Electronic Supplementary Information

Li+-Zn2+ tailored nanostructured metallohydrogel based mixed ionic-electronic conductor

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EXPERIMENTAL SECTION

Materials and Physical Methods:

The solvents were distilled and dried by following standard procedures prior to their use. Reagents and solvents used in the experiment were purchased from Finar Ltd, Ahmedabad, Gujarat (India), S. D. Fine Chem. Ltd, Mumbai, India and used as received without further purification. Methanol was purchased from Advent chembio Pvt. Ltd, Navi Mumbai, Maharastra (India). Lithium hydroxide and 1H-Imidazole-4-Carbaldehyde were purchased from Spectrochem Pvt. Ltd., Mumbai (India), Hydrazine hydrate (80%) and Zinc Acetate Dihydrate were purchased from Sisco Research Laboratories Pvt. Ltd. Mumbai (India). Mandelic acid hydrazide was purchased from Alfa Aesar. UV-Vis study was done on UV2600 Schimazdu spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a AVANCE III 400 Ascend Bruker BioSpin International AG spectrometer. Electrospray ionization mass (ESI-MS) spectra were recorded on a Waters (Micromass MS Technologies) QTof Premier. FT-IR data were recorded on spectrum two PerkinElmer FT-IR spectrometer. FE-SEM images were captured by JOEL-7610 F Plus and TEM images were captured using a JEOL JEM 2100. Powder XRD data was collected on Rigaku SmartLab between angle $2\theta = 5$–80°.

Rheological Study:

Rheological data were recorded using rheometer MCR 102 (Anton Paar) equipped with stainless steel parallel plates (20 mm diameter, 1.0 mm gap). Experiments were conducted on freshly prepared gels (1.5% w/v). Linear viscoelastic regions of the gel samples were determined by measuring the storage modulus, G′ and the loss modulus, G″ as a function of stress and strain amplitude (At constant angular frequency of 10 rad s^{-1}). Dynamic oscillatory frequency sweep was carried out 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 120 °C at a constant frequency of 10 rad/sec and strain of 0.5%.

Electrochemical impedance spectroscopic (EIS) measurements:

Nyquist impedance plot and conductivity measurement-

Nyquist impedance plot for Metallohydrogel (**MHG**) was obtained using a CH instruments CHI604E electrochemical workstation within the frequency range 10^6 Hz to 1 Hz at a small perturbation voltage of 10 mV. The electrochemical measurements were performed on an indigenously build cylindrical electrochemical cell consisting of two stainless steel disc electrodes separated at a fixed distance. Nyquist plot was fitted with a suitable equivalent electrical circuit by an inbuilt software provided by CH instruments. The conductivity (σ) of the **MHG** was calculated using the following relation:

$$\sigma = \frac{1}{R} \cdot \frac{d}{S} \qquad \text{.......................................(1)}$$

Where, R is resistance of the **MHG**, d is the distance between two electrodes and S is area of the electrodes.[1] All the electrochemical impedance measurements were performed at room temperature.

Bode impedance plot and measurement of ionic and electronic conductivity separately

Bode impedance plots for **MHG** were recorded using a CH instruments CHI604E electrochemical workstation within the frequency range 10^6 Hz to 10^{-4} Hz at a small perturbation voltage of 10 mV. The electrochemical measurements were performed on an indigenously build cylindrical electrochemical cell consisting of two stainless steel disc electrodes separated at a fixed distance. From Bode magnitude plot the total impedance of the high frequency (HF) plateau was taken as ionic resistance and was used to calculate the ionic conductivity with the help of equation-1. Whereas electronic conductivity was calculated by taking the total impedance of low frequency (LF) plateau as electronic resistance followed by putting the obtained resistance value in equation-1 to get value of electronic conductivity.[2]

Impedance *vs* time plot-

The electrochemical experiments to obtain impedance *vs* time measurements at higher (10^6 Hz) and lower (0.1 Hz) frequency were performed in a cylindrical electrochemical cell with three electrodes system. The electrodes are; Ag/AgCl reference electrode, platinum wire counter electrode and glassy carbon working electrode.

Current-voltage (I-V) characteristic curve-

I-V characteristic curve was obtained in Linear Sweep voltammetry (LSV) mode of the electrochemical work station. A 10 mm diameter and 2 mm thick pellet of dried **MHG** was prepared using pelletizer. The pellet was placed between two copper disc plate of an indigenously built screw push-type sample holder. The copper discs were used to provide electrical contact.

