Electronic Supplementary Information

Itaconic and citraconic acid directed thixotropic and self-healable supramolecular metallogels of M(II) (M=Co, Cu, Zn, and Cd) for the growth-inhibitory potency against human pathogenic microbes

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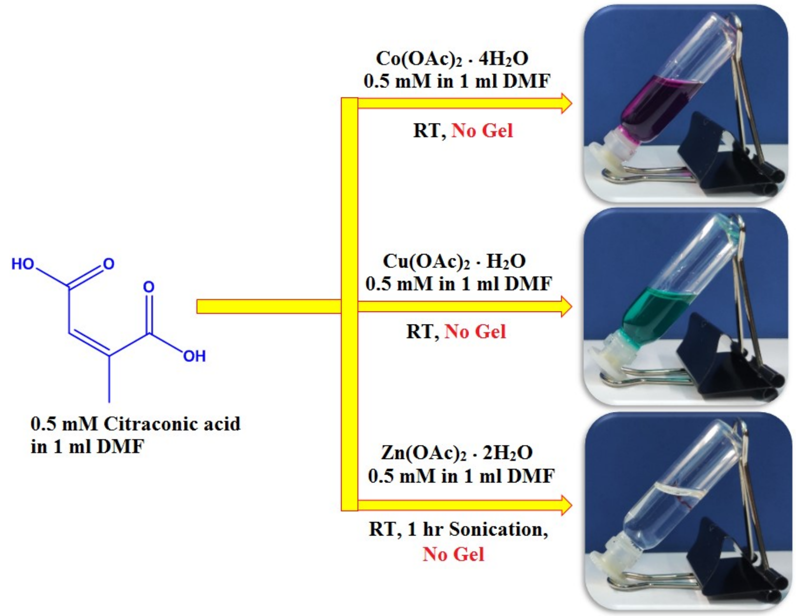
1. Gelation ability of different metal salts with the citraconic acid



Scheme S1. Gelation ability of different metal salts like Co(II) acetate tetrahydrate, Cu(II) acetate monohydrate, Zn(II) acetate dihydrate with the citraconic acid in DMF solvent medium.

2. Gelation ability of Cd(II) metal salt with the itaconic acid

Scheme S2. Gelation ability of Cd(II) acetate dihydrate with the itaconic acid in DMF solvent medium.

3. Minimum Critical Gelation Concentration (MGC) of the synthesized Co-IA, Cu-IA, Zn-IA, and Cd-CA Metallogels

The minimum critical gel concentrations (MGC) of Co-IA, Cu-IA, Zn-IA and Cd-CA metallogels have been evaluated. For all the itaconic acid based metallogels, the concentrations of gel-forming chemical-ingredients i.e. $Co(CH_3COO)_2{\cdot}4H_2O$, $Cu(CH_3COO)_2{\cdot}H_2O$ and $Zn(CH_3COO)_2{\cdot}2H_2O$ and itaconic acid were maintained as 1:1, w/w. Likewise, for the citraconic acid based metallogel, the concentrations of gel-forming chemical-ingredients i.e. $Cd(CH_3COO)_2{\cdot}2H_2O$ and citraconic acid were also maintained as 1:1, w/w. Following this stoichiometric aspect the concentration of metal salt and organic gelator were varied.

The best quality gel of the supramolecular Co-IA metallogel was appeared when the concentration of Co(II)-salt and itaconic acid were taken as 99.6 and 52.0 mg/ml respectively (Table S1 showing the concentrations of gel-forming chemicals and the serial no designated as (i), (ii), (iii), (iv) and (v) are shown in Fig. S1 respectively).

Table S1

Serial No	Metal Concentration (in 1 ml DMF)	Gelator concentration (in 1 ml DMF)	Phase
(i)	12.4 mg/ml	6.5 mg/ml	Sol
(ii)	24.9 mg/ml	13.0 mg/ml	Viscous sol
(iii)	49.8 mg/ml	26.0 mg/ml	More viscous sol
(iv)	74.7 mg/ml	39.0 mg/ml	Weak gel
(v)	99.6 mg/ml	52.0 mg/ml	Gel

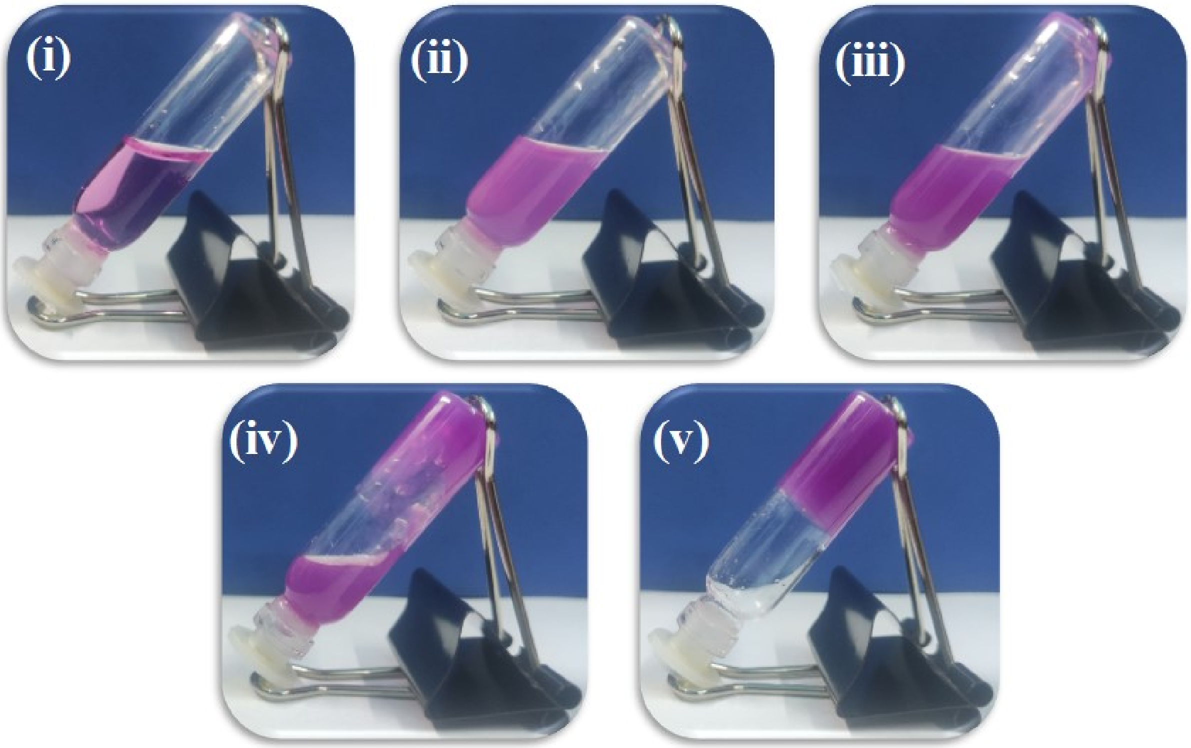


Fig. S1. Determination of Minimum Critical Gelation Concentration of the **Co-IA** metallogel with step-wise photography of **Co-IA** metallogel forming chemical constituents having varied concentrations.

The best quality gel of the supramolecular Cu-IA metallogel was appeared when the concentration of Cu(II)-salt and itaconic acid were taken as 59.9 and 39.0 mg/ml respectively (Table S2 showing the concentrations of gel-forming chemicals and the serial no designated as (i), (ii), (iii), (iv), and (v) are shown in Fig. S2 respectively).

