG-5** (12 equivalent LiOH).

Gel samples	R_{st} (Ω)	R_{ct} (Ω)	C (in F)	CPE (F. s^n)	R(Ω)	Conductivity (S/cm)	Error (%)
MBLG-2	127.6	1220	1.158×10^{-10}	3.367×10^{-5} , n= 0.5	1347	2.73×10^{-3}	4.95
MBLG-4	2.014	199.9	4.346×10^{-10}	3.085×10^{-4} , n= 0.5	201.91	1.82×10^{-2}	1.04
MBLG-5	7.31	130.5	1.084×10^{-9}	3.291×10^{-4}, n= 0.65	137.50	2.67×10^{-2}	1.28
MBLG-5 (12 eqv. LiOH)	24.0	17.39	2.62×10^{-6}	3.414×10^{-4}, n= 0.7	41.39	8.90×10^{-2}	4.86

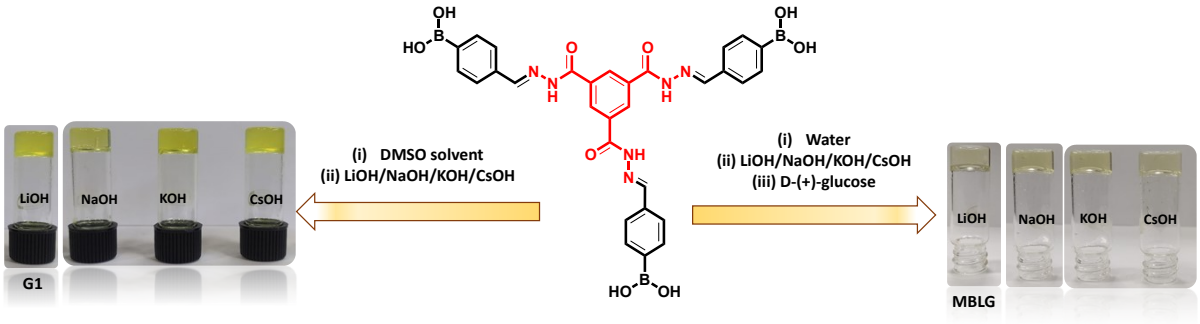


Figure S6: The representation of two separate kind of gel formation processes in DMSO and water solvents from the gelator **MB**, following different gelation protocols as mentioned in Table S3. While the hydrogel (**MBLG**) formation is highly D-(+)-glucose selective, DMSO gel (**G1**) only requires strong alkali bases.

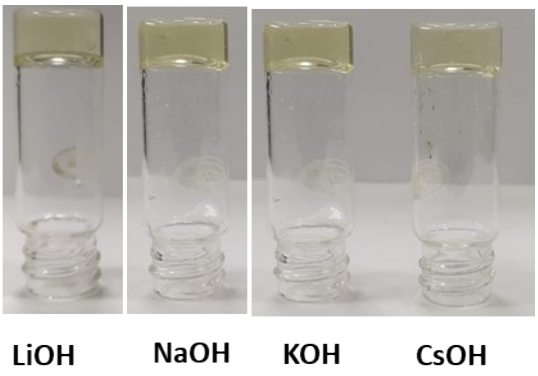


Figure S7: Hydrometallogelation of **MB** gelator (2 wt%) in presence of (i) LiOH, (ii) NaOH, (iii) KOH and (iv) CsOH.

Figure S8: Gelation behaviour of **MB** gelator with varying wt% in presence of 6 equivalent LiOH and 1.5 equivalent D-(+)-glucose. *= CGC of **MB**.

Figure S9: Gelation behaviour of **MB** gelator (2 wt %) with varying equivalence of D-(+)-glucose.

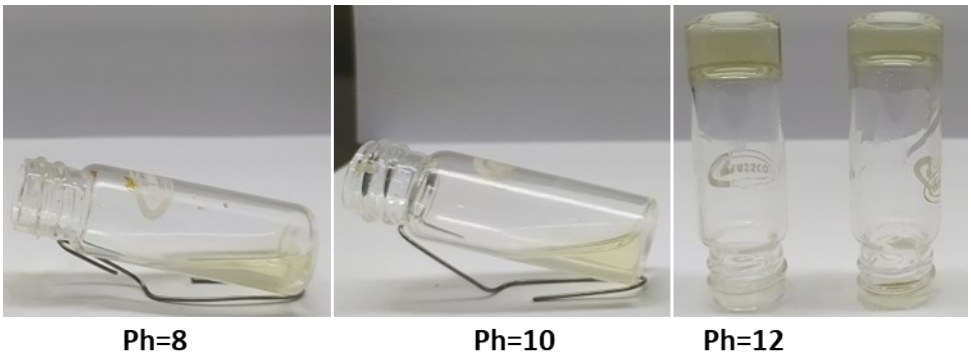


Figure S10: Hydrogel formation from **MB** and D-(+)-Glucose at varying pH, showed that gel forms at pH≥ 12.