Transport number evaluation

The ionic transport number (t_{Li+}) was evaluated using the d.c. polarization technique. In this technique, an electrochemical cell SS| **MHG** |SS was polarized by applying a step potential of 0.01V and the resulting current was recorded as a function of time (Figure S10). The value of t_{Li+} was calculated using the Vincent–Evans equation:

$$t_{Li+} = \frac{I_S(\Delta V - I_0 R_0)}{I_0(\Delta V - I_S R_S)}$$

where I_0 and I_S are the initial and steady state current, respectively. R_0 and R_S are the cell resistance before and after polarization measured by nyquist impedance plot. ΔV is the applied step potential.[3]

Synthesis and characterization:

(E)-N'-((1H-imidazol-5-yl)methylene)-2-hydroxy-2-phenylacetohydrazide (H₂IML)

A methanolic solution of 1H-imidazole-4-carbaldehyde (0.2 g, 2.083 mmol) was added dropwise to a

solution of mandelic acid hydrazide (0.345 g, 2.083 mmol) dissolved in methanol, and the overall solution was stirred at room temperature for 8 hours. The reaction yielded white coloured solid compound which was further washed with methanol and diethyl ether and dried under vacuum. Yield 0.450 g (88%). Anal.calcd.for $C_{12}H_{12}N_4O_2$: C, 59.01; H, 4.95; N, 22.94; Found: C, 59.15; H; 5.2 N, 22.86. ^{1}H NMR (D_2O, 400 MHz, δ_H, ppm) 5.09 (s, 1H, -CH), 6.33 (s, 1H, -OH), 7.60-7.3 (m, 5H, Ar-H), 7.75 (s, 1H, H imdz), 7.89 (s, 1H, H imdz), 8.09 (s, 1H, NH imdz), 8.39 (s, 1H, -HC=N), 13.83 (s, 1H, NH alph). ESI-MS m/z: [**H₂IML** + H]$^+$, 245.1 (*calcd.* 245.1).

Synthesis of metallohydrogel (MHG)

H₂IML (15 mg, 0.061 mmol) was dissolved in deionised water (0.5 mL) followed by deprotonation with $LiOH.H_2O$ (5.11 mg, 0.122 mmol) subsequent sonication of the dissolved mixture resulted in a colourless solution. A freshly prepared $Zn(OAc)_2.2H_2O$ (6.68 mg, 0.031 mmol) solution in deionised water (0.5 mL) was added dropwise to the colourless solution, the resulting solution gradually turned in white coloured gel,which was confirmed by the inverted vial test. Anal. calcd. for $(C_{24}H_{20}N_8O_4ZnLi_2.5H_2O)$: C, 44.15; H, 4.63; N, 17.17; Found: C, 44.21; H, 4.69; N, 17.11. ESI-MS (diluted gel) m/z: [$(C_{24}H_{20}N_8O_4ZnLi_2)$ + H]$^+$, 563.1 (*calcd.* 563.1).
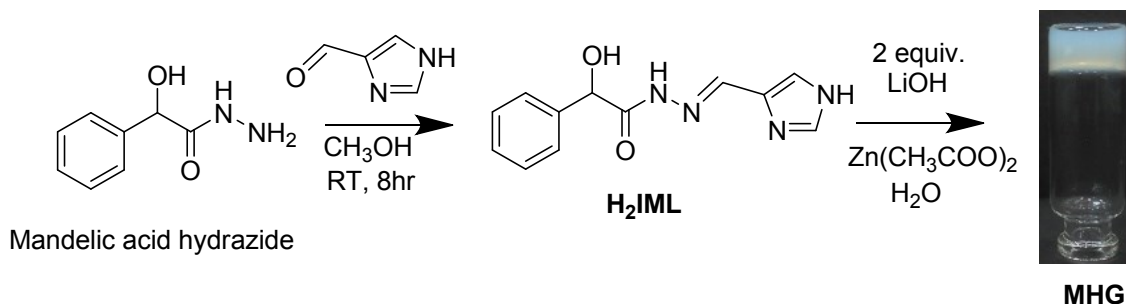
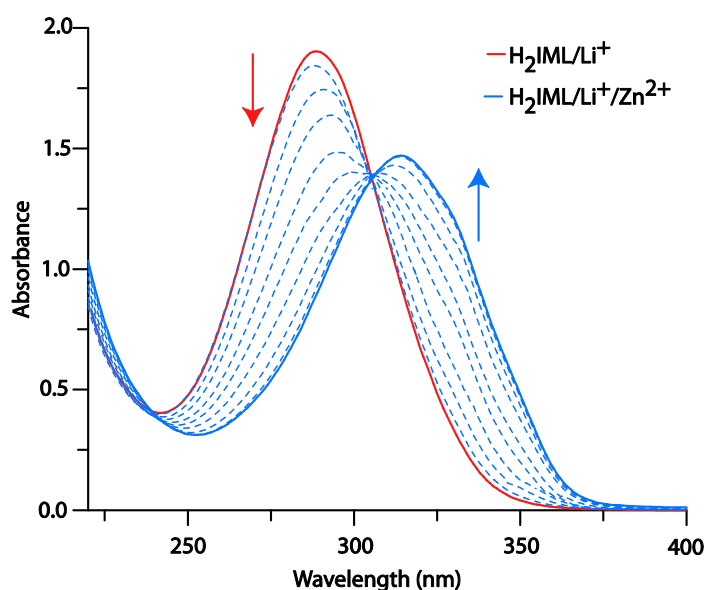**Scheme S1:** Synthetic route addopted for the synthesis of **H₂IML** and **MHG**.

