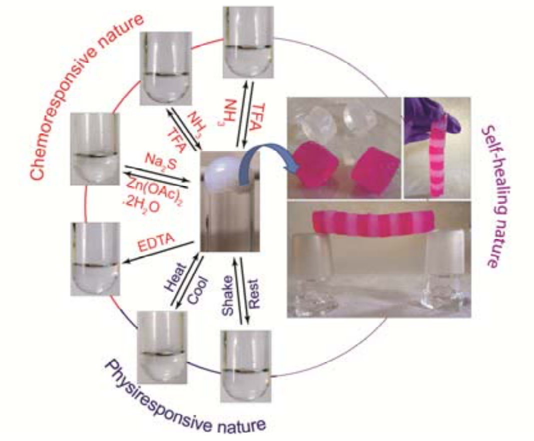
Supporting Information

Amino Acid Based Multiresponsive Low Molecular Weight Metallohydrogels with Autonomous and Rapid Self-healing Ability

Subhadeep Saha, Jürgen Bachl, Tanay Kundu, David Díaz Díaz and Rahul Banerjee**



Contents List

page

S1. Preparation of ligands ……..…………………………………................................. 11
S2. Optimization of stock solution and preparation of hydrogels …………………………. 13
S3. Effect of chirality of the ligand ………………………………………………………... 13
S4. Microscopy images …………………………………………………………………… 15
S5. Viscoelastic properties ………………………………………………………………... 15
S6. MALDI-TOF analysis…… ……………………………………………………....... 17
S7. Structure property relationship………………… ……………………………………… 19

S1. ***Preparation of amino acid based ligands:*** The ligand system VP 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 30% perchloric acid (for the ligand L-VP)/ 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 which 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-VP): 1.4 g, 70% yield. Yield (L-VA): 1.25g, 65%. The ligand has been crystallized from the aqueous solution the both. L-VA and L-VP. Crystals were collected and utilized for its characterization. IR (KBr, cm^{-1}):ν_{OH},3421; ν_{as}(CO2), 1562; ν_s(CO2), 1409.^{1}H NMR (D_2O, ppm): -CH_3(1.21, d, 3H), -CH_3 (1.35, d, 3H), -CH (3.20, m, 1H), -HN-CH (3.65, m, 1H), -CH2 (3.82, dd, 2H), py-H (7.34, d, 2H), py-H (8.38, d, 2H).

S2. ***Optimization of stock solution and preparation of hydrogels:*** Scheme 1 illustrates the synthesis of ZAVP gel which forms upon mixing the aqueous solutions of the two components (0.5 ml each), *viz.* zinc acetate dihydrate (ZA, 0.2 M) and ligand system L-VP (derived from L-valine; 0.4 M), which turns into a gel (CGC=84 gL^{-1}) within a few seconds at room temperature. Physical mixture of pure V and sodium perchlorate (P) also has the potential of forming gels. ZPVA gel (CGC=91 gL^{-1}) has also been synthesized under similar condition by mixing 0.5 ml aqueous solution of Zinc Perchlorate hexahydrate (ZP; 0.2 M) and ligand system L-VA (derived from L-valine; 0.4 M).

S3. ***Effect of chirality of the ligand:*** As often observed with other chiral gelators,[i] the enantiomeric purity of the ligand was found to play a key role on the formation of stable gels. Thus, the most stable gels were obtained when using enantiomerically pure ligands, although complete gelation could be observed when the enantiomeric excess (ee) was 85% ≤ ee ≤ 100%. In contrast, only partial gelation was achieved in the range 60-80% ee, and no gelation was observed when the ee was < 60%. Moreover, we notice that the bulk gels remained stable during sonication. Notably, if two different ZAVP gel blocks made up of L-VP and D-VP are kept in contact to each other, they don't gets attached together (don't heal). On the contrary, they both degrade with time to sol phase.

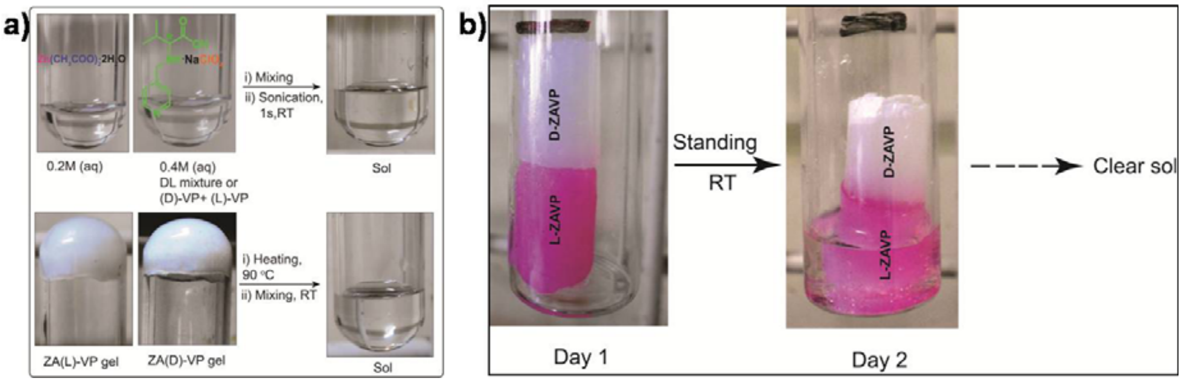


Figure S1. a) formation of sol phase in 50% enantiomeric excess ligand. b) Destruction of self-standing gels [L-ZAVP (made from L-VP) and D-ZAVP (made from D-ZAVP) to gel phase kept in contact to each other.