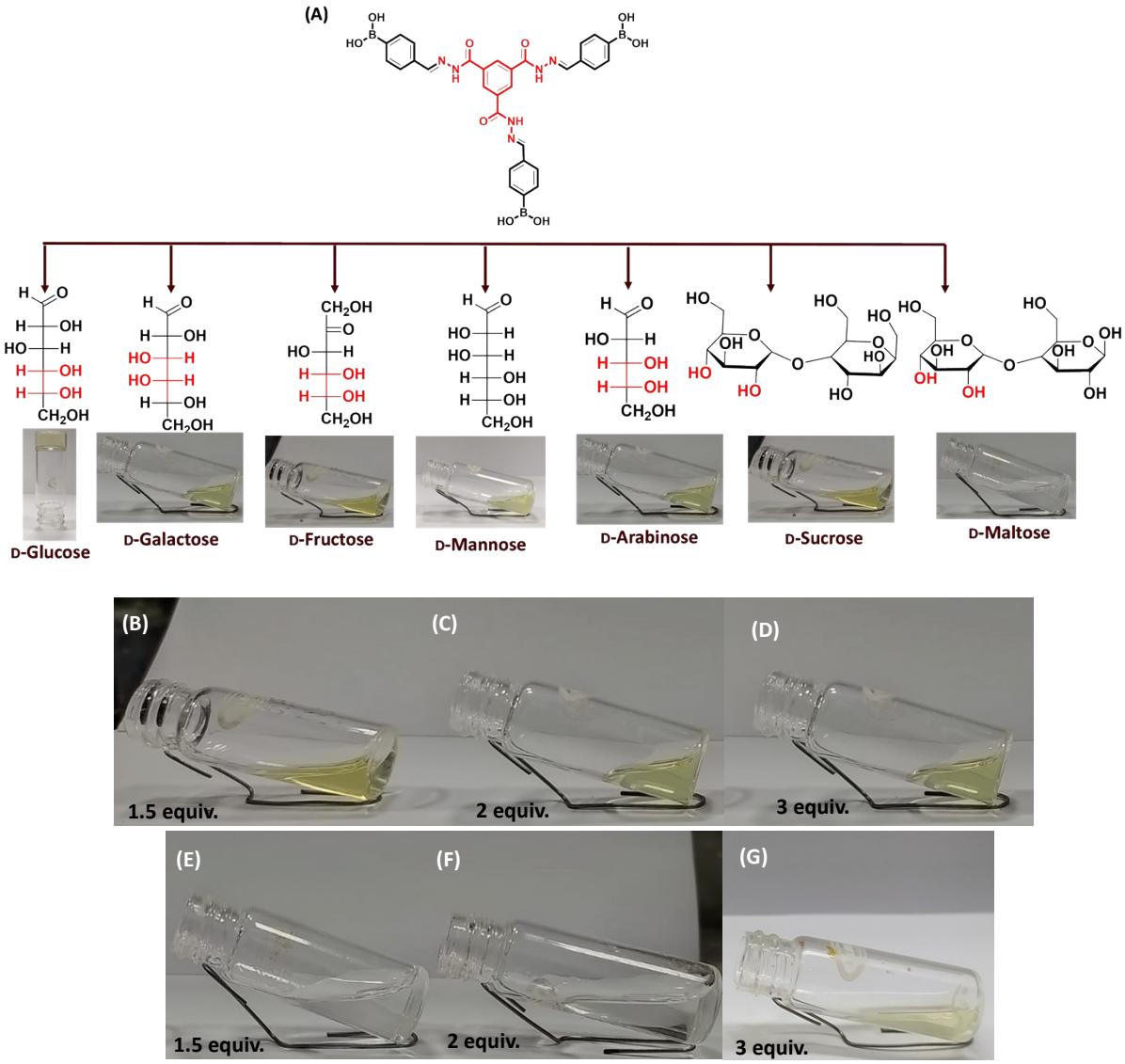


Figure S11: (A) Gelation behaviour of **MB** with varying sugar molecules, showing high selectivity towards D-(+)-glucose, Gelation test of LiOH deprotonated **MB** (2 wt%) by varying the (B-D) Sucrose and (E-G) Maltose concentrations.

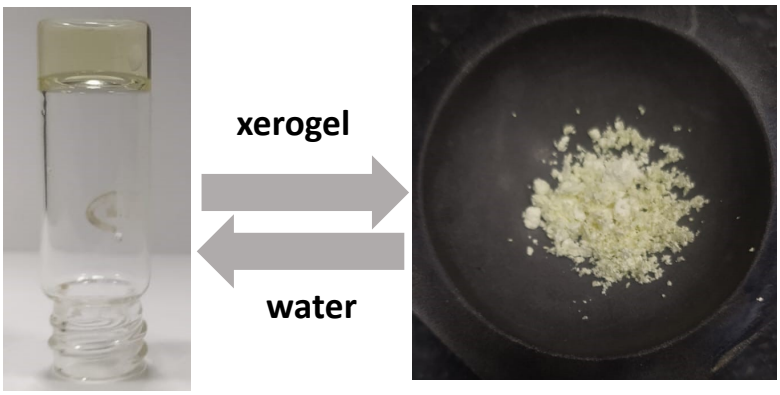


Figure S12: Gel to xerogel to gel regeneration in **MBLG** metallogel.