Figure S1. UV-vis titration spectra of **H₂IML**+ Li$^+$ (1×10^{-4} M, H_2O, red line) *vs* Zn^{2+} (1×10^{-2} M, H_2O, blue

lines) shows nice isosbestic point at 305 nm which suggests the formation of complex **H₂IML**+ Li⁺+ Zn²⁺.
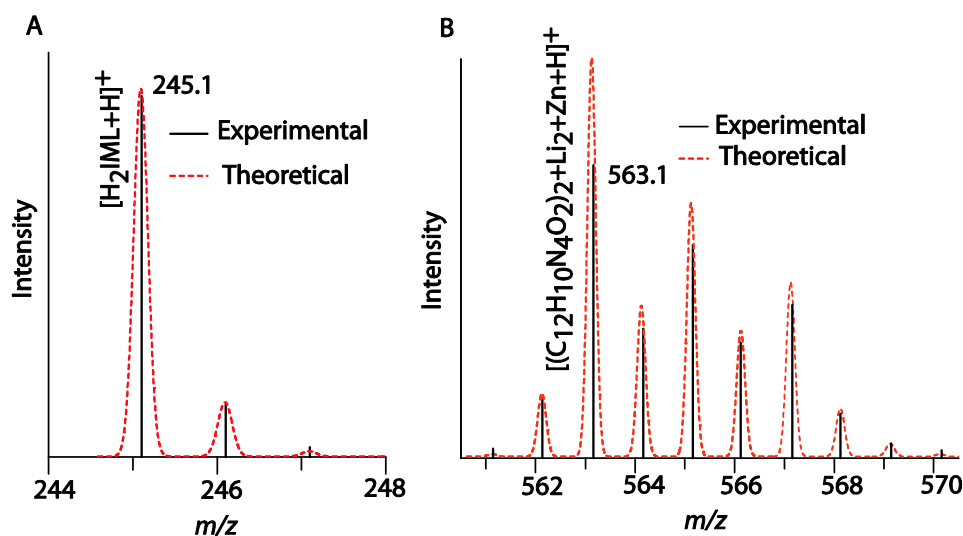

Figure S2. Simulated (red dotted line) and experimental (black line) ESI-MS spectra for (A) **H₂IML** and (b) diluted **MHG**.
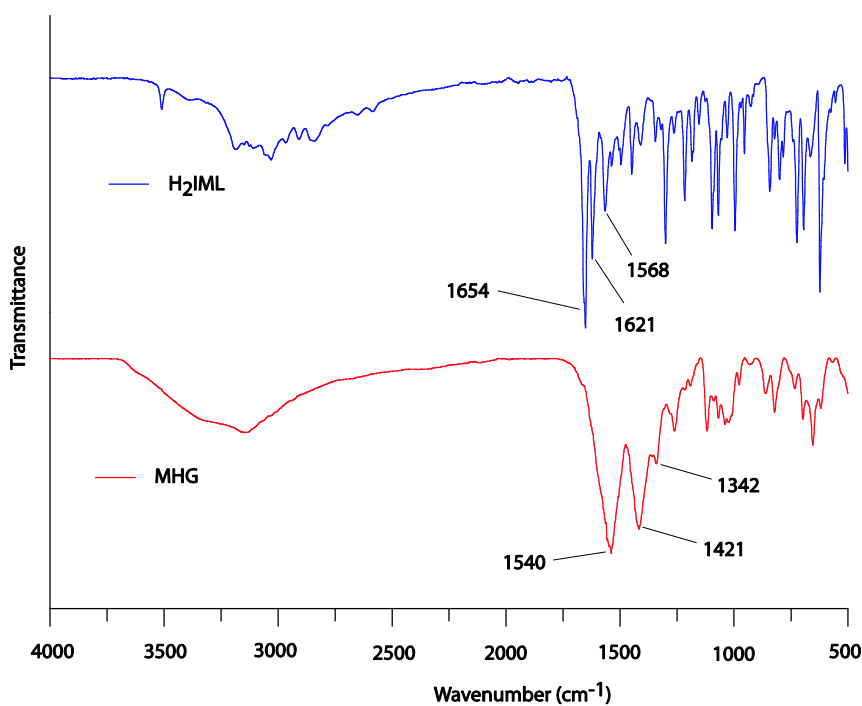