S4. ***Microscopy images:***

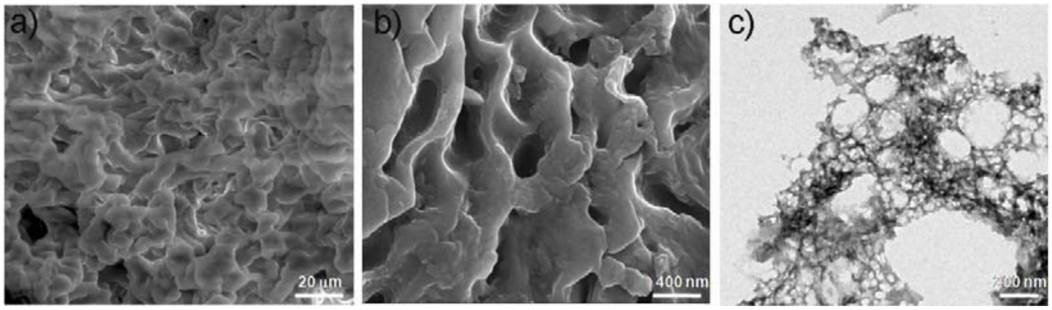


Figure S2. a) ESEM, b) FESEM, c) TEM images of ZAVP xerogel illustrates its fibrillar nature.

S5. Viscoelastic properties

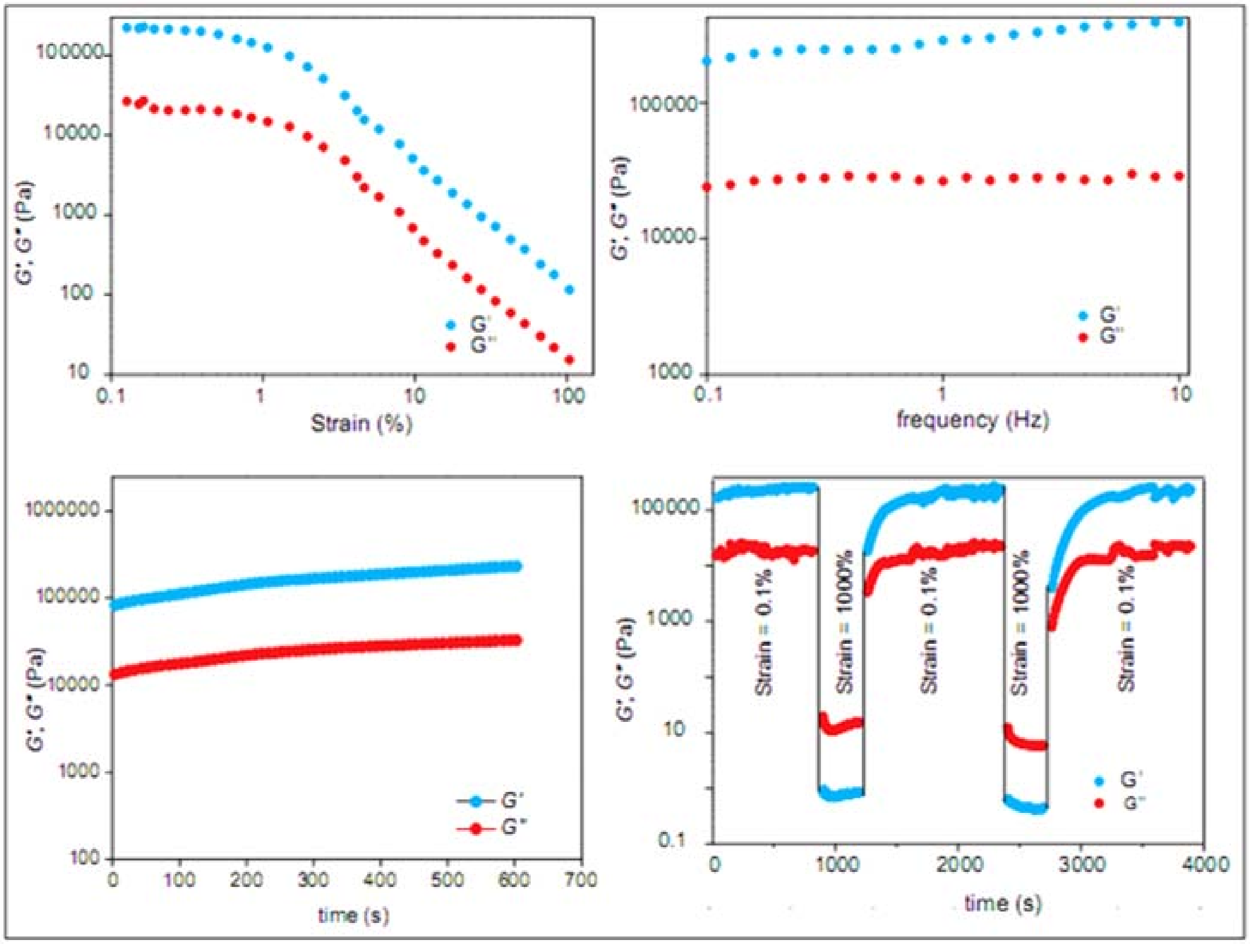


Figure S3. Oscillatory rheology of ZAVP hydrogel prepared at the CGC: a)DSS experiment at constant frequency of 1 Hz, b) DFS experiment at strain = 0.1%, c) DTS experiment at constant strain at 0.1% and frequency constant at 1 Hz c) b) Thixotropy-loop test via continuous step-strain measurements at 0.1 Hz frequency.