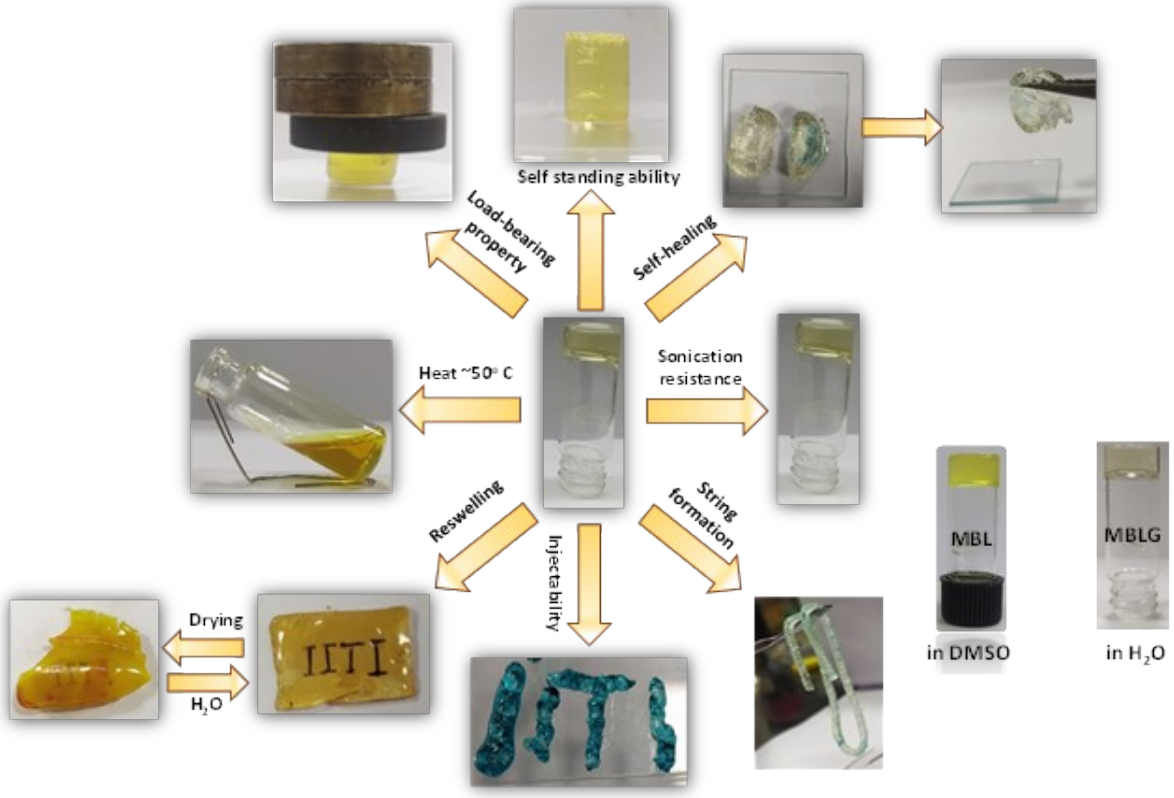


Figure S13: Miscellaneous physical properties exhibited by **MBLG** metallogel.

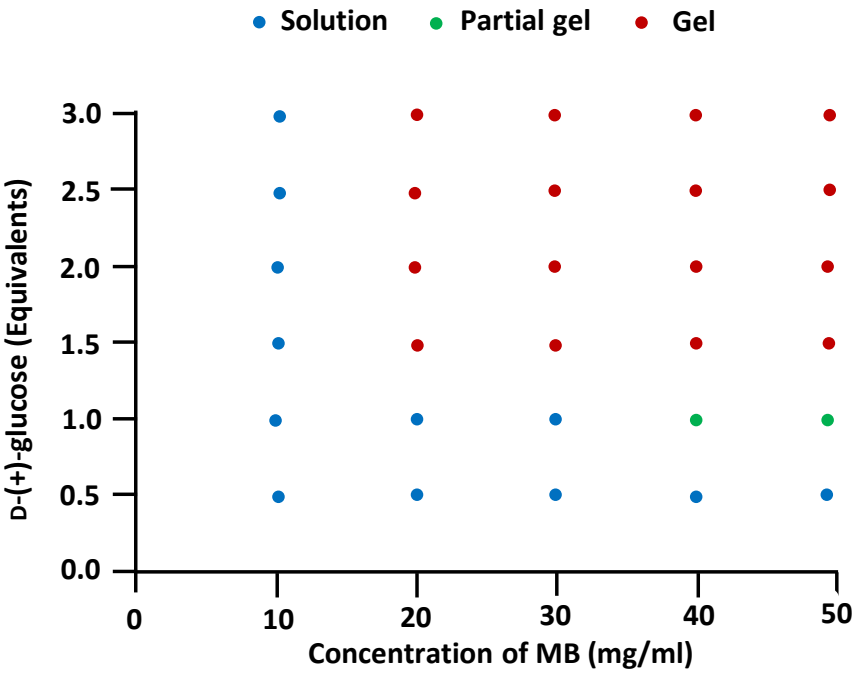


Figure S14: Gelation test chart prepared by varying the weight percentage of both gelator **MB** and D-(+)-glucose.

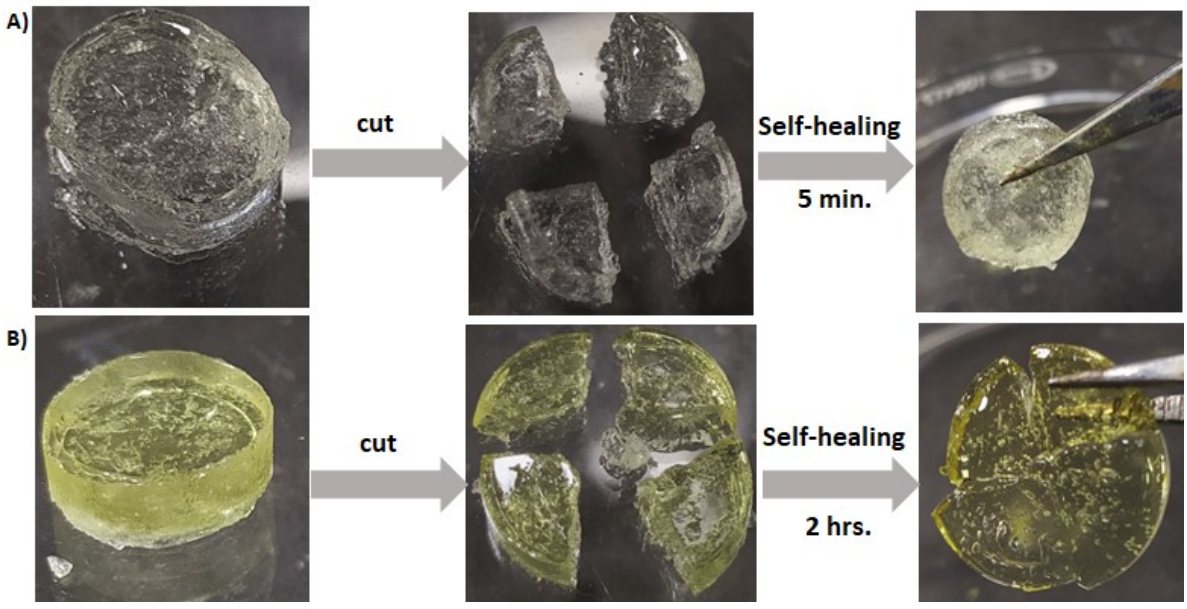


Figure S15: Self-healing behaviour of (A) **MBLG-2** and (B) **MBLG-5**, showing rapid self-healing for low loading of **MB,** while **MBLG-5** needed longer time.