Table S2

Serial No	Metal Concentration (in 1 ml DMF)	Gelator concentration (in 1 ml DMF)	Phase
(i)	9.9 mg/ml	6.5 mg/ml	Sol
(ii)	17.9 mg/ml	11.7 mg/ml	Viscous sol
(iii)	19.9 mg/ml	13.0 mg/ml	More viscous sol
(iv)	39.9 mg/ml	26.0 mg/ml	Weak gel
(v)	59.9 mg/ml	39.0 mg/ml	Gel

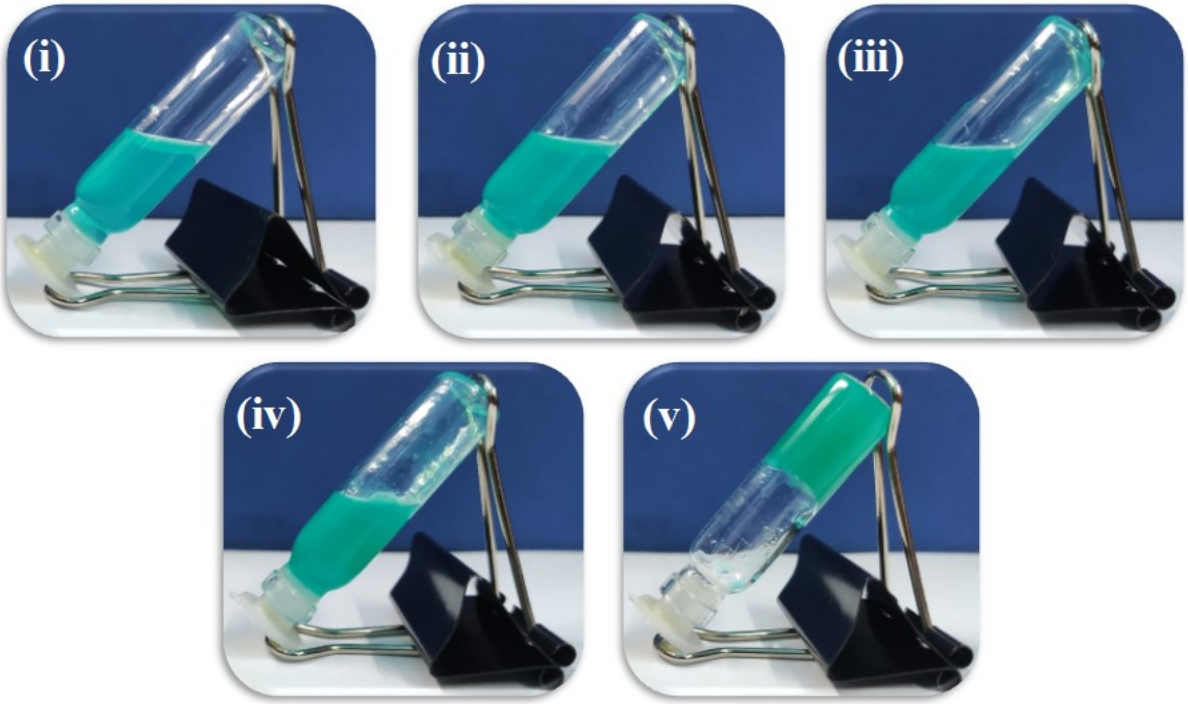


Fig. S2. Determination of Minimum Critical Gelation Concentration of the **Cu-IA** metallogel with step-wise photography of **Cu-IA** metallogel forming chemical constituents having varied concentrations.

The best quality gel of the supramolecular Zn-IA metallogel was appeared when the concentration of Zn(II)-salt and itaconic acid were taken as 329.2 and 195.1 mg/ml respectively (Table S3 showing the concentrations of gel-forming chemicals and the serial no designated as (i), (ii), (iii), (iv), (v), and (vi), are shown in Fig. S3 respectively).

Table S3

Serial No	Metal Concentration (in 1 ml DMF)	Gelator concentration (in 1 ml DMF)	Phase
(i)	21.9 mg/ml	13.0 mg/ml	Sol
(ii)	131.7 mg/ml	78.0 mg/ml	Viscous sol
(iii)	219.5 mg/ml	130.1 mg/ml	Weak gel
(iv)	263.4 mg/ml	156.1 mg/ml	Weak gel
(v)	329.2 mg/ml	195.1 mg/ml	Gel

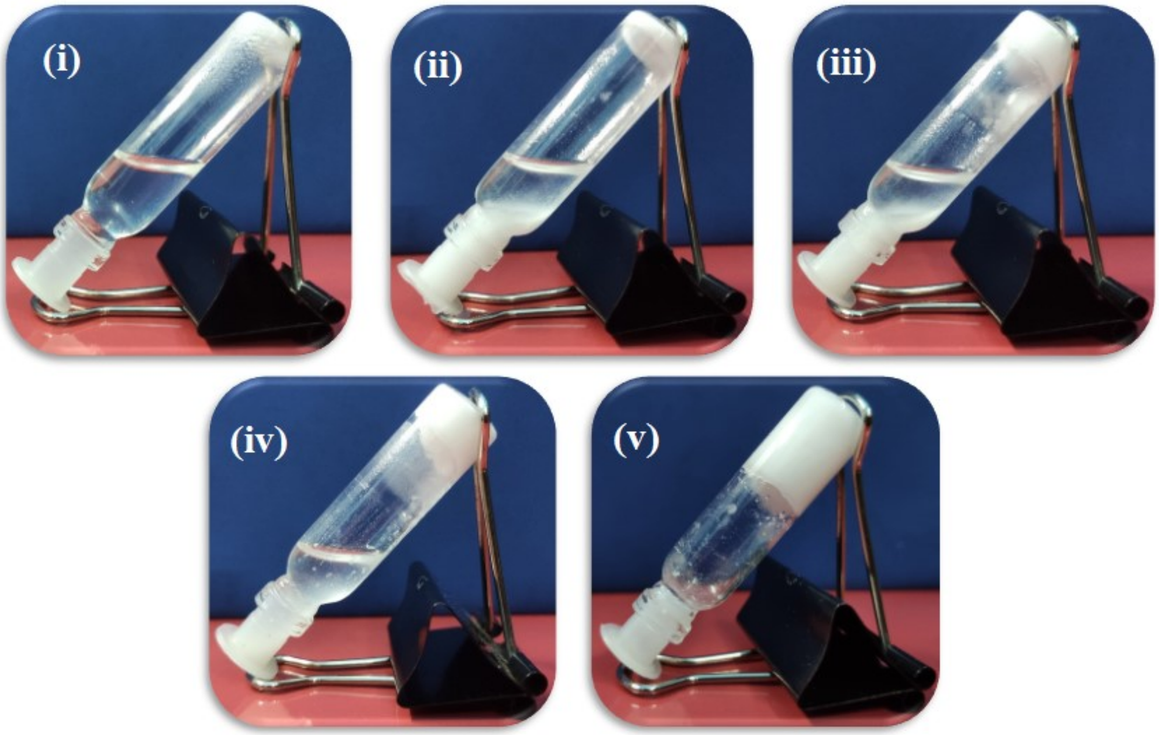


Fig. S3. Determination of Minimum Critical Gelation Concentration of the **Zn-IA** metallogel with step-wise photography of **Zn-IA** metallogel forming chemical constituents having varied concentrations.

The best quality gel of the supramolecular Cd-CA metallogel was appeared when the concentration of Cd(II)-salt and citraconic acid were taken as 10.6 and 5.2 mg/ml respectively (Table S4 showing the concentrations of gel-forming chemicals and the serial no designated as (i), (ii), (iii) and (iv) are shown in Fig.S4,respectively).