Figure S3. FT-IR spectrum of **H₂IML** gelator (blue) showing υ(-OH) at 3514 cm⁻¹, υ(-NH) at 3191 cm⁻¹, υ(-C=O) at 1654, 1621 cm⁻¹ and υ(-C=N) at 1568 cm⁻¹. FT-IR spectrum of dried **MHG** (xerogel) showing υ(-C=O) at 1540, 1421 cm⁻¹ and υ(-C=N) at 1342 cm⁻¹. The large shift in C=O and C=N vibrations in the xerogel FT-IR spectrum supports the coordination of Zn²⁺ with N, N, O site. Further, the disappearance of -OH and broadening of -NH vibrations support the binding of Li⁺ to -OH and -NH groups.
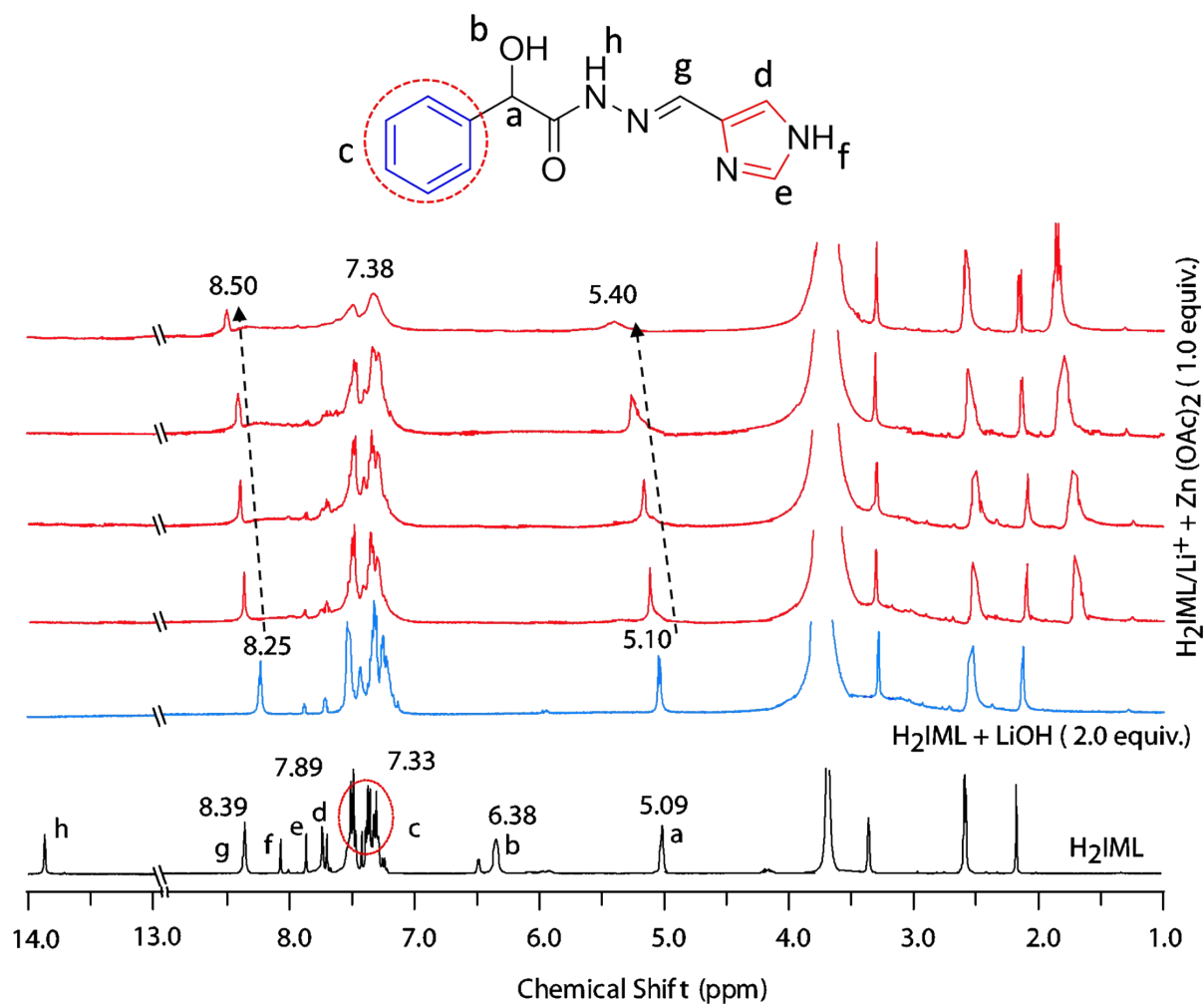
Figure S4. ¹H NMR titration spectra of **H₂IML** with LiOH.H₂O and Zn(OAc)₂.2H₂O.
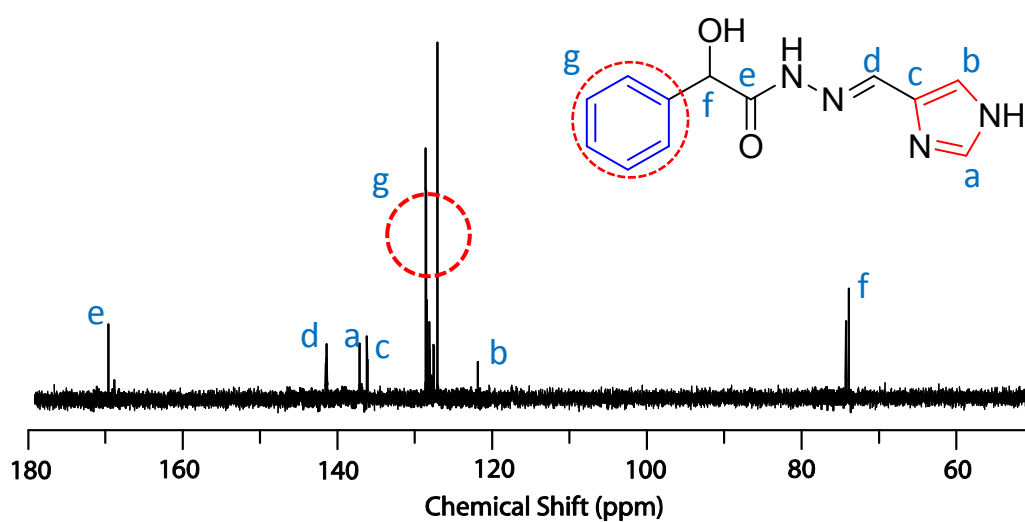