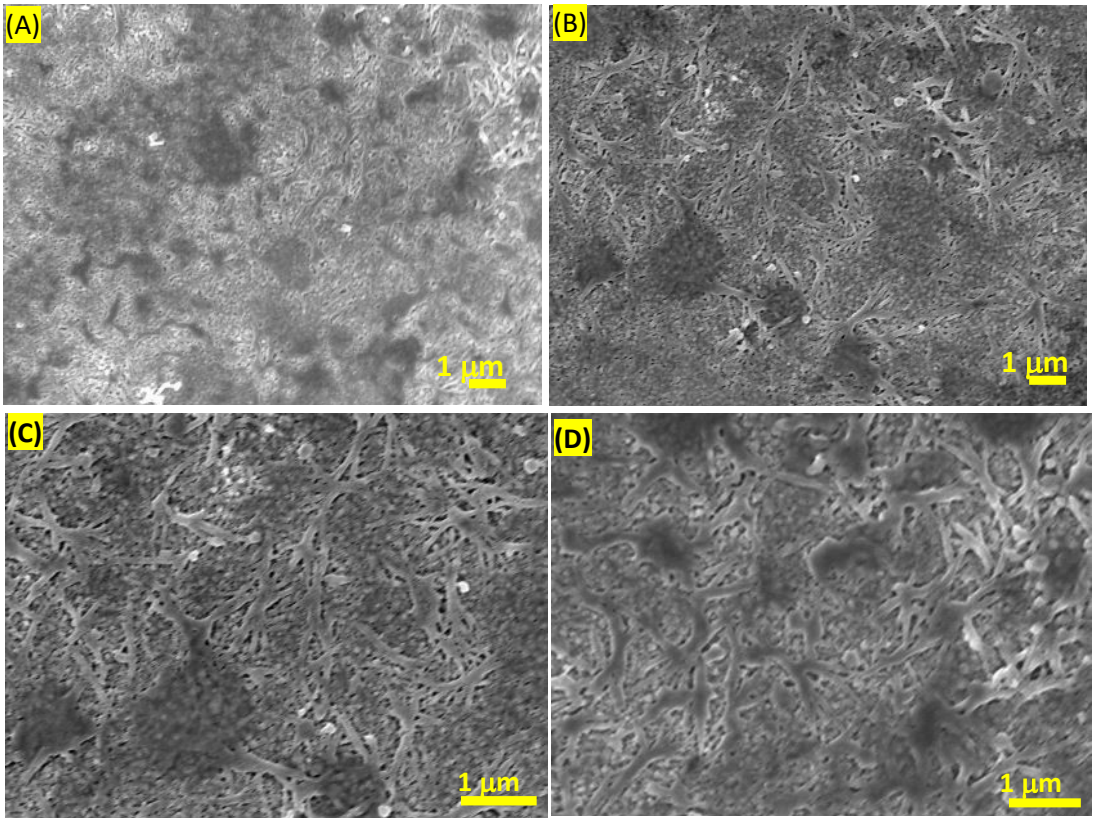


Figure S16: FESEM images of vacuum dried organometallogel **G1**.

Note: As evident from the FE-SEM images, the arrangement of intricate gel fibres of **MBLG** was quite different from the **G1.** The **G1** gel exhibited entangled, long nanofibrous gel milieu with an average fibre diameter of ~40 nm.