Table S4

Serial No	Metal Concentration (in 1 ml DMF)	Gelator concentration (in 1 ml DMF)	Phase
(i)	2.6 mg/ml	1.3 mg/ml	Sol
(ii)	5.3 mg/ml	2.6 mg/ml	More viscous sol
(iii)	7.9 mg/ml	3.9 mg/ml	Weak gel
(iv)	10.6 mg/ml	5.2 mg/ml	Gel

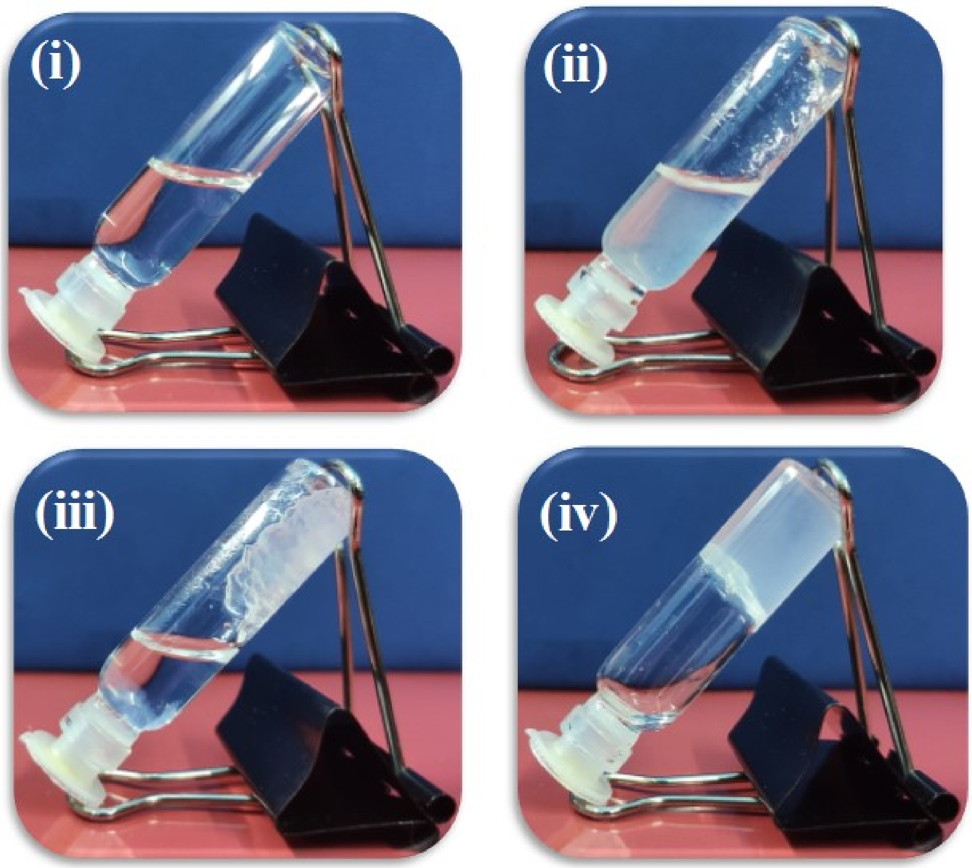


Fig. S4. Determination of Minimum Critical Gelation Concentration of the **Cd-CA** metallogel with step-wise photography of **Cd-CA** metallogel forming chemical constituents having varied concentrations.

4. Testing of gelation ability of different solvents in forming stable metallogels of Co-IA, Cu-IA, Zn-IA, and Cd-CA

The role of diverse solvents ranging from polar to non-polar categories was tested to get the stable metallogels of Co-IA, Cu-IA, Zn-IA, and Cd-CA. Solvents like water, DMSO, acetonitrile, THF, chloroform, ethyl acetate, methanol, ethanol, dichloromethane, acetic acid, acetone, and petroleum ether are being involved in testing the gelation capability. The stoichiometric quantity of gel-constituting chemical agents like metal salts and the gelators were retained as per the minimum critical gelation concentrations for the every solvent directed metallogelation studies for each metallogels respectively. The gelation process mentioned in the experimental section has been adopted for every solvent-directed attempt. The 'inversion-vial' has been accomplished for individual cases and the outcome of individual solvent-based experiments is collected in Fig. S5, Fig. S6, Fig. S7 and Fig. S8 for Co-IA, Cu-IA, Zn-IA and Cd-CA metallogels respectively. The experimental outcome clearly confirms that DMF is the optimum solvent to achieve the stable Co-IA, Cu-IA, Zn-IA and Cd-CA metallogels under ambient experimental conditions.

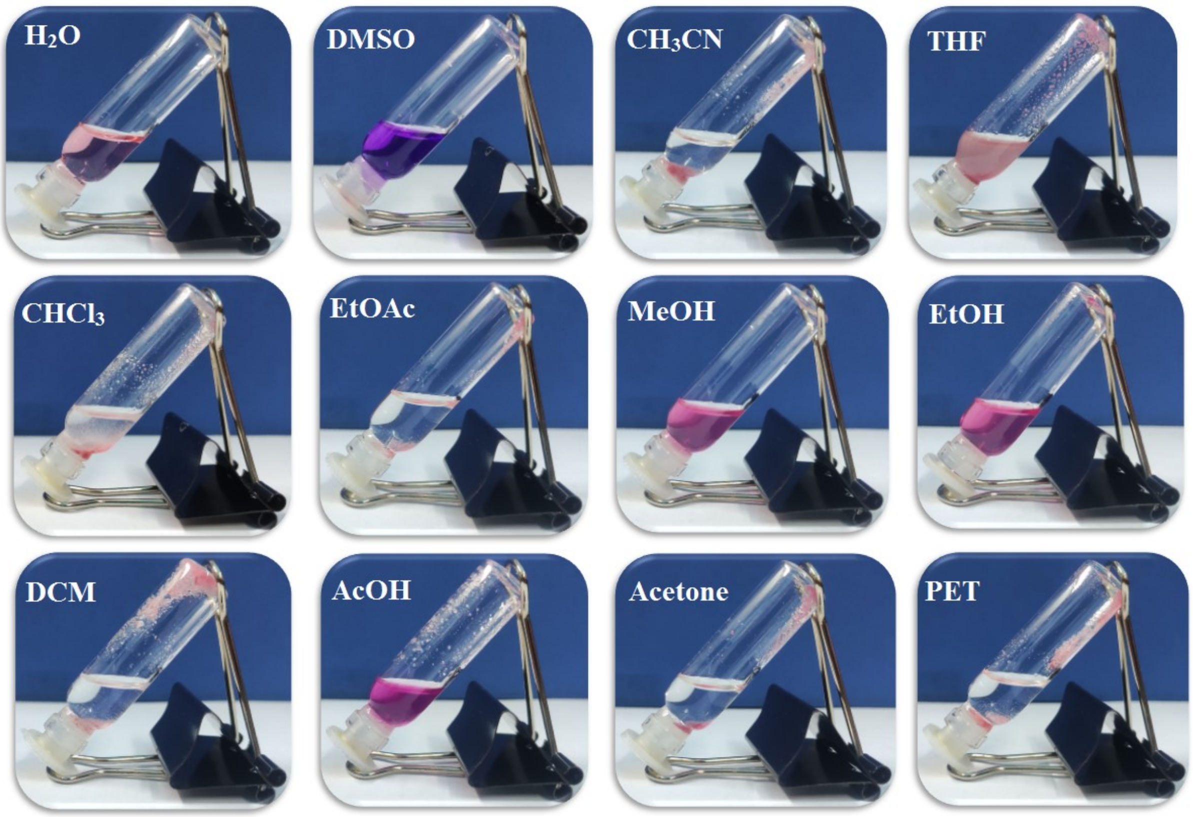


Fig. S5. Role of versatile solvents in forming stable metallogel of **Co-IA**.