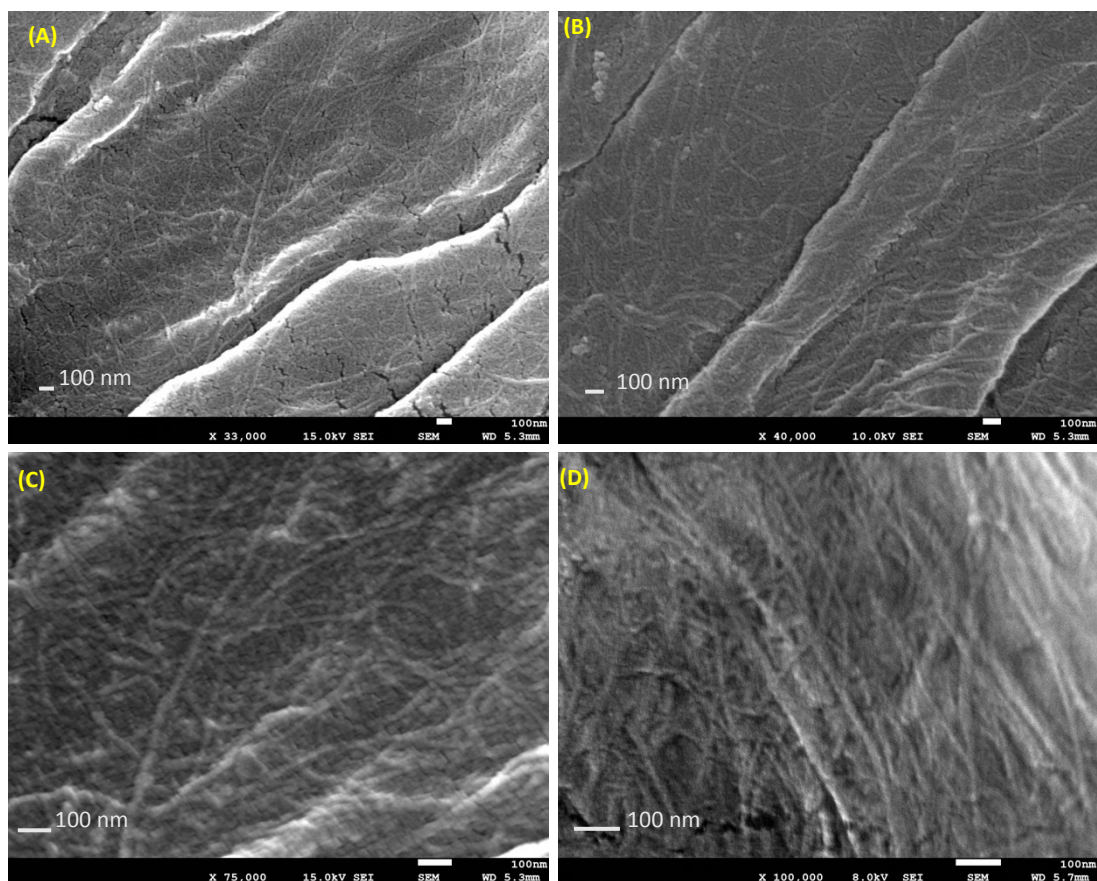**Figure S5.** ^{13}C NMR (400 MHz, D₂O, 298 K) spectrum of **H₂IML**.

