Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Dissolvable Metallohydrogels for Controlled Release: Evidence of a Kinetic Supramolecular Gel Intermediate

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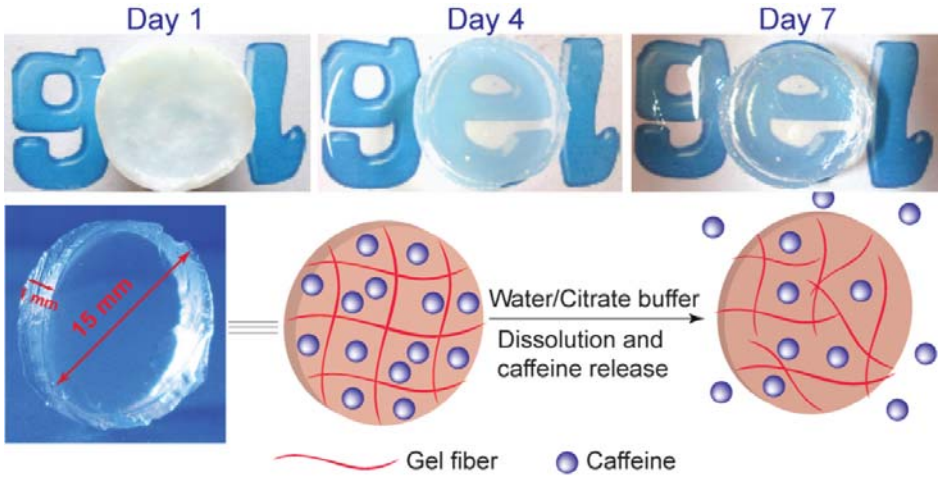

Contents List

S1. Preparation of ligands and gel

Preparation of amino acid based ligand: The ligand system VA was prepared following a modified literature procedure. To an aqueous solution (8 mL) of L-valine (1g, 8.5 mmol) and Na_2CO_3 (0.46 g, 4.25 mmol), 4-pyridinecarboxaldehyde (0.92 g, 8.5 mmol) in MeOH (5 mL) was added slowly. The solution was stirred for 3 h and cooled in an ice bath. $NaBH_4$ (0.38 g, 10.2 mmol) was added to the solution slowly. The mixture was stirred for 12 h, and 50% acetic acid (for the ligand L-VA) was used to neutralize the basic (pH~12) reaction mixture and adjust the pH to 7.1-7.2. As a result, in the reaction mixture sodium perchlorate/ sodium acetate (for perchloric acid and acetic acid, respectively) gets generated this eventually plays a very important role in the gelation process. The solution was stirred further for 1 h and then evaporated to dryness. The solid was extracted in hot and dry EtOH, and the filtrate was evaporated to get a white powder. L-VP has been prepared using same procedure. Yield (L-VA): 1.25g, 65%. The ligand has been crystallized from the aqueous solution Crystals were collected and utilized for its characterization. IR (KBr, cm^{-1}): ν_{OH}, 3421; $\nu_{as}(CO_2)$, 1562; $\nu_s(CO_2)$, 1409. ^1H NMR (D_2O, ppm): -CH_3(1.21, *d*, J= 1.11, 3H), -CH_3 (1.35, *d*, J= 1.1, 3H), -CH (3.20, m, 1H), -HN-CH (3.65, m, 1H), -CH_2 (3.82, *dd*, 2H), py-H (7.34, *d*, 2H), py-H (8.38, *d*, 2H).

Optimization of stock solution and preparation of hydrogels: Figure 1 illustrates the synthesis of ZNVA and ZPVA hydrogels which forms upon mixing the aqueous solutions of the two components (0.5 mL each), *viz.* zinc nitrate hexahdrate (ZN, 0.2 M; for ZNVA)/ zinc perchlorate hexahdrate (ZP, 0.2 M; for ZPVA) and ligand system L-VA (derived from L-valine; 0.4 M), which turns into a gel within a few seconds at room temperature.