S5. MALDI-TOF analysis

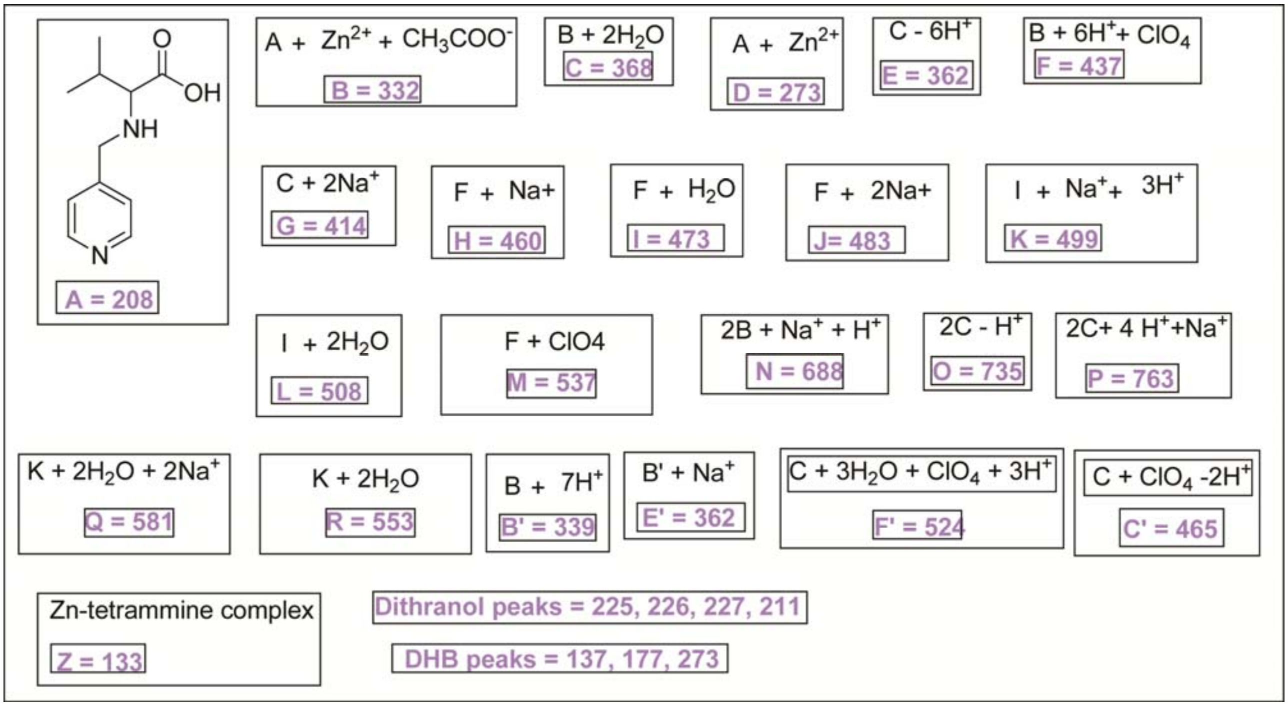


Figure S4. Index of peaks appearing in MALDI-TOF spectra.