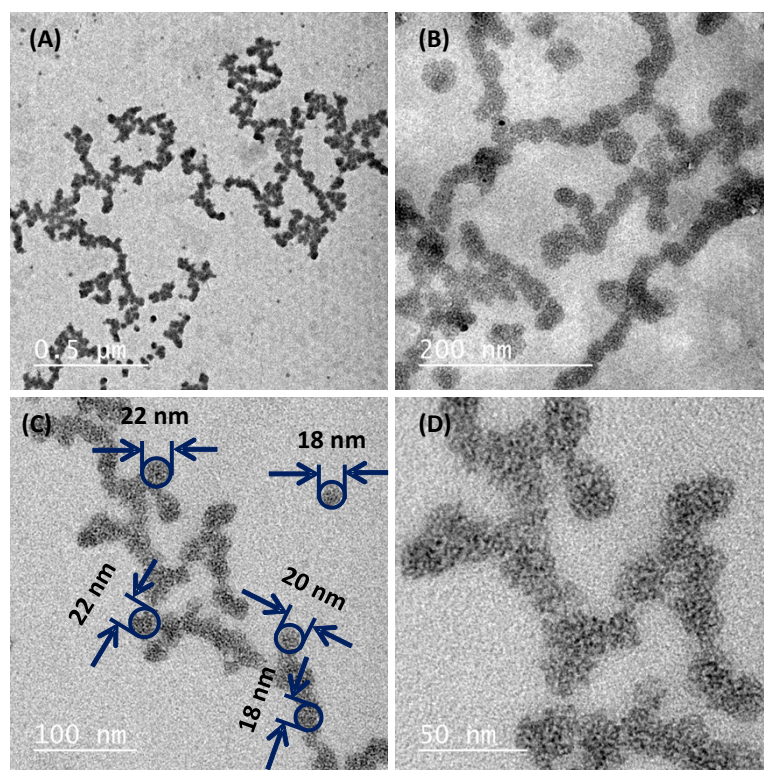**Figure S6.** FE-SEM images of dried **MHG** at different magnification.