S2. Viscoelastic properties

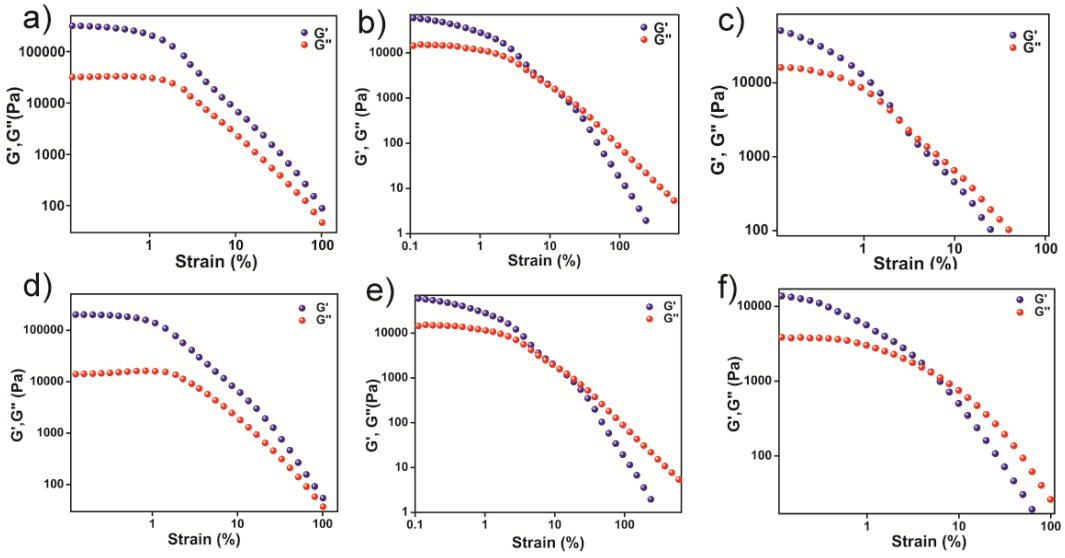

Figure S1. Oscillatory rheology of ZNVA and ZPVA hydrogels prepared at the CGC: DSS experiment at constant frequency of 1 Hz of a) of 6 h old, b) 3 days old and c) 7 days old ZNVA gel and c) 6 h old, b) 3 days old and c) 7 days old ZPVA gel.