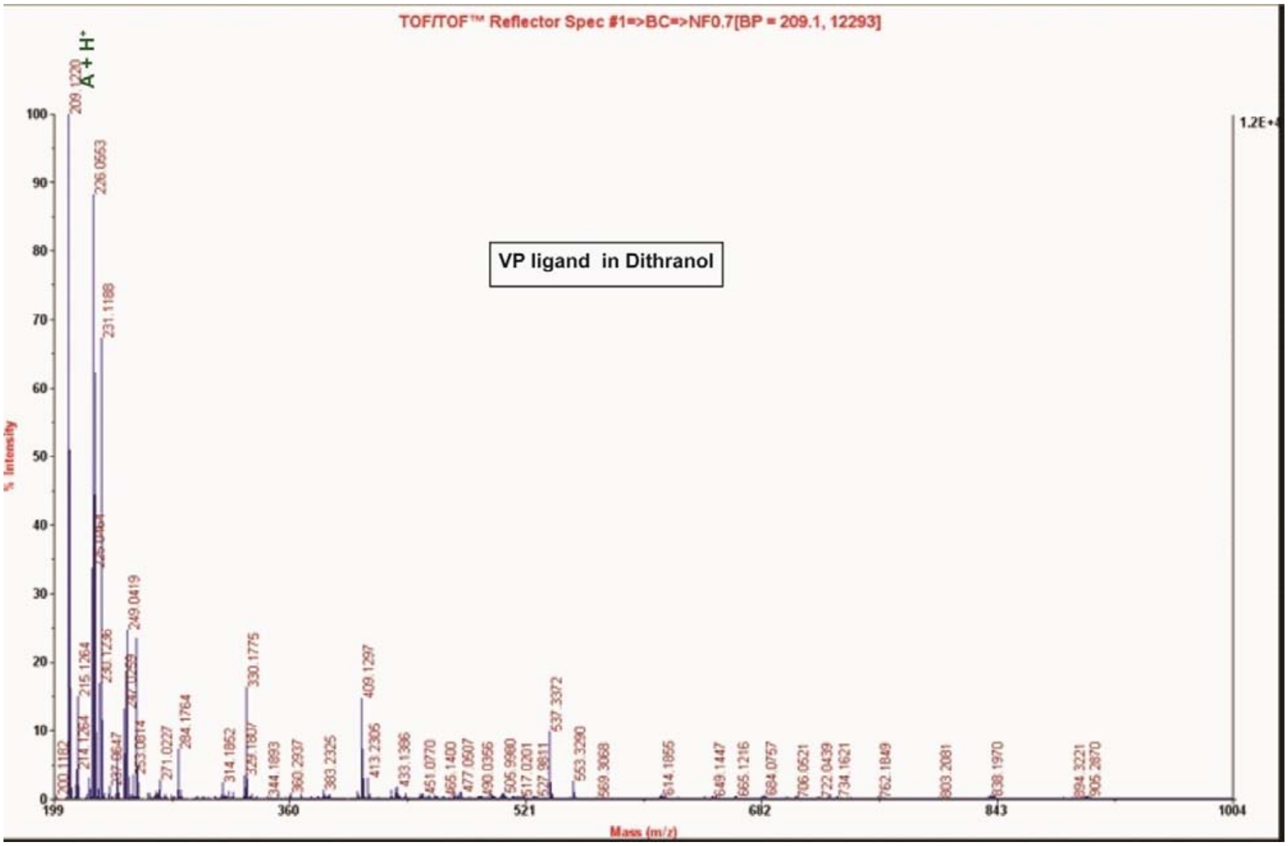


Figure S5. MALDI-TOF spectra of VP ligand in water.

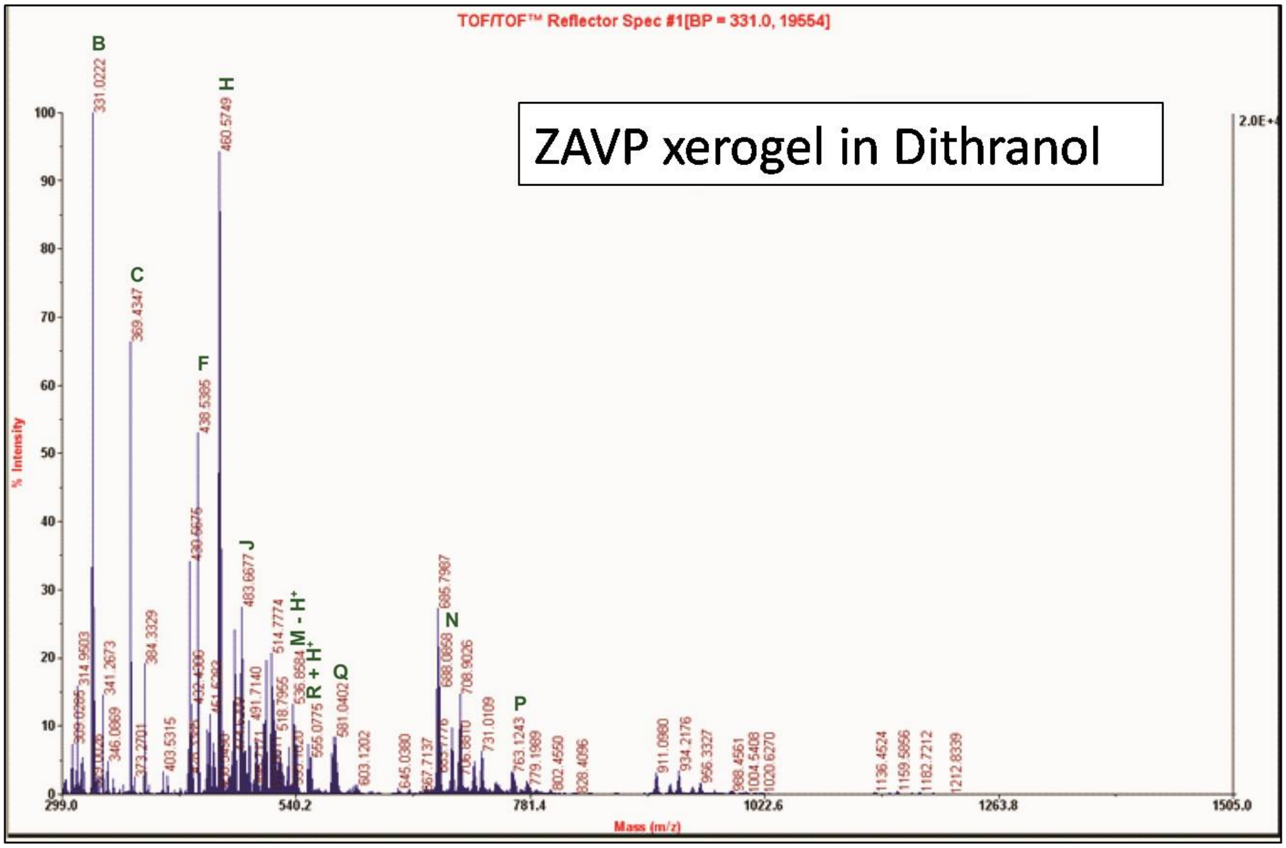


Figure S6. MALDI-TOF spectra of ZAVP xerogel in water (1mg/ml)