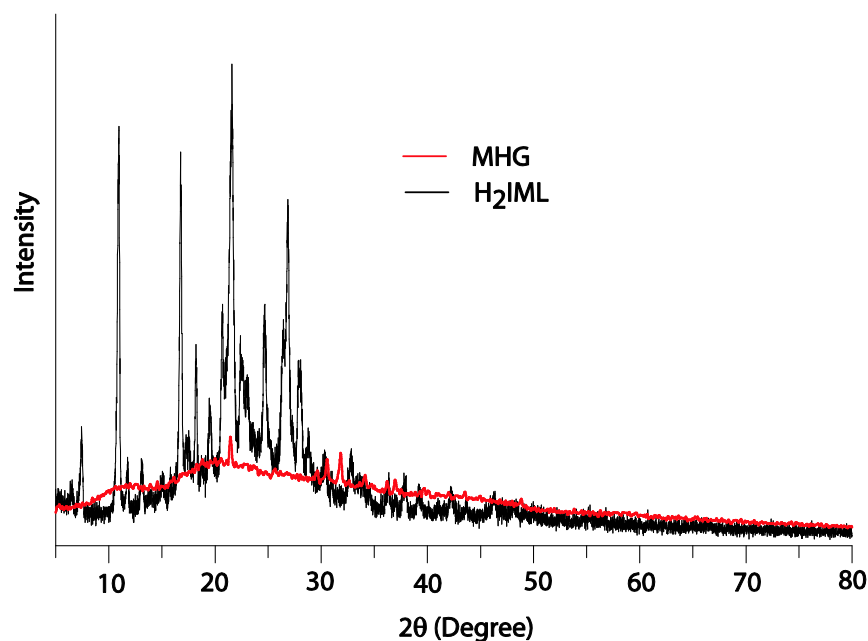**Figure S7.** TEM images of dried **MHG** at different magnification.

Figure S8. Powder XRD patterns of **H₂IML** gelator and dried **MHG**.
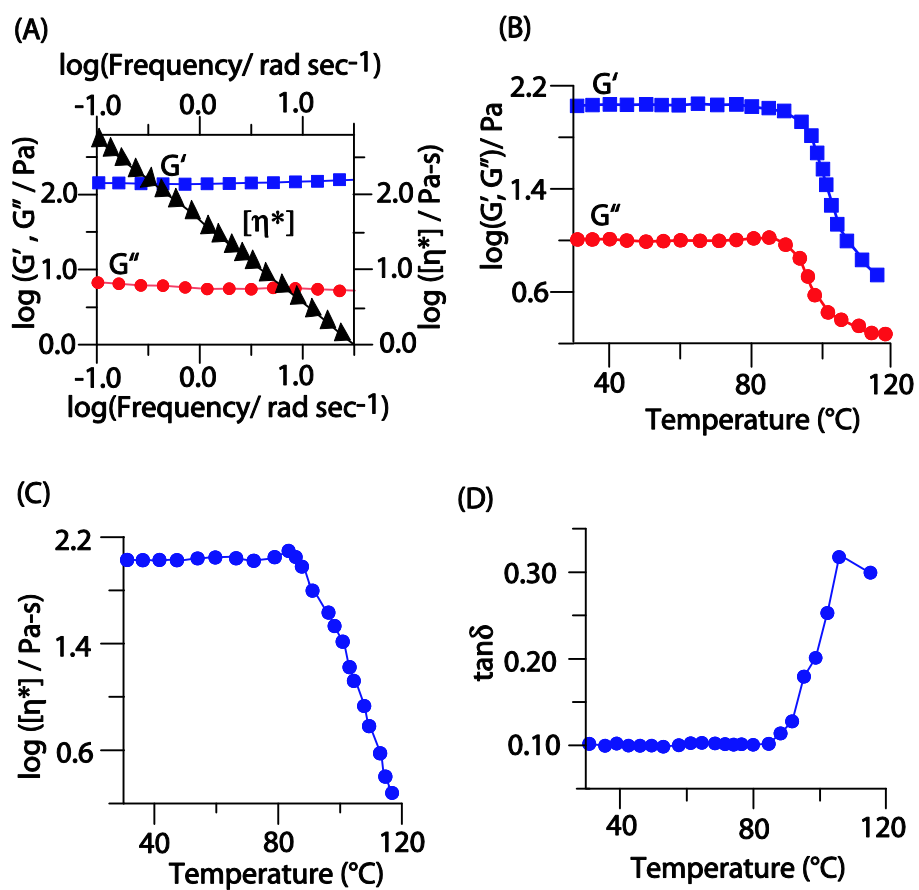