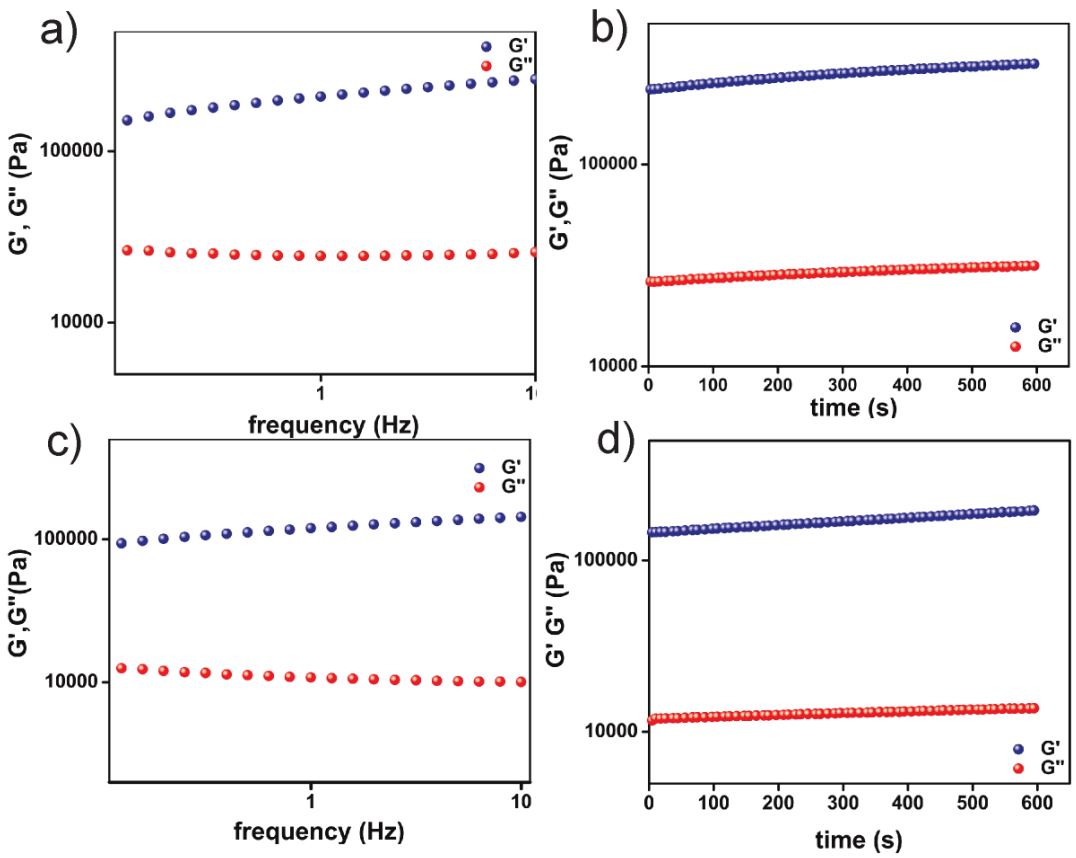

Figure S2. Oscillatory rheology of ZNVA and ZPVA hydrogels prepared at the CGC: Dynamic frequency sweep (DFS) experiment at constant strain of 0.1% of a) ZNVA and c) ZPVA hydrogel. b) and d) shows dynamic time sweep measurement at constant frequency of 1 Hz and constant strain of 0.1%.

S3. Thermogravimetric analyses

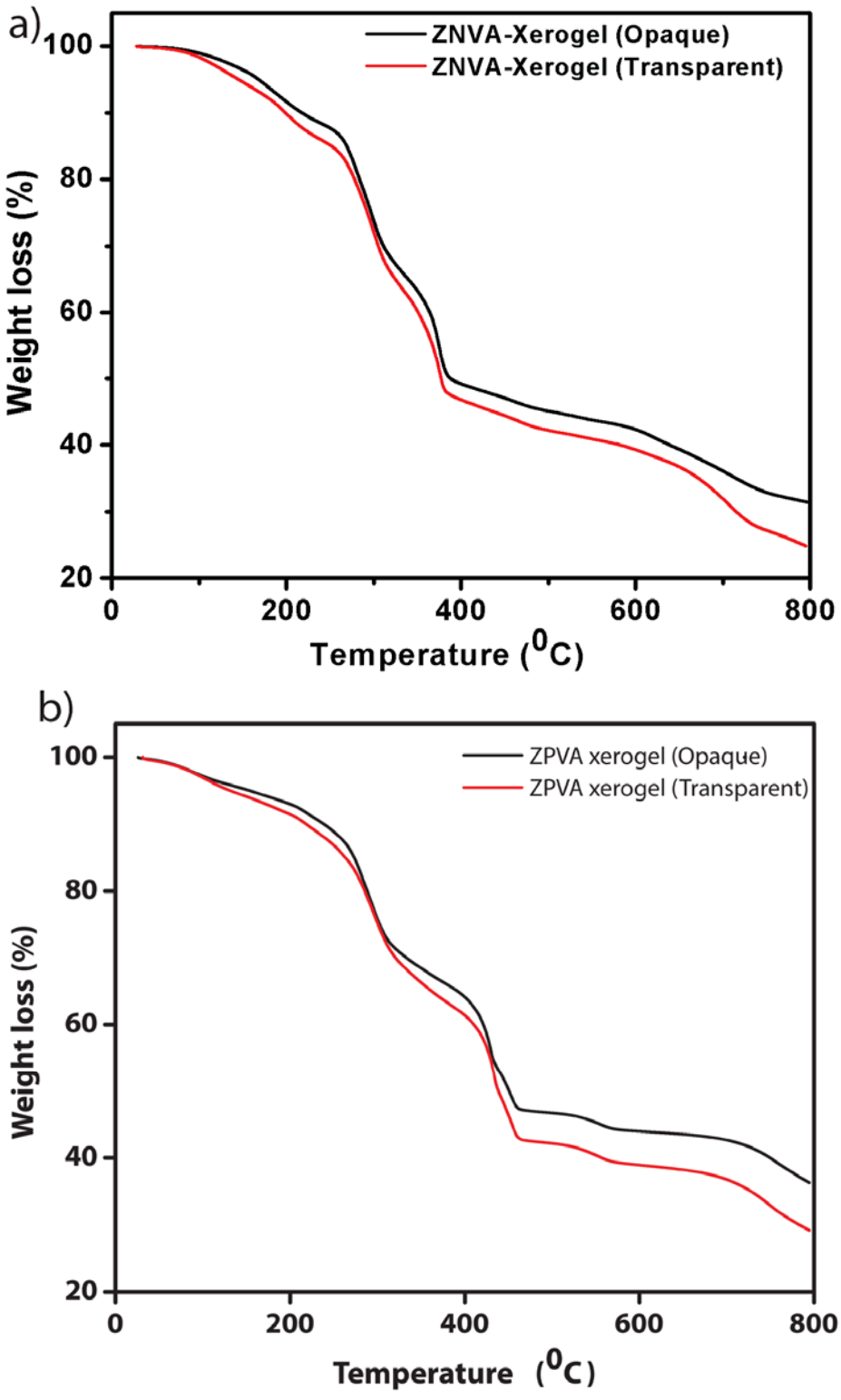

Figure S3. TGA traces for (a) ZNVA hydrogels and (b) ZPVA hydrogels (Black: Opaque and Red: Transparent gel).