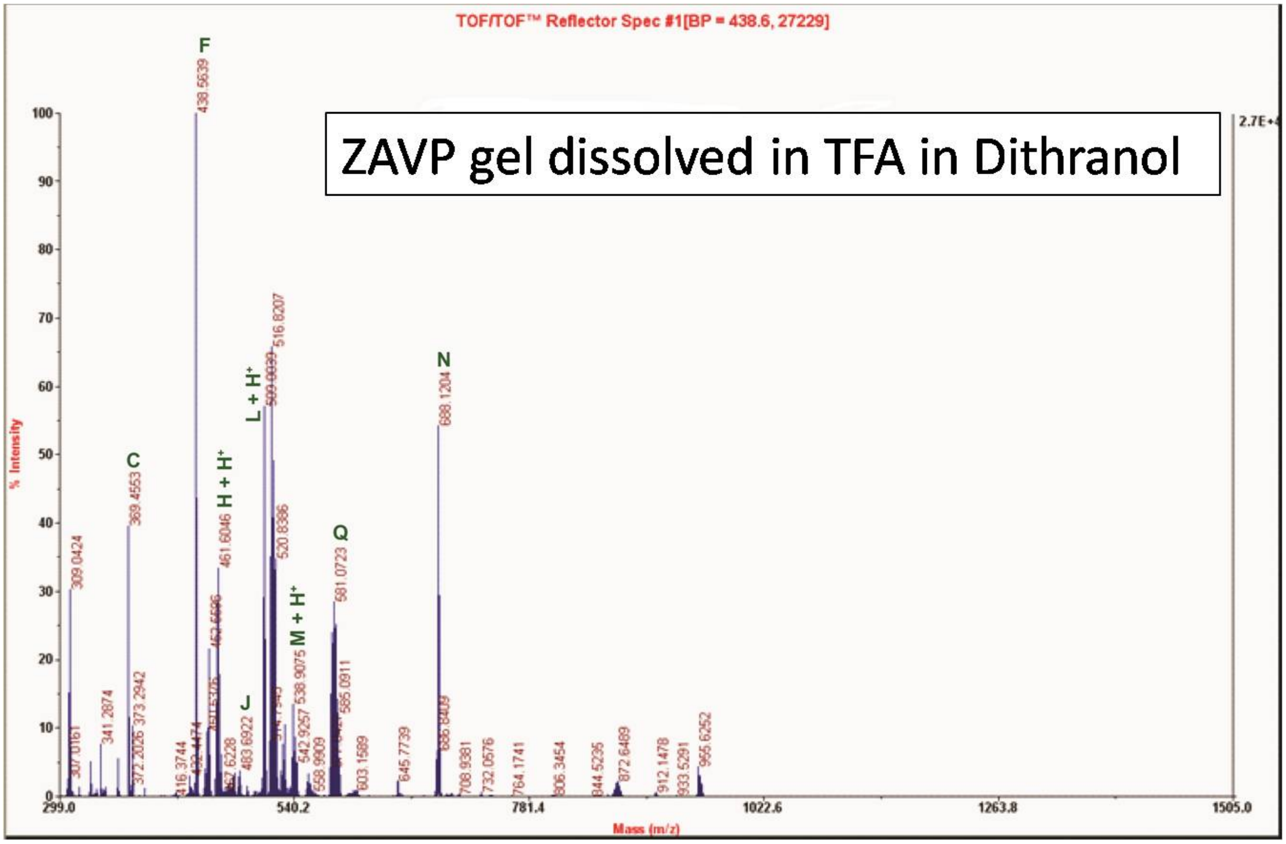


Figure S7. MALDI-TOF spectra of ZAVP gel dissolved in 1M in TFA.