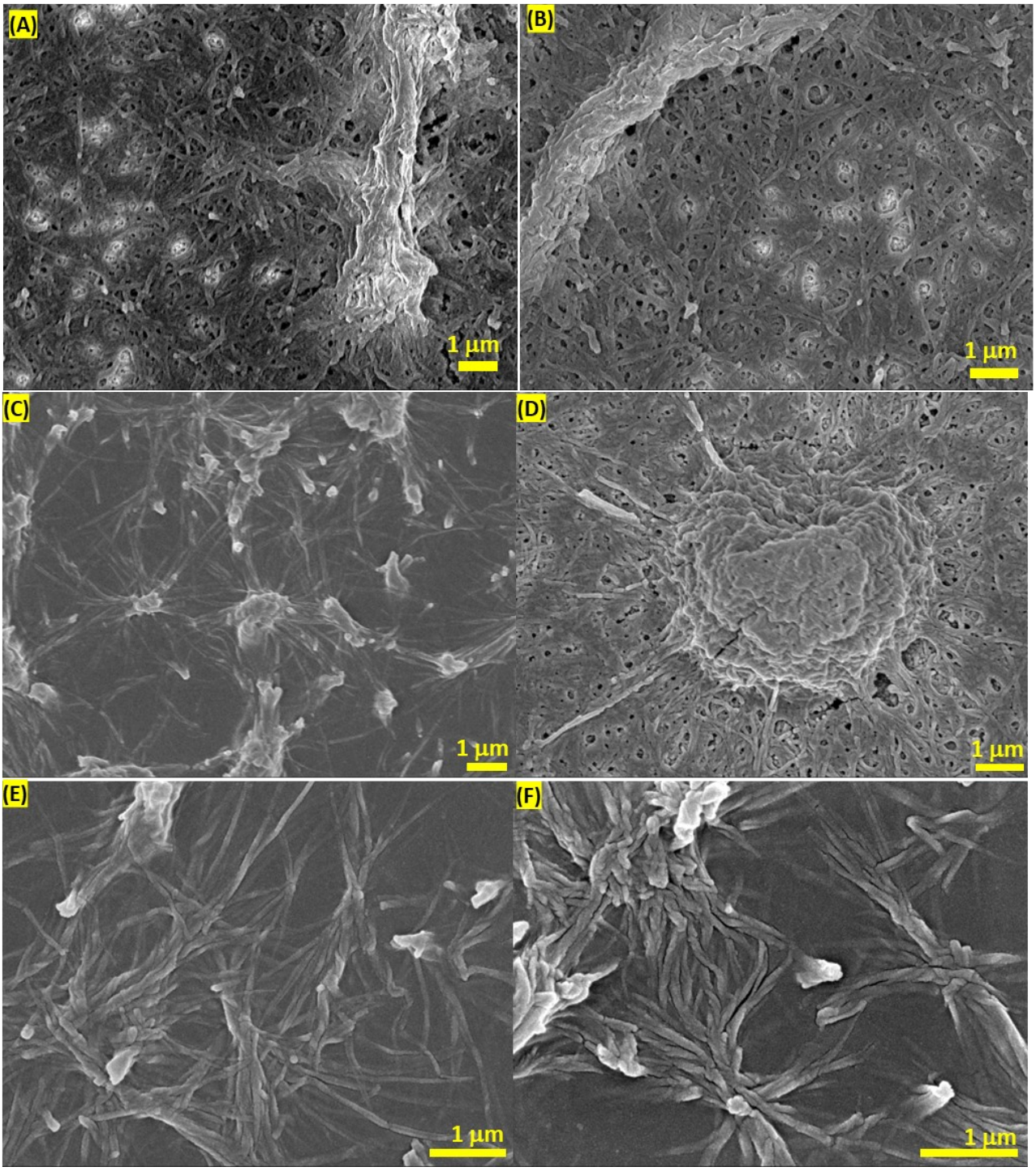


Figure S17: FESEM images of vacuum-dried (A-B) **MBLG-2** and (C-F) **MBLG-5** gels.

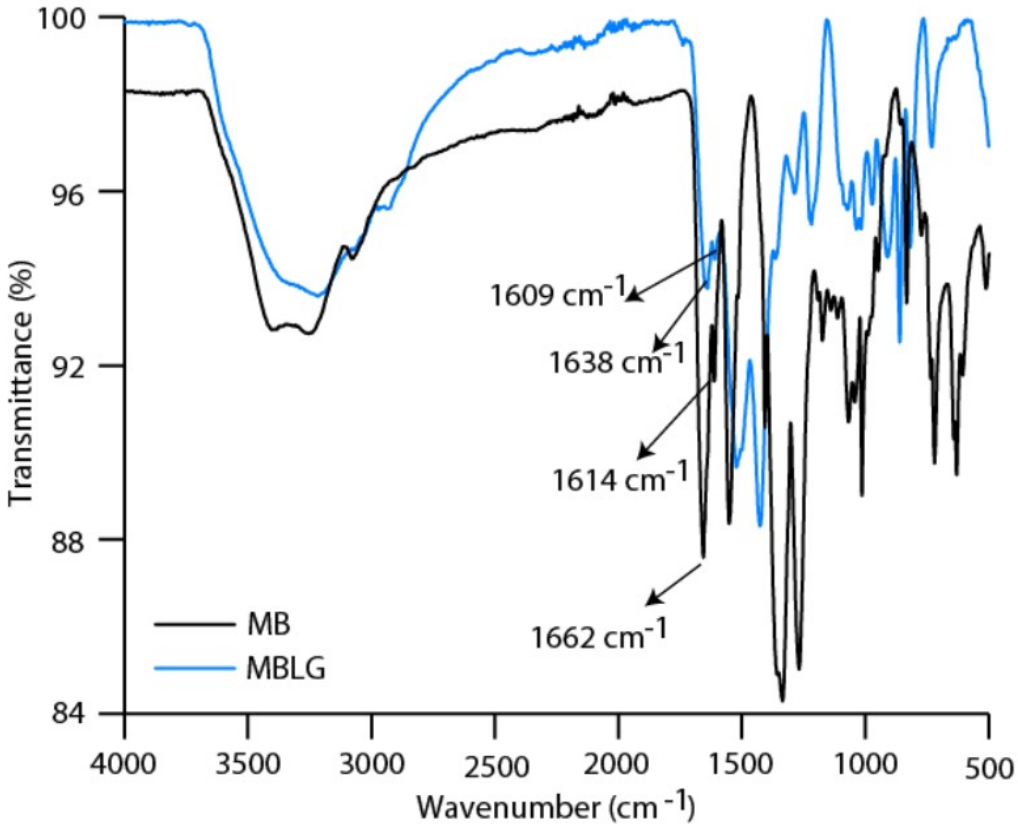


Figure S18: FTIR spectra of **MB** and **MBLG** xerogel.