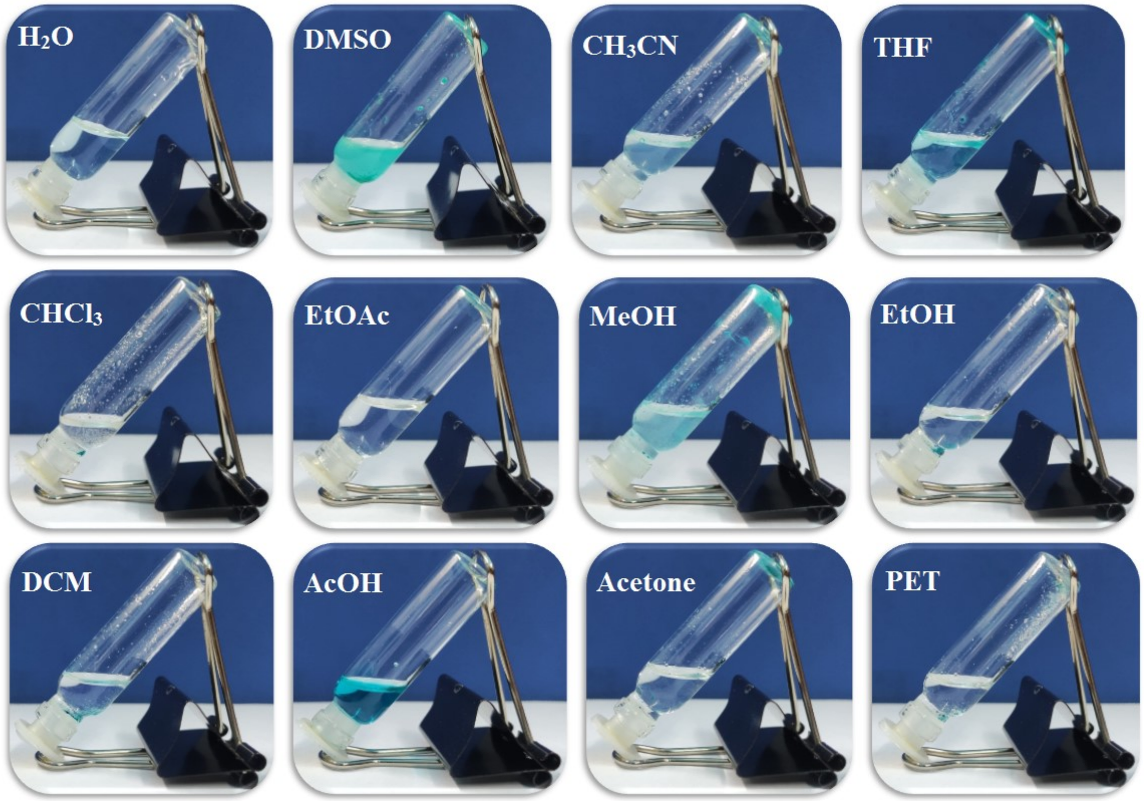


Fig. S6. Role of versatile solvents in forming stable metallogel of **Cu-IA**.

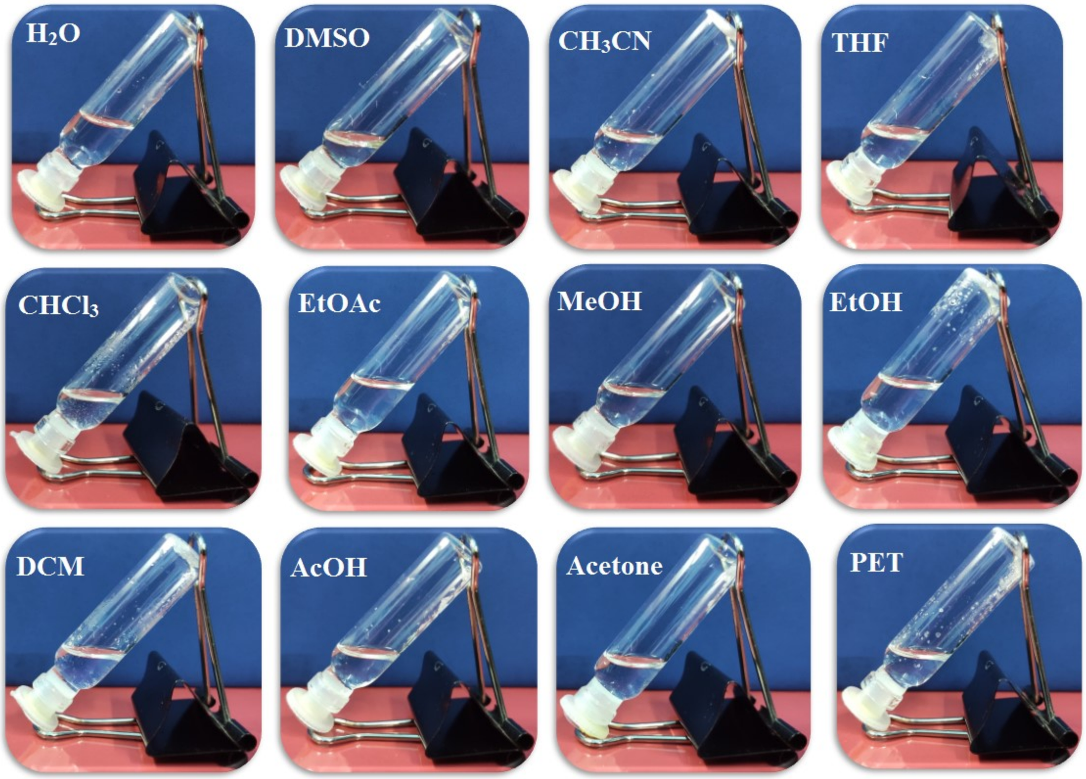


Fig. S7. Role of versatile solvents in forming stable metallogel of **Zn-IA**.

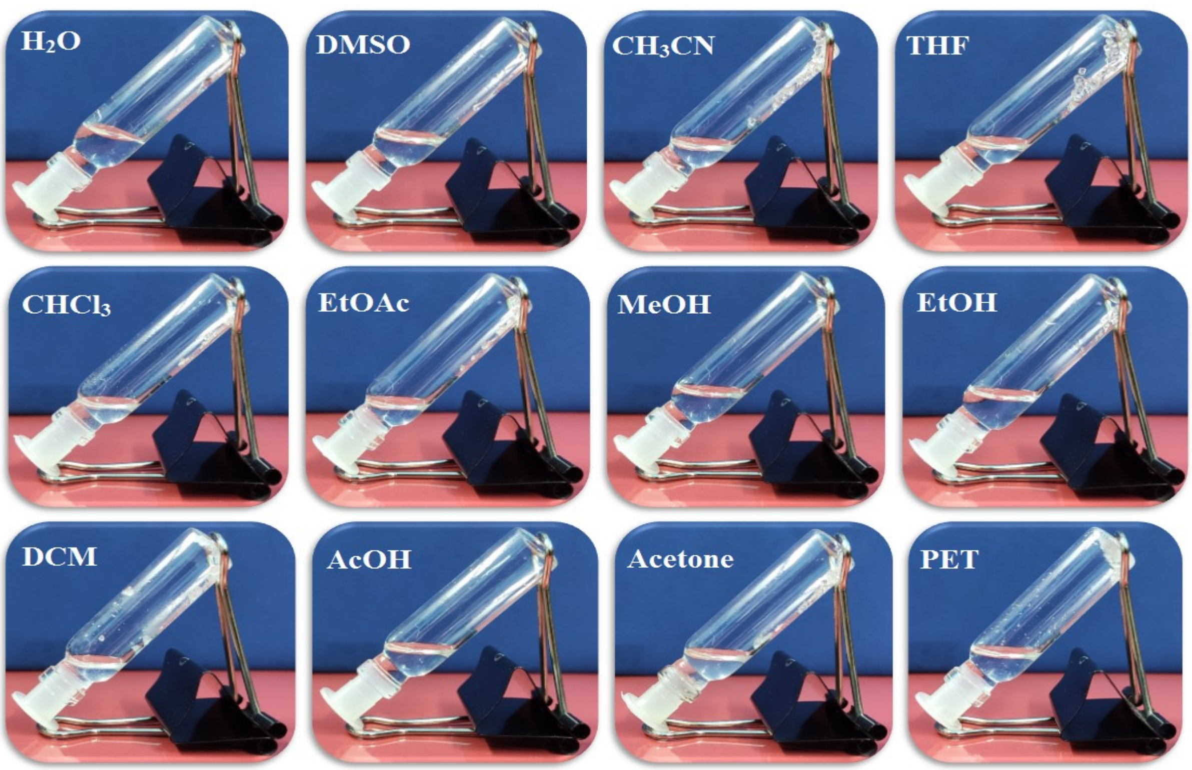


Fig. S8. Role of versatile solvents in forming stable metallogel of **Cd-CA**.