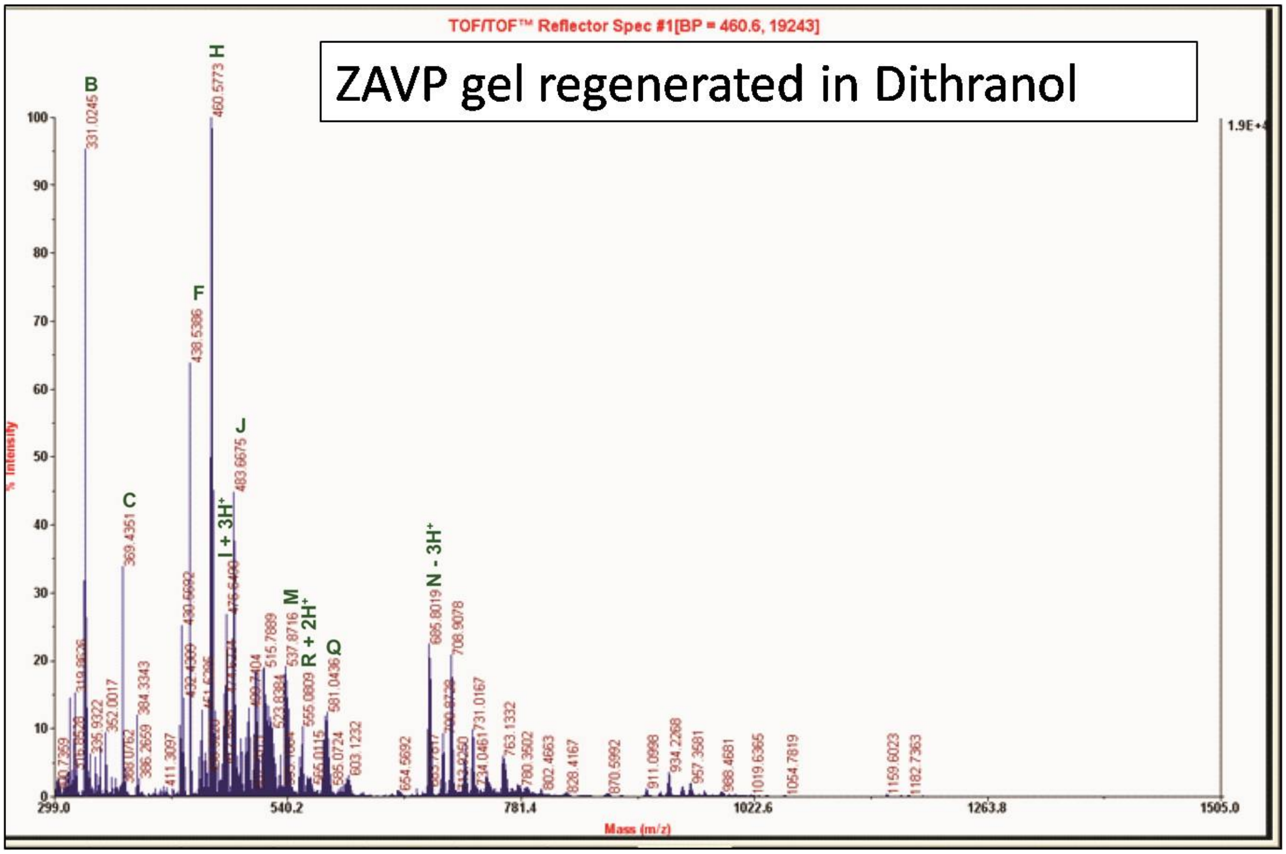


Figure S8. MALDI-TOF spectra of regenerated ZAVP gel form TFA dissolved solution upon addition of liq. Ammonia (1M).

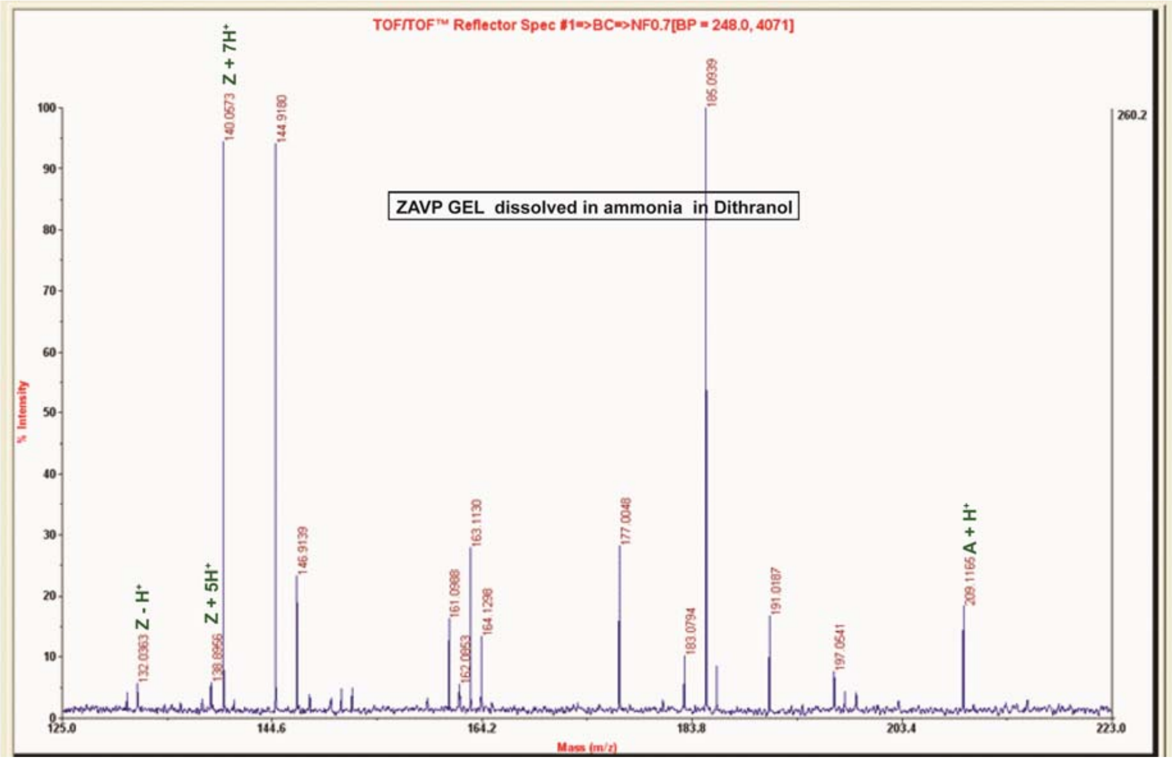


Figure S9. MALDI-TOF spectra of the dissolved ZAVP gel dissolved in liq. ammonia (4M).