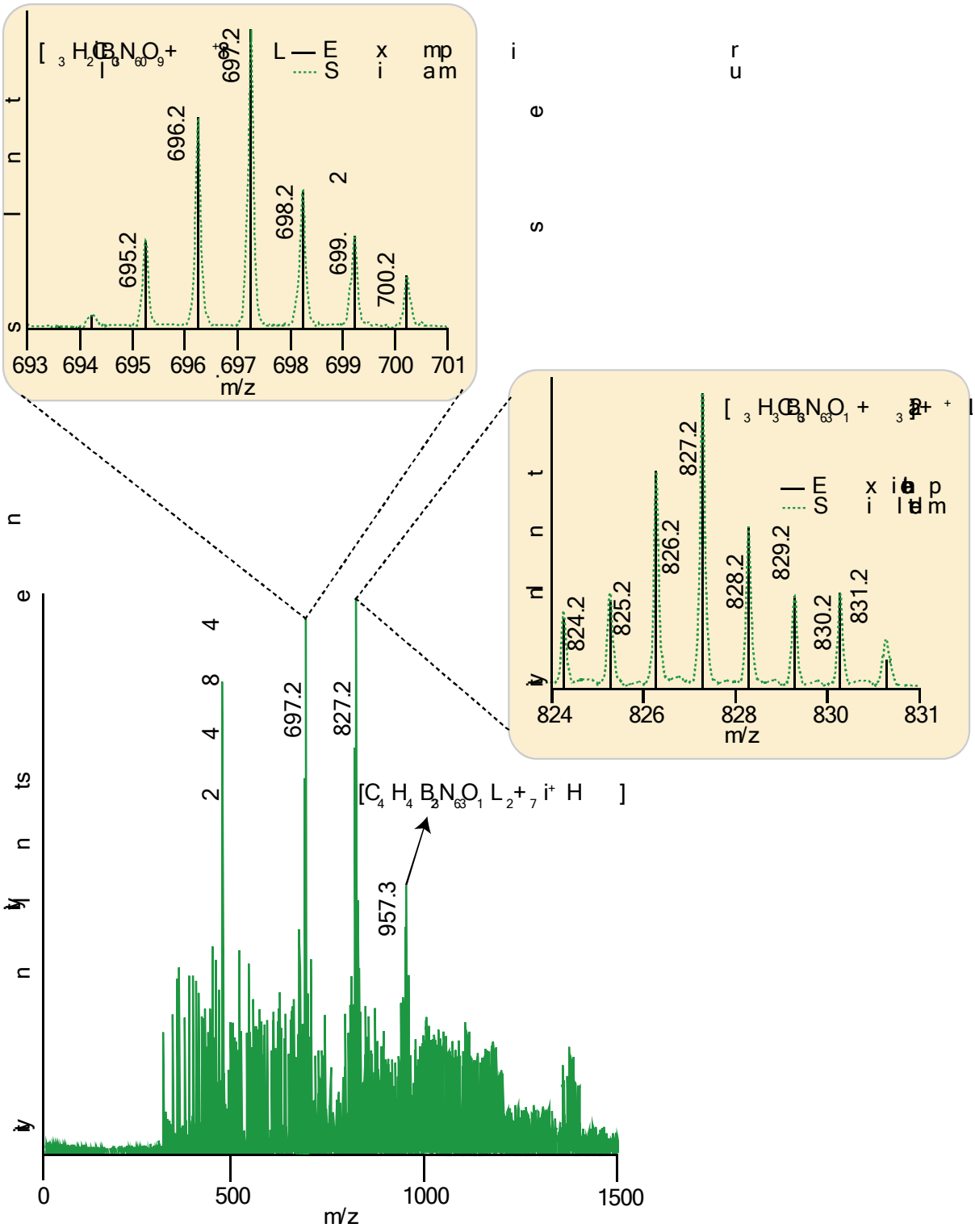


Figure S19: ESI-MS spectrum of **MBLG.**

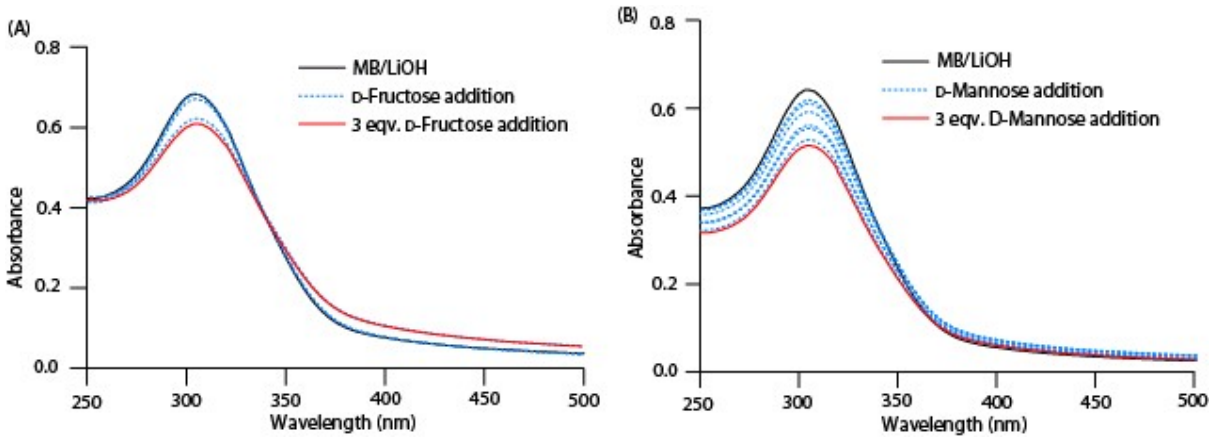


Figure S20. UV-Vis titration study performed between deprotonated **MB** (10^{-5} M, H_2O) and **(A)** D-Fructose/ (B) D-Mannose**,** (10^{-3} M, H_2O).

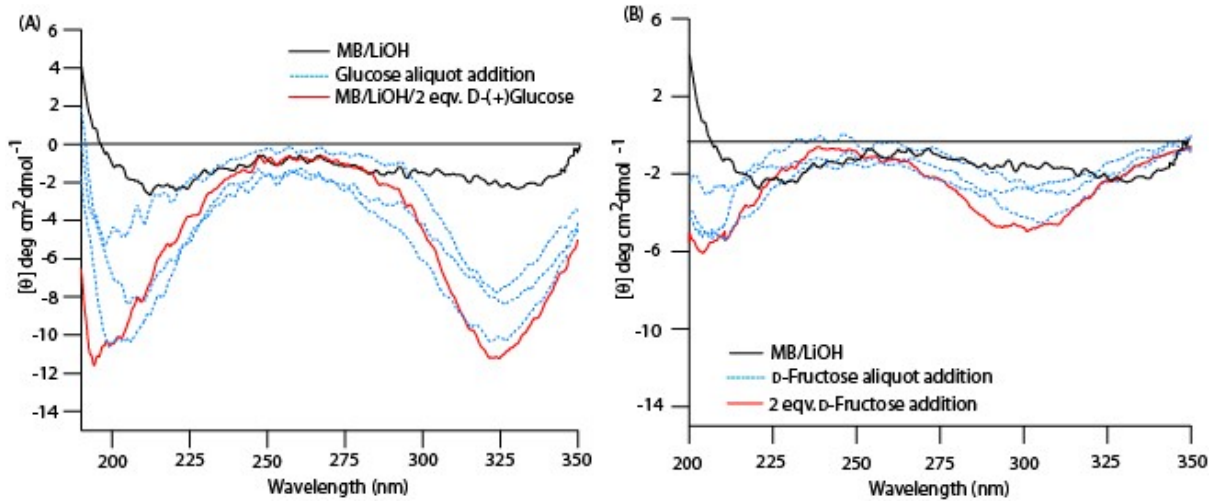


Figure S21. CD titration performed between deprotonated **MB** (0.5 x 10^{-4} M) and **(A)** D-(+)-glucose/ (B) D-Fructose (10^{-2} M).