5. FT-IR Analysis

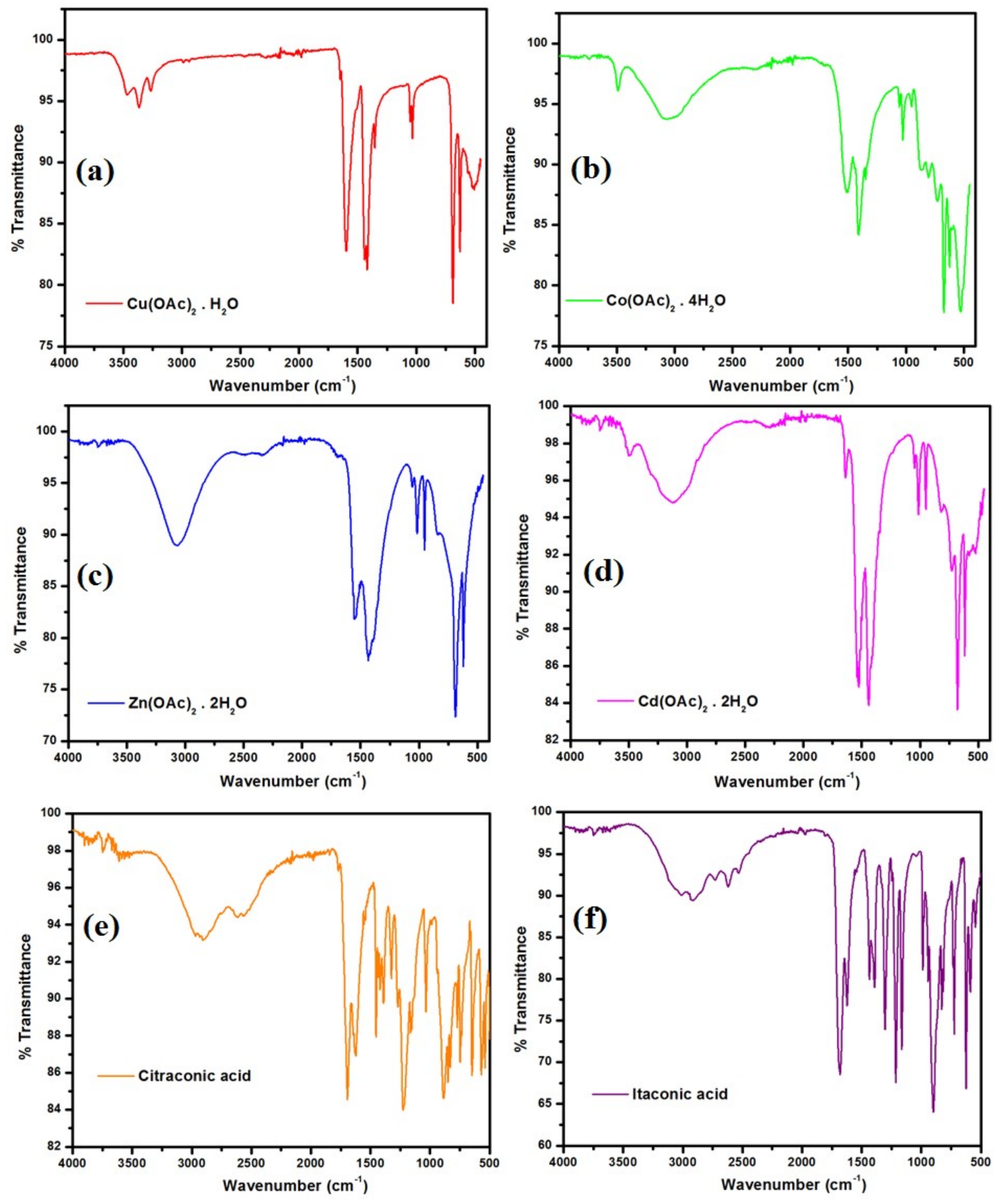


Fig. S9. Infrared Spectral data of the gel-forming chemical-ingredients involving (a) Copper acetate monohydrate, (b) Cobalt acetate tetrahydrate (c) Zinc acetate dihydrate (d) Cadmium acetate dihydrate (e) Citraconic acid, and (f) Itaconic acid.

6. UV-Vis spectroscopic Study

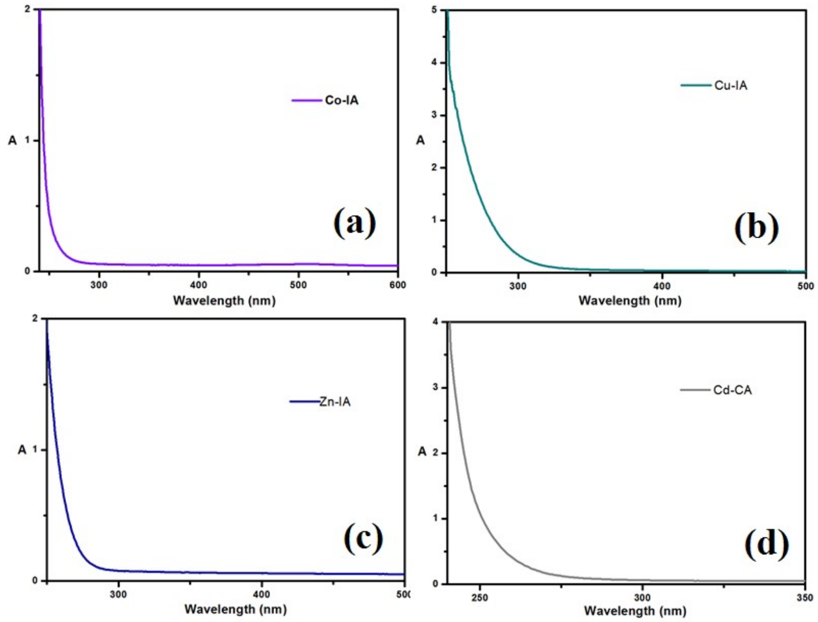


Fig. S10. Representation of UV-Vis Spectral data of (a) Co-IA (b) Cu-IA, (c) Zn-IA and (d) Cd-CA metallogel solutions. The peaks at around 250 nm, 275 nm, 270 nm and 250 nm for Co-IA (1.3 mg/ml), Cu-IA (2.5 mg/ml), Zn-IA (2.2 mg/ml) and Cd-CA (2.0 mg/ml), respectively, are observed. These might be due to the n-π^* and/or π-π^* transitions of water solution of metallogels.