S6. Mechanistic considerations.

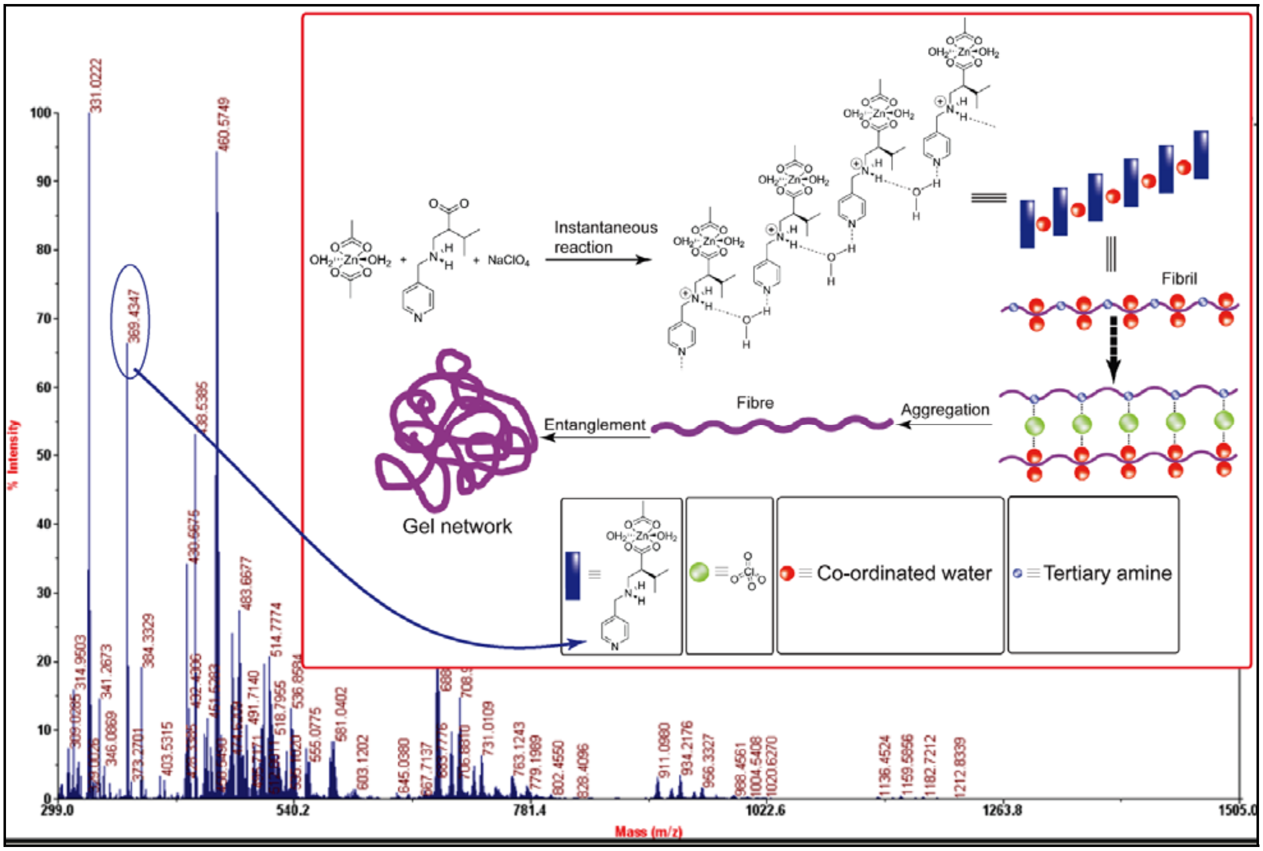


Figure S10. Structure of the gel based on MALDI-TOF data. The interaction between two fibrils has been shown in a simplified way for clarity. Mass (m/z) for the intense peaks at 331,438, 460 and 688 indicates fragments/ aggregates of the Zn- complex (Please see figure S5)