S4. PXRD spectra

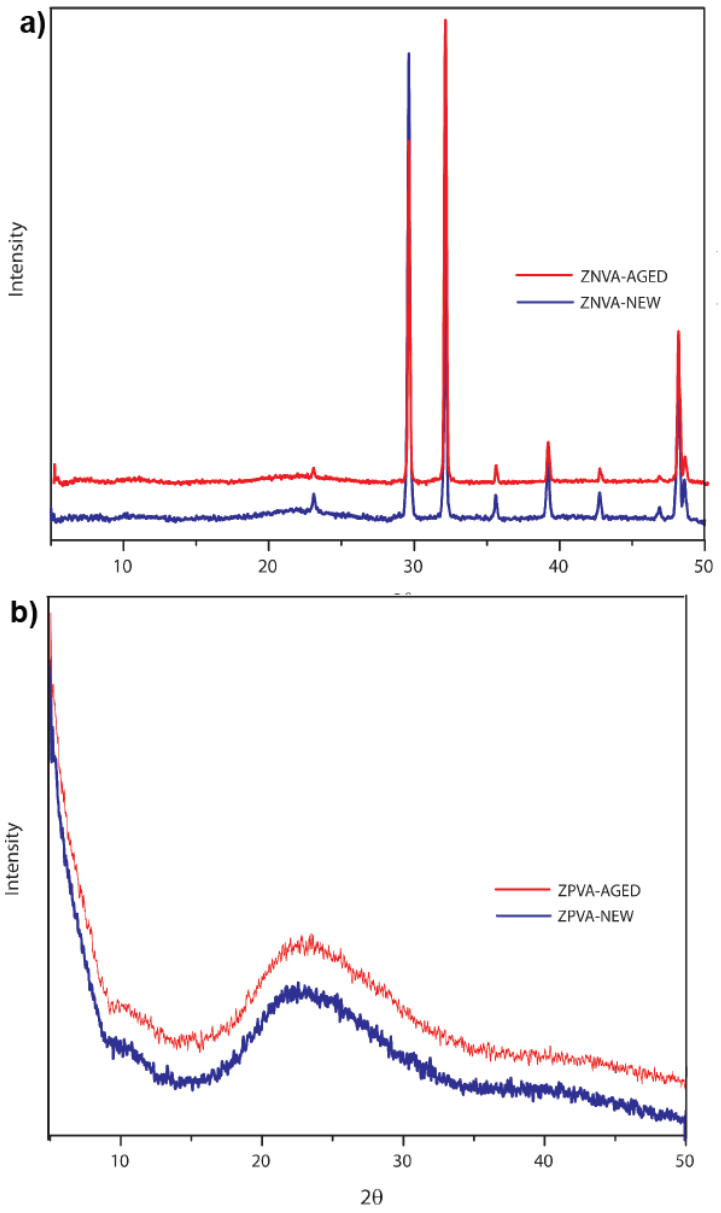

Figure S4. PXRD spectra for (a) ZNVA hydrogels and (b) ZPVA hydrogels (Blue: Opaque and Red: Transparent gel).