7. ESI-Mass spectroscopic Study

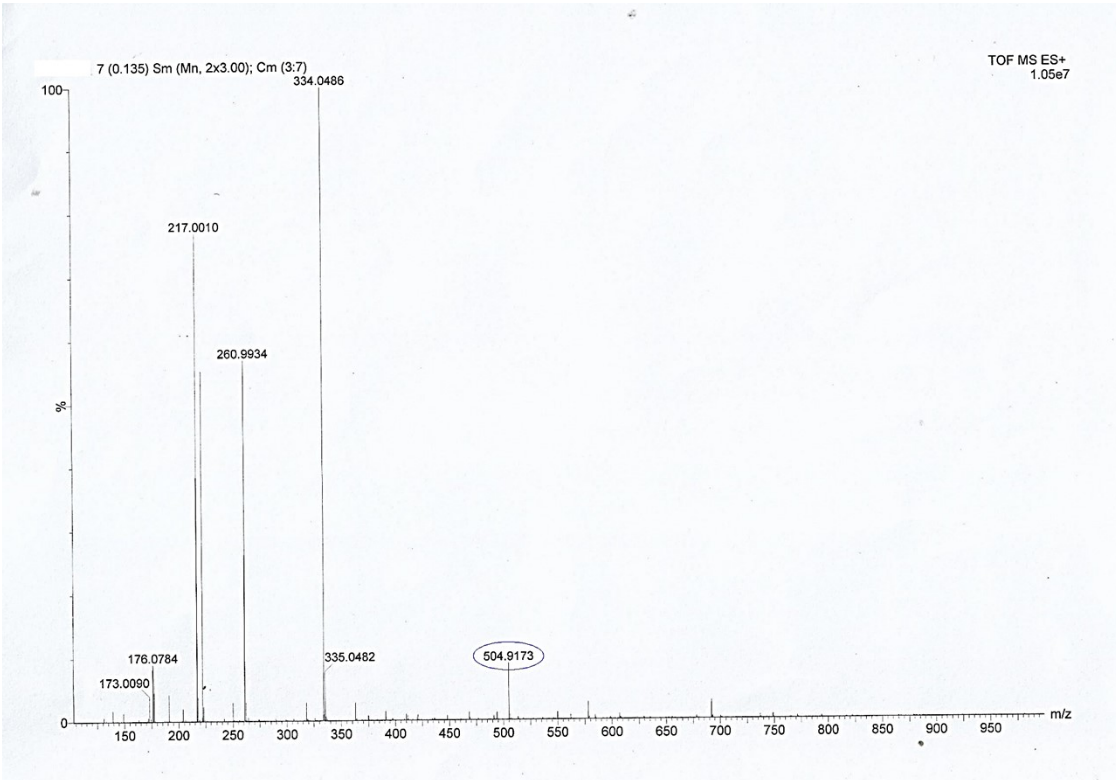


Fig. S11. The ESI-Mass spectral analysis of Co-IA metallogel.

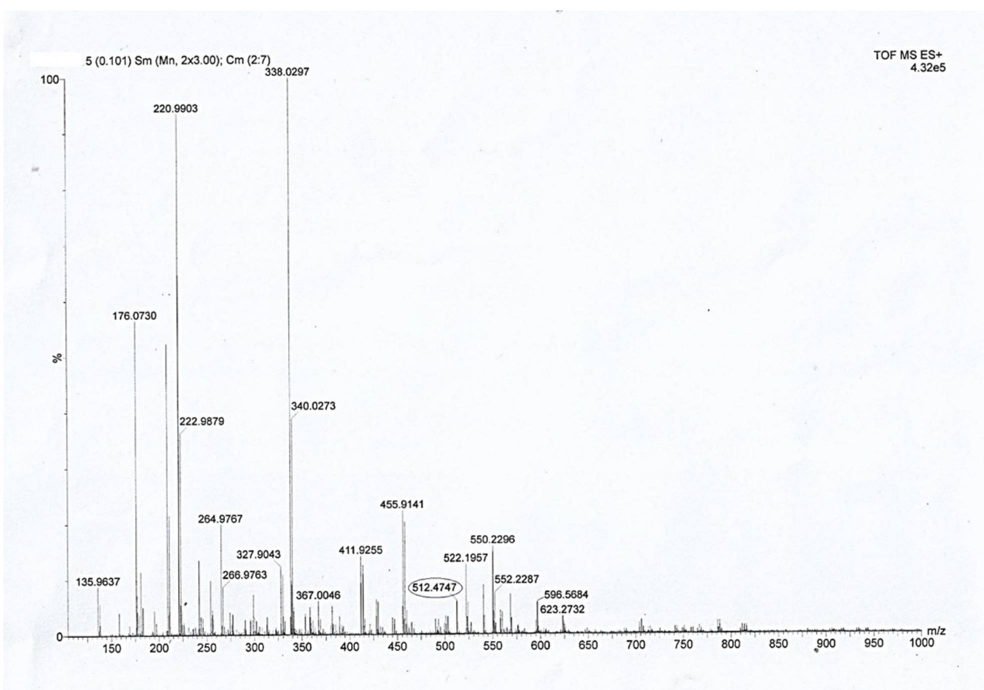


Fig. S12. The ESI-Mass spectral analysis of Cu-IA metallogel.

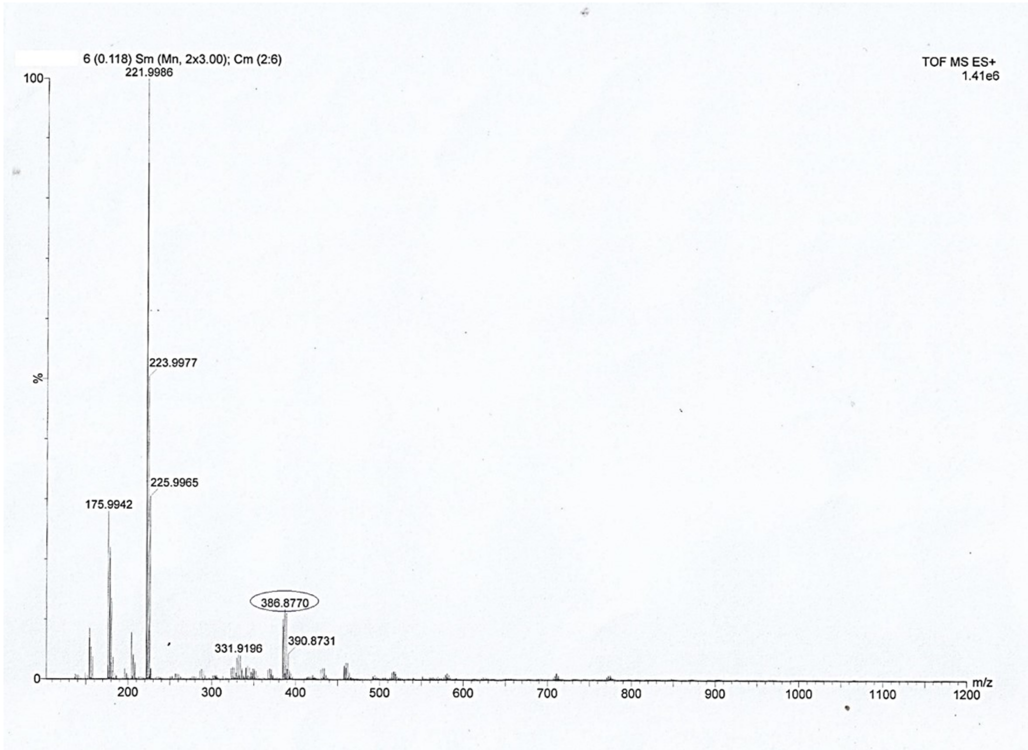


Fig. S13. The ESI-Mass spectral analysis of Zn-IA metallogel.