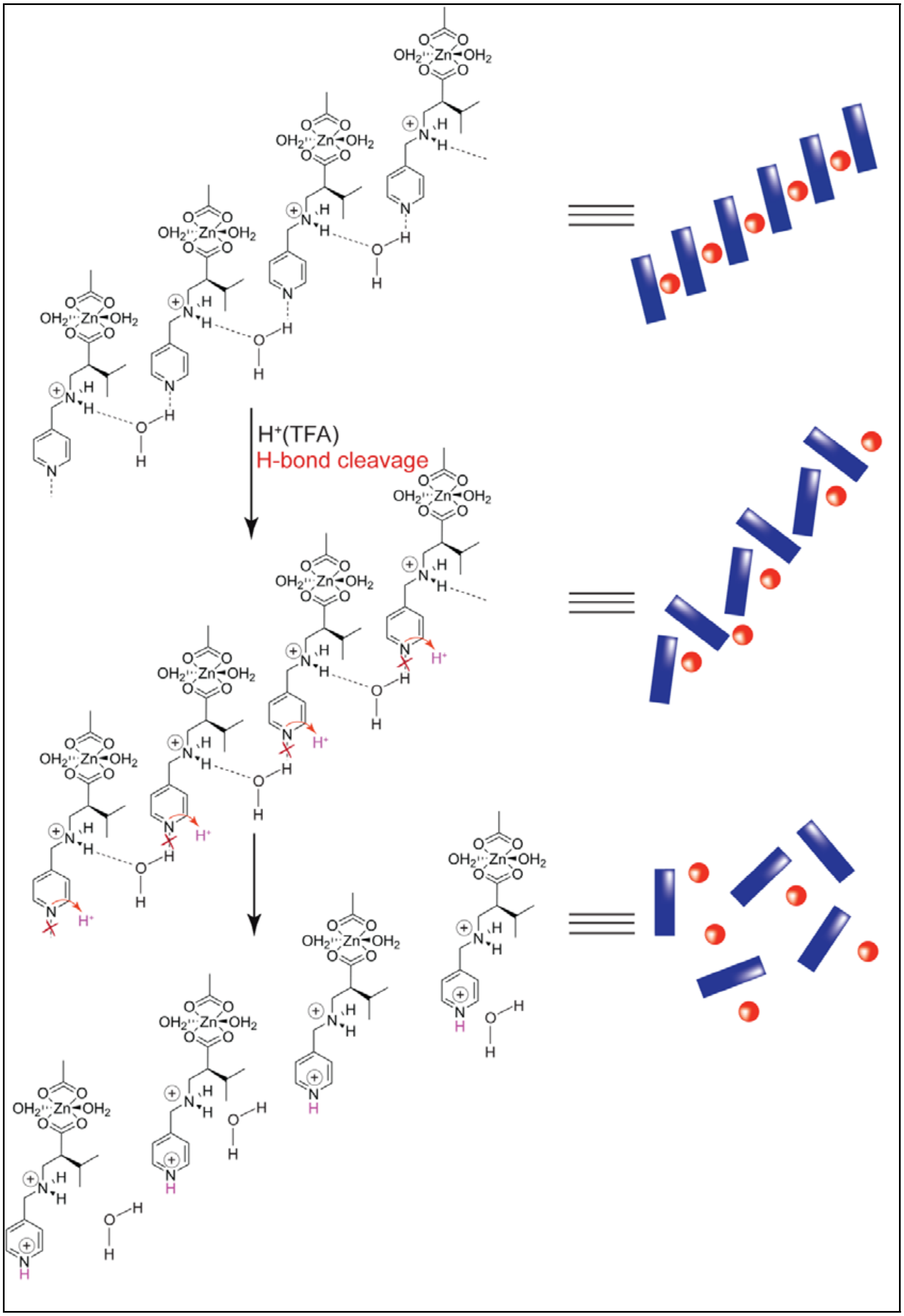


Fig S11. Plausible Dissolution mechanism in presence of 1M TFA.

Plausible explanation: The unique self-healing response and the multiresponsive nature of ZAVP motivated us to investigate the structure of the gelator and nature of the supramolecular forces responsible for their assembly. We were able to determine the molecular weight of the gelator by MALDI-TOF analysis of a dispersion of ZAVP xerogel in water (1 mg/ml). Analysis of the obtained spectra shows the intense peaks appear in the low molecular weight region rather the high molecular weight region (Figure S8) which proves the gelator is low molecular weight (LMW) one, not a co-ordination polymer (co-ordination polymers give prominent peaks at high molecular weight region). After considering all of the intense peaks visible in the LMW region, we could conclude that the peak appearing at 368/369 could be the molecular weight of the gelator (Figure S5 and S6). Based on the components used for the formation of the gel, we proposed the structure of the gelator which is an octahedral Zn^{2+} complex Zn^{2+} in the complex is chelated by the two carboxylates from acetate and the ligand (V) and the two axial positions are occupied by two water molecules (Figure S6 and S12). We have also proposed the mechanism of self-assembly of the gelators. The metal complexes assemble via water molecules by means of H-bonding and form fibrils (Figure S12). These fibrils assemble via H-bonding (perchlorate mediated) to form fiber which eventually entangle to form 3D gel network. This structure of the fibers also accounts for the properties like self-healing and solubility of the gel in acid. Proton from TFA protonates the pyridinic N thereby disrupting water-pyridinic N H-bonding which results degradation of fibril to gelator. Upon addition of liq. ammonia equivalent amount of TFA the gel phase gets restored. When a block of gel is cut, the H-bonding among the gelators/ fibrils gets disrupted. But, if the cut blocks are allowed to attach along the cut surfaces, they reunites to form a single block similar to the original one as the refurbishment of disrupted H-bonding takes place.