S5. IR spectra

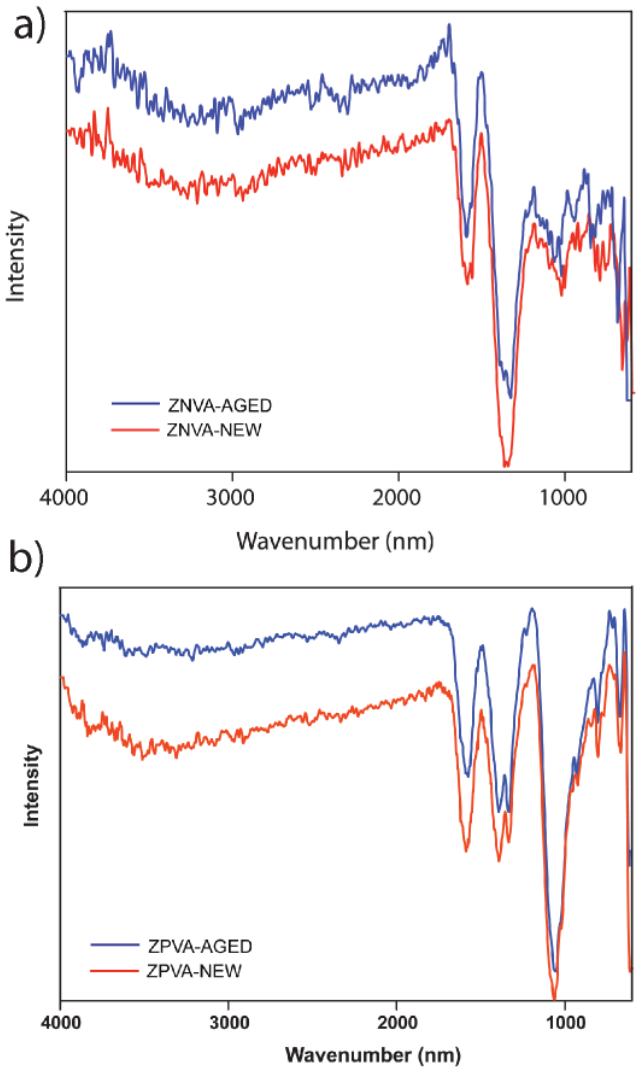

Figure S5. FTIR spectra for (a) ZNVA and (b) ZPVA hydrogels (Blue: Opaque and Red: Transparent gel).

S6. Multiresponsive nature

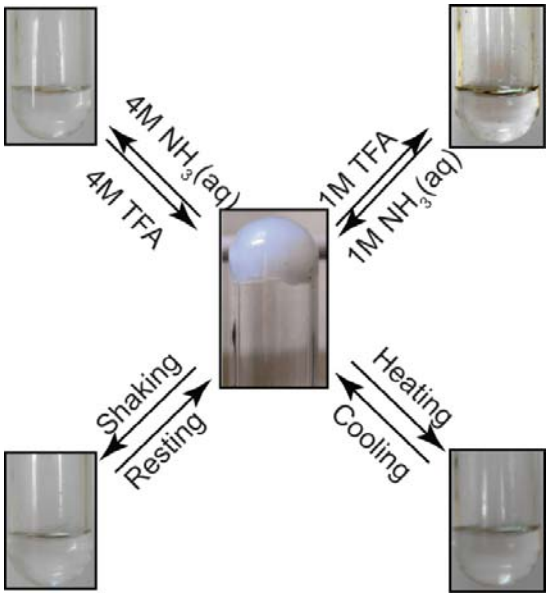

Figure S6. Multistimuli-responsive nature of ZNVA and ZPVA hydrogels.