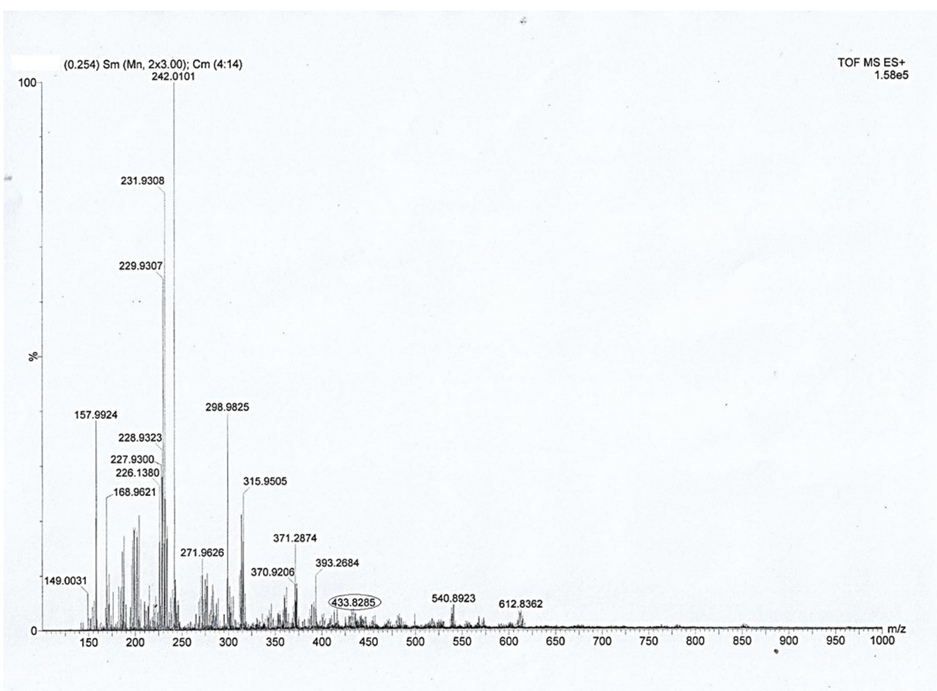
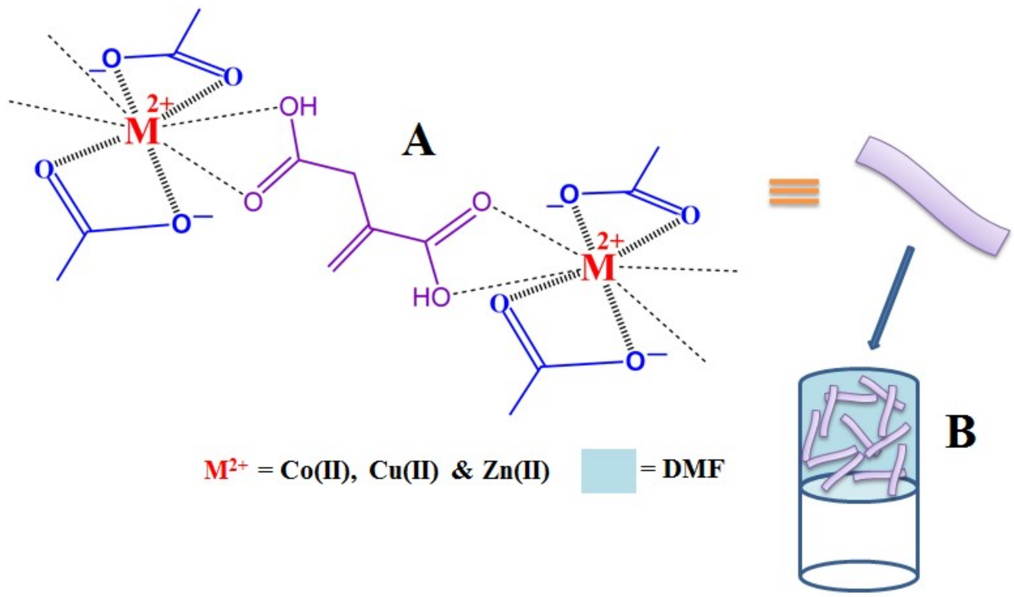
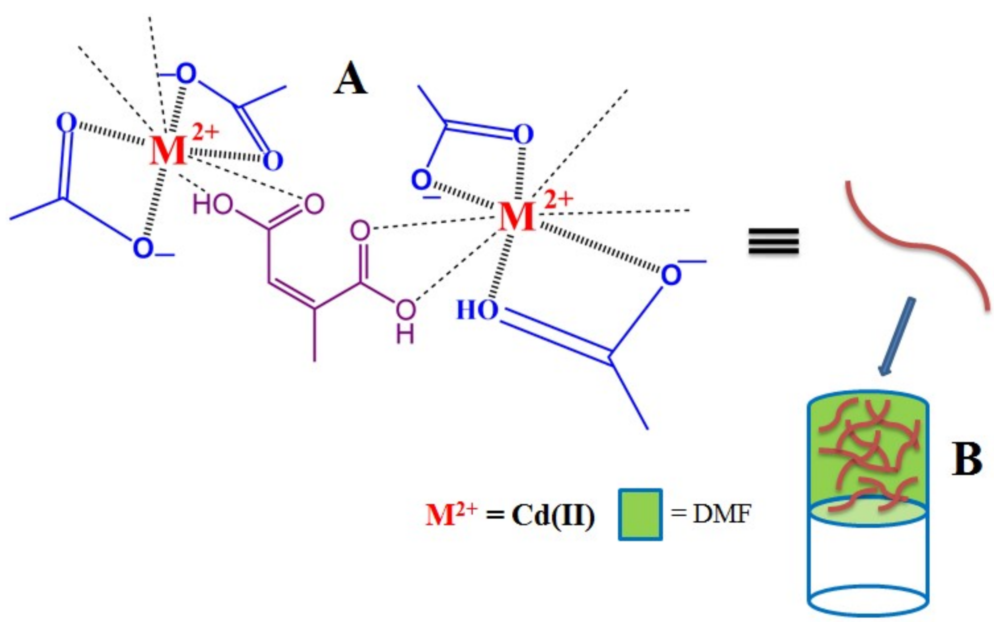


Fig. S14. The ESI-Mass spectral analysis of Cd-CA metallogel.

8. Plausible formation strategies of itaconic and citraconic acid based metallogels (Co-IA, Cu-IA, Zn-IA and Cd-CA)



Scheme S3. Plausible construction strategy of itaconic acid based metallogels in DMF (Co-IA, Cu-IA and Zn-IA). (A and B stand for the proposed network and the inverted image of metallogels in vial, respectively.).



Scheme S4. Plausible construction strategy of citraconic acid based metallogel in DMF (Cd-CA). (A and B stand for the proposed network and the inverted image of metallogel in vial, respectively.).