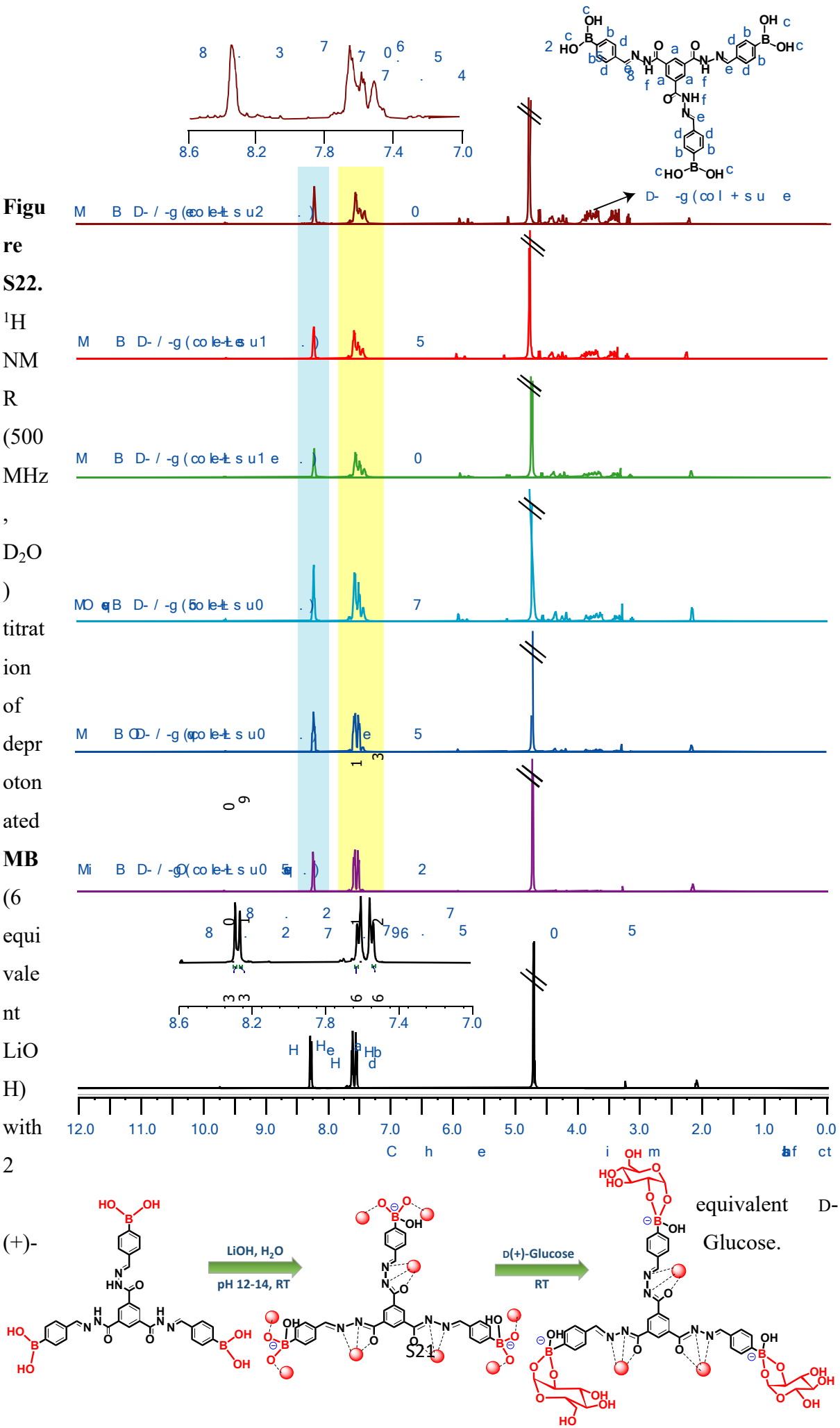


Figure S22. ^{1}H NMR (500 MHz, D_2O) titration of deprotonated **MB** (6 equivalent LiOH) with 2 equivalent D-(+)-Glucose.

Figure S23: A schematic representation of Glucose binding to boronic acid core in presence of LiOH or **MB-**Glucose adduct formation triggered metallogel **MBLG** formation.