S7. MALDI-TOF spectra

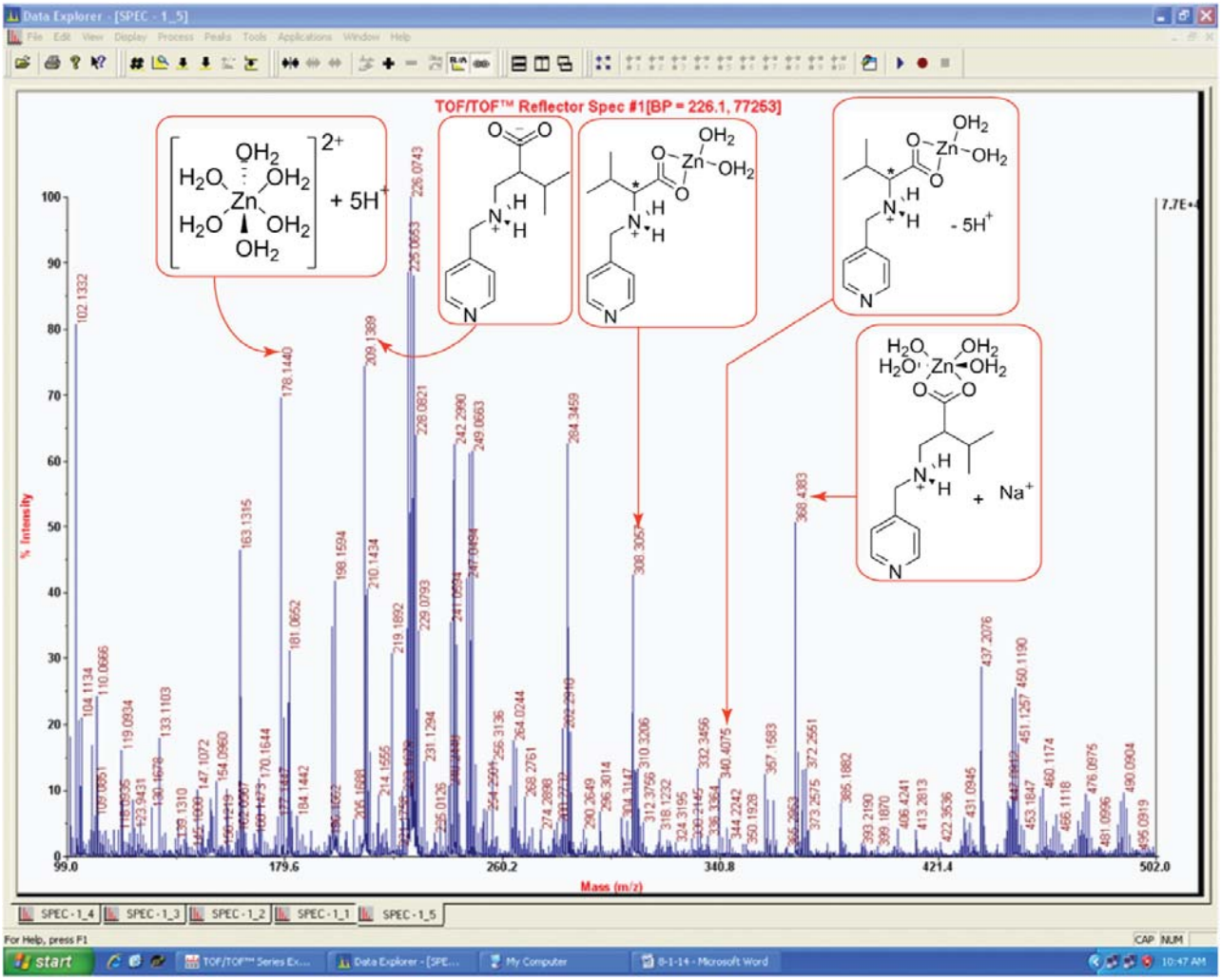

Figure S7. MALDI-TOF spectra and possible fragments for ZNVA hydrogel in dithranol matrix (*m/z* = 211, 225, 226 and 247 denote dithranol matrix peaks; *m/z* = 178.1440 and 209.1369 are from metal ion precursor and ligand; m/z = 340 and 368 peaks corresponding to the gelator complex).