9. PXRD analysis

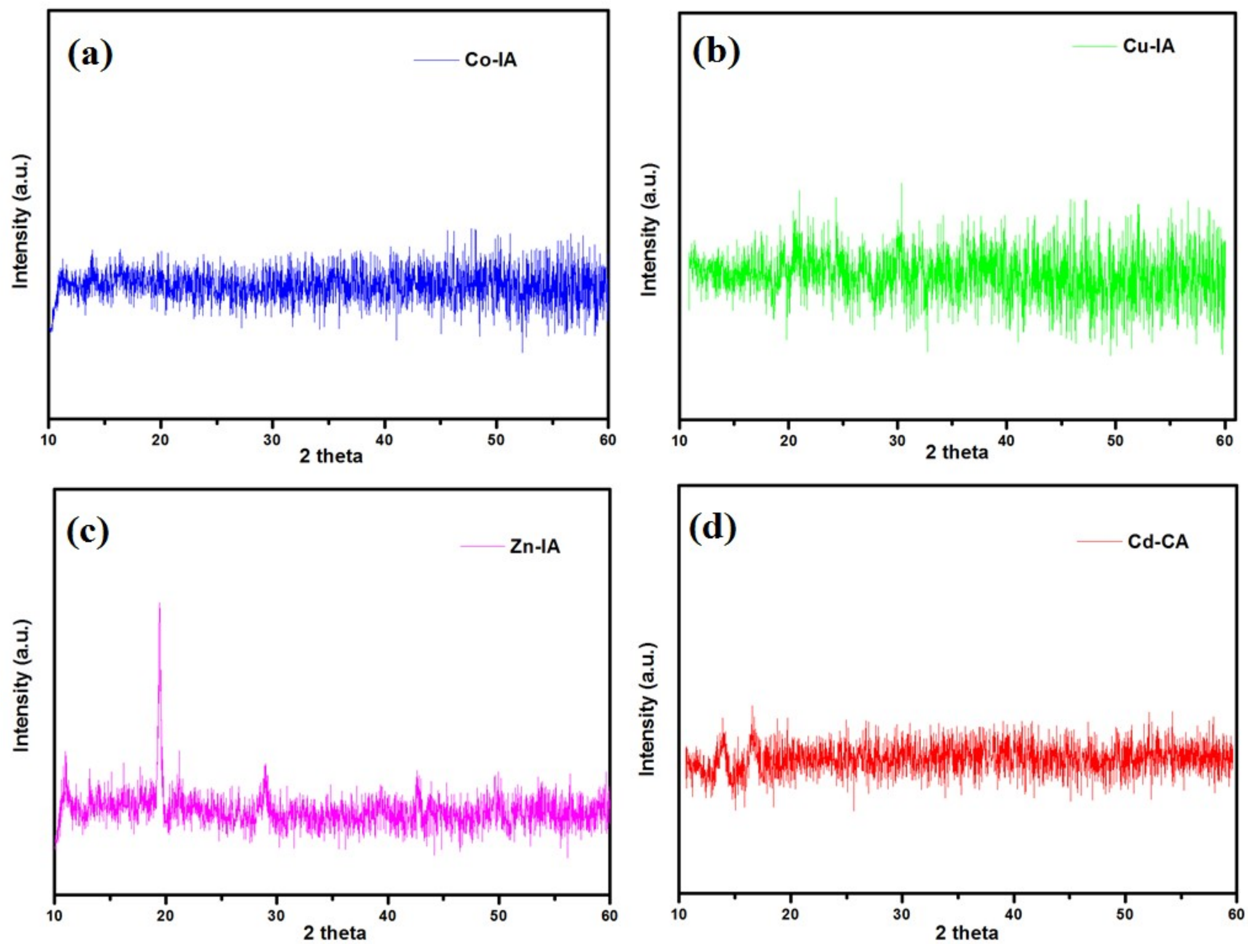


Fig. S15. Powder X-Ray diffraction (PXRD) studies of the xerogel-forms of (a) Co-IA, (b) Cu-IA, (c) Zn-IA, and (d) Cd-CA metallogels.

10. Assessment of inhibitory potential of individual metallogel forming precursors against potent pathogenic microorganisms

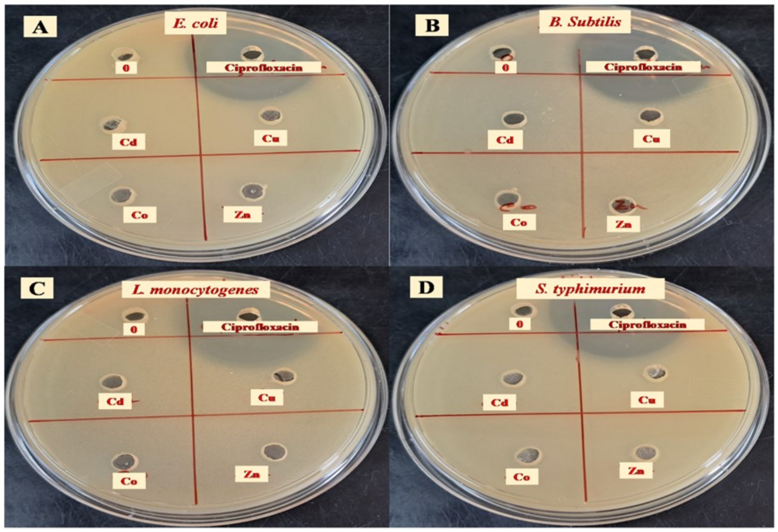


Fig. S16. Effect of all four metallic salts on the bacterial growth, *E. coli* (A), *B. subtilis* (B), *L. monocytogenes* (C), and *S. typhimurium* (D).

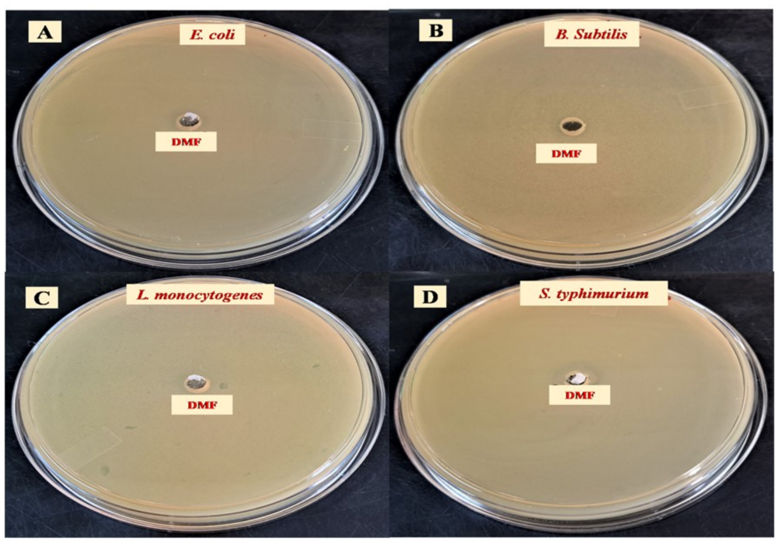


Fig. S17. Effect of all DMF on the bacterial growth, *E. coli* (A), *B. subtilis* (B), *L. monocytogenes* (C), and *S. typhimurium* (D).

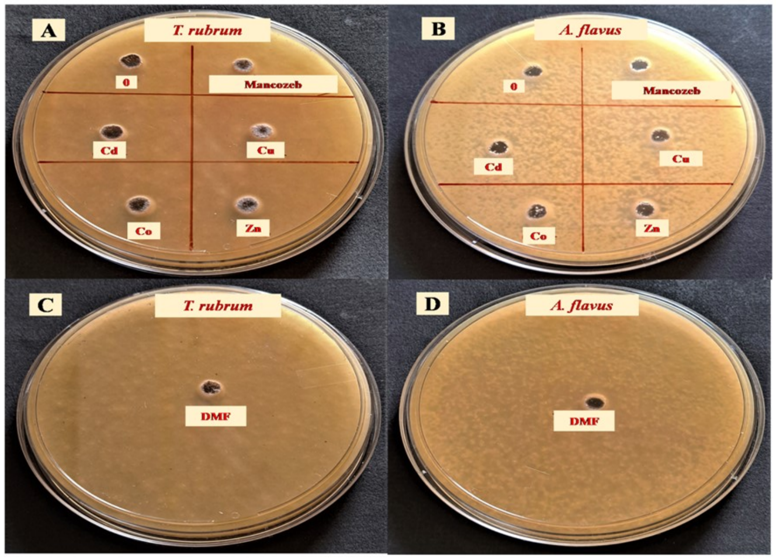


Fig. S18. Effect of all four metallic salts on the fungal growth, *T. Rubrum* (A), and *A. flavus* (B), and inhibitory effect of DMF on fungal growth *T. Rubrum* (C), and *A. flavus* (D).