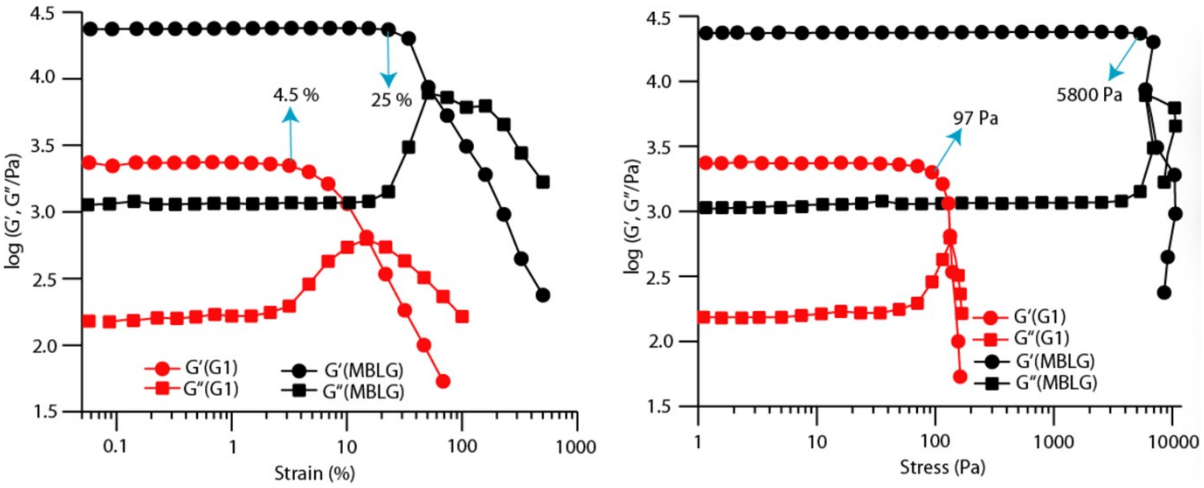


Figure S24: Rheological study of **G1** (5 wt%) and **MBLG-5**: loss modulus and storage modulus variation upon (A) dynamic strain and (B) Dynamic stress sweep.

Note: The **G1** gel formed in DMSO solvent also showed true gel phase nature, however, it was mechanically less stiff than the **MBLG** gels as demonstrated in figure S24. Hence, the latter gel appeared more suitable for the practical purpose of device fabrication than the former.

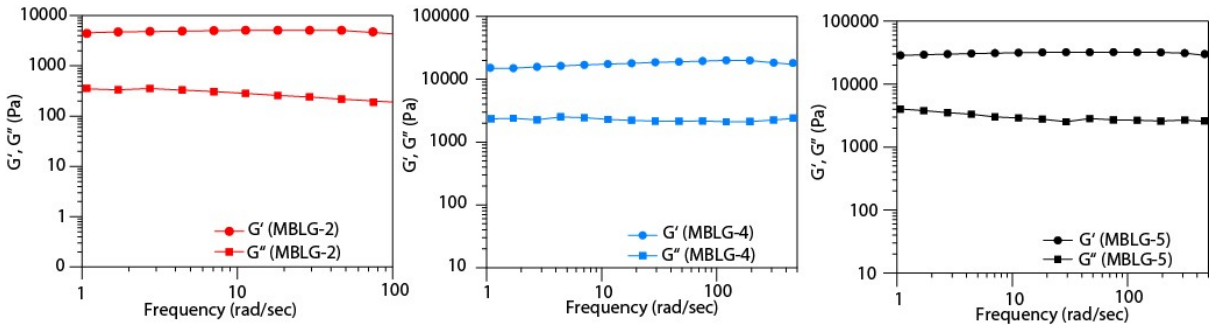


Figure S25: Oscillatory frequency sweep measurement; variation of G' and G" against oscillatory frequency for (A) **MBLG-2** (B) **MBLG-4** and (C) **MBLG-5.**

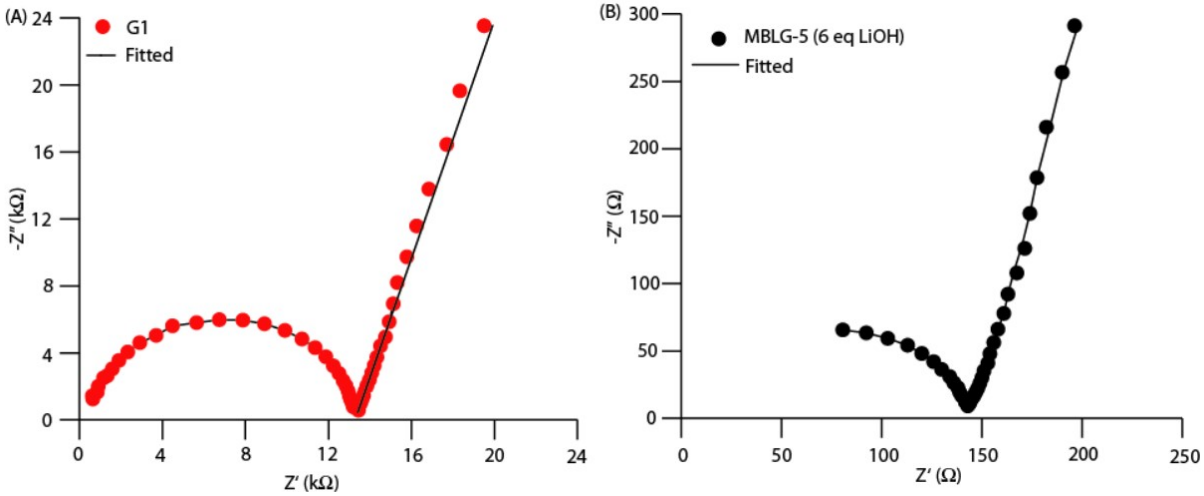


Figure S26: Nyquist impedance plots for **G1** and **MBLG-5** metallogels (both gels at 5 wt%).

Note: As evident from Table S4, S5 and Figure S25, S26, the DMSO solvent congealed organometallogel **G1** derived from **MB** gelator, overall exhibited much inferior mechanical and electronic properties than the D-(+)-glucose induced **MBLG** hydrometallogel. The striking change in the properties exemplify the pivotal role of co-gelator D-(+)-glucose and solvent in the superior gel network formation from the gelator scaffold **MB**.[3]

References:

1. C. Mahendar, M. K. Dixit, Y. Kumar and M. Dubey, *J. Mater. Chem. C*, 2020, **8**, 11008.
2. X. Li, Q. Gao, J. Wang, Y. Chen, Z.-H. Chen, H.-S. Xu, W. Tang, K. Leng, G.-H. Ning, J. Wu, Q.-H. Xu, S. Y. Quek, Y. Lu and K. P. Loh, *Nat. Commun.*, 2018, **9**, 2335.
3. J. J. B. van der Tol, G. Vantomme and E. W. Meijer, *J. Am. Chem. Soc.*, 2023, **145**, 17987.