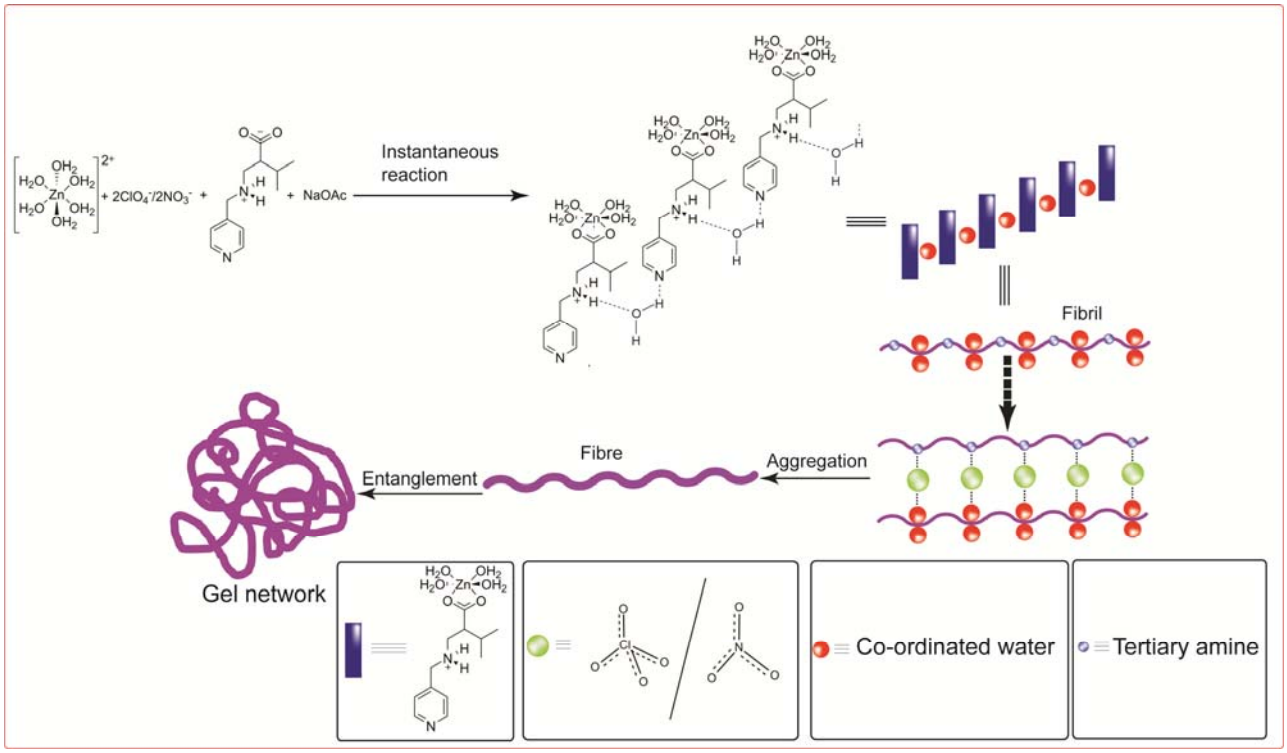

Figure S8. Plausible mechanism of formation of the gelator complex and subsequent formation of supramolecular aggregate.

S8. TEM images

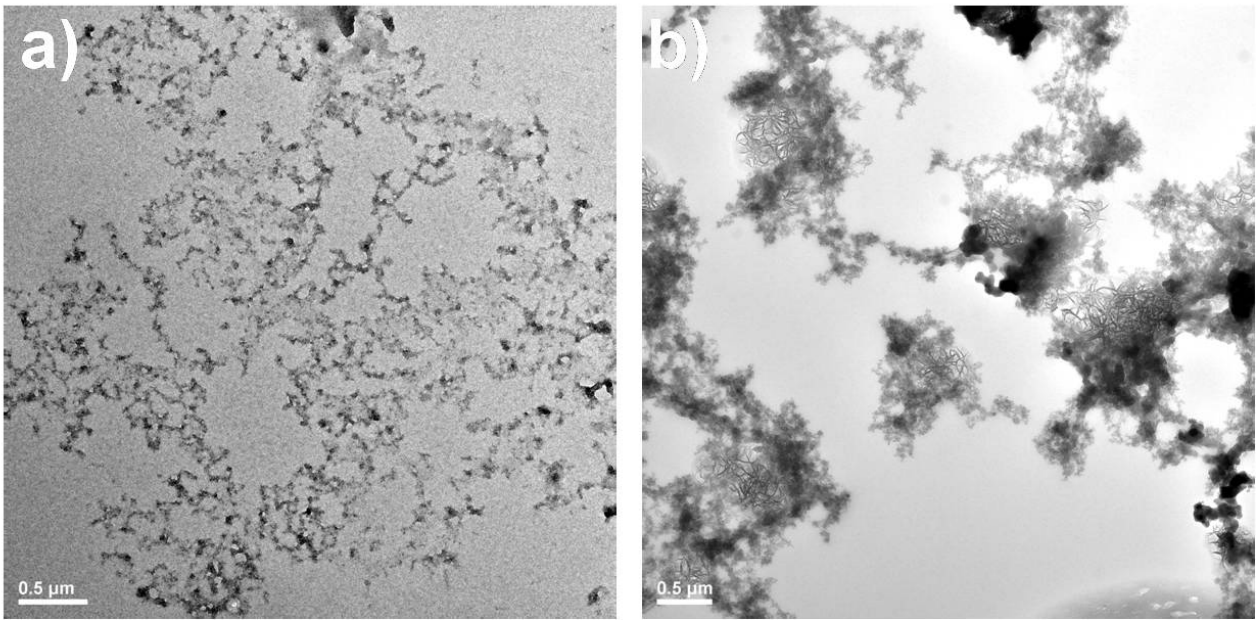

Figure S9. TEM images of a) opaque and b) and transparent ZPVA metallohydrogels.