Figure S9. (A) Oscillatory frequency measurements (B) Dynamic temperature ramp *vs* G' and G" (C) Dynamic temperature ramp of complex viscosity (D) Temperature ramp of loss tangent (tanδ =G"/G') plot which indicates the critical temperature (T_{gel}) 85 °C for **MHG**.
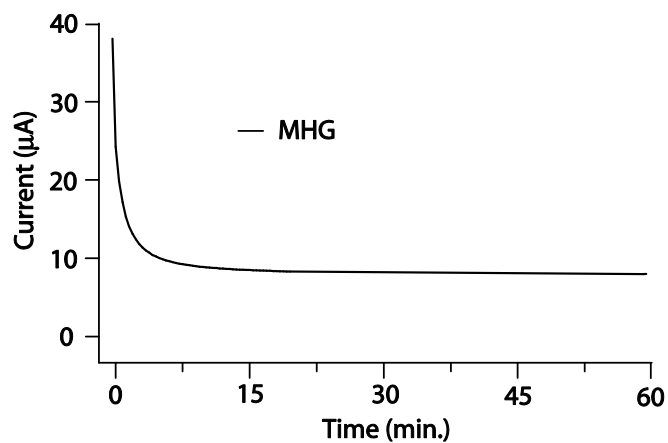
Figure S10. D.C. polarization curve of cell: SS|**MHG**|SS with applied step potential of 0.01 V
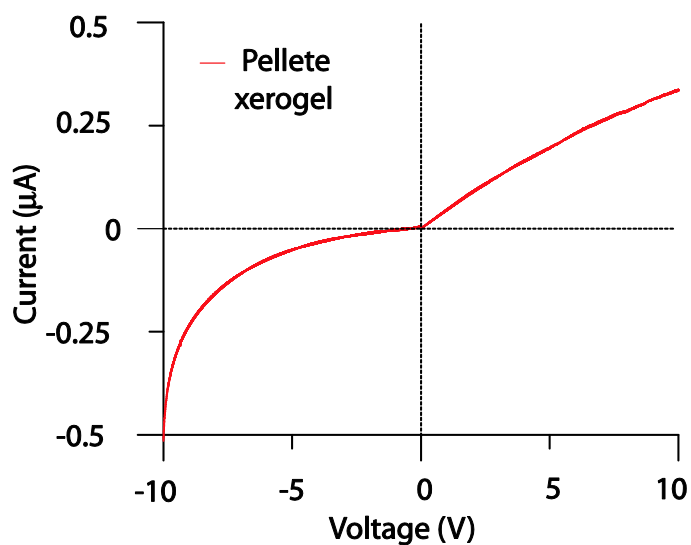

Figure S11. Current-voltage (I-V) characteristic of the dried **MHG** (xerogel) pellet.
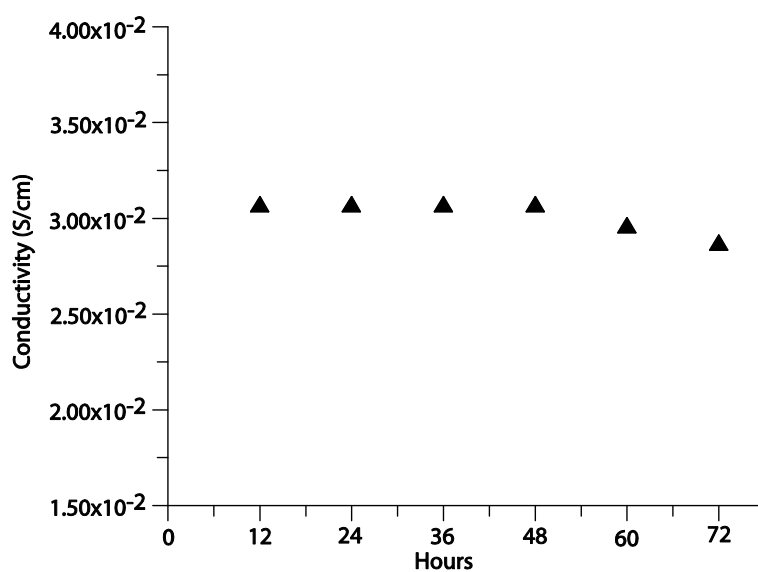

Figure S12. Variation in conductivity of **MHG** with respect to time.

References:

1   V. K. Pandey, M. K. Dixit, S. Manneville, C. Bucher and M. Dubey, *J. Mater. Chem. A*, 2017, **5**, 6211.

2   E. Skovroinski, R. J. Oliveira and A. Galembeck, *J. Colloid Interface Sci.,* 2019, **533**, 216.

3   Shalu, V. K. Singh and R. K. Singh, *J. Mater. Chem. C*, 2015, **3**, 7305.