

Electronic Supplementary Information†

Multistimuli-Responsive Self-Healable Supramolecular Copper(II)-Metallogel Derived from L-(+) Tartaric Acid: An efficient Schottky barrier diode†

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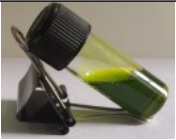







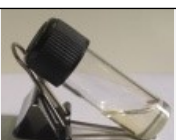


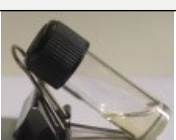

‡SD and SKO should be treated as joint first authors.

Table S1. Molar ratios of Copper acetate (CuA) : Tartaric acid for gelation in DMF

Entry	Copper Acetate : Tartaric Acid (mM)	Total Vol	Phase^a	Picture
1.	0.5:0.5	1ml	S	
2.	0.5:1.0	1ml	PG	
3.	1.0:0.5	1ml	S	
4.	1.0:1.0	1ml	PG	
5.	1.0:1.5	1ml	PG	
6.	1.0:2.0	1ml	G	

^aG: gel; PG: partial gel; S: sol.

Table S2. Effect of the copper salts with different counter-anions on the gelation ability of CuA-Tar metallogel system^a













Entry	Metal Salt	[Metal Salt]	[Ligand]	Vol ^b	Phase	Picture
1.	 CuCl ₂ ·2H ₂ O	1 mM	 2mM	1mL	S	
2.	 Cu(NO ₃) ₂ ·3H ₂ O	1 mM	 2mM	1mL	S	
3.	 CuSO ₄ ·5H ₂ O	1 mM	 2mM	1mL	S	
4.	 Cu(OH) ₂	1 mM	 2mM	1mL	P	
5.	 CuCl ₂	1 mM	 2mM	1mL	S	





Abbreviations: S, solution; P, precipitates. ^aGelation tests were performed as described in the Experimental Section. ^bTotal volume of solvent.

Gelation ability Procedure of CuA-Tar metallogel in different solvents:

The gelation ability procedure of Copper(II) acetate monohydrate and tartaric acid, was tested in different solvents maintaining the minimum critical gel concentration of CuA-Tar metallogel from the synthetic method of CuA-Tar metallogel, described in the experimental section.^a The gel formation strategy of CuA-Tar metallogel in different solvents were checked by ‘inversion of the vial’ test. The experimental result (Table S3) clearly revealed that the Copper(II) acetate monohydrate and tartaric acid based mechanically stable CuA-Tar metallogel can exclusively form in DMF solvent medium (Fig. 1).




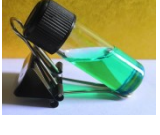





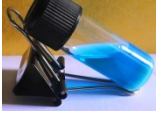


Table S3. Gelation process of CuA-Tar metallogel^a with $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ in various solvents^b

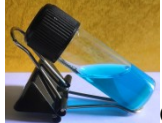


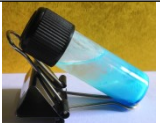
Entry	Solvent ^b	Phase	Conc. ^c	Vol. ^d	Gelation Time ^e	Gel-Phase Colour ^f	Picture
1.	 Xylene	I	500	1	-	-	
2.	 MSO	S	500	1	15min	Blue	
3.	 1-Propanol	I	1200	1	-	-	
4.	 n-Octanol	I	500	1	-	-	
5.	 acetone	S	500	1	15min	Blue	
6.	 MeOH	S	500	1	15min	Blue	

7.	 CH ₃ CN	P	500	1	15min	Blue	
8.	 C cyclohexane	I	500	1	-	-	

^aGelation tests were performed as discussed in the Experimental Section: Cu(OAc)₂·H₂O (0.199 g, 1 mmol) in DMF (500 μl) and tartaric acid (0.300 g, 2 mmol) in DMF (500 μl). The temperature of the ultrasonic bath was 30 ± 2 during the sonication. ^bSolvent abbreviations: CH₃CN = Acetonitrile, DMSO = Dimethyl sulfoxide, MeOH = Methanol. ^cMinimum Gelation Concentration (MGC) of CuA-Tar metallogel is 500 mg mL⁻¹. ^dTotal volume of the solvents. ^eAll gels were completely opaque. ^fAbbreviations: S = Solution; I = insoluble; P = precipitate.

Table S4. Gelation process of CuA-Tar metallogel^a with Cu(NO₃)₂·3H₂O in various solvents^b





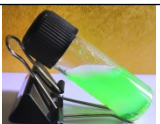




Entry	Solvent ^b	Phase	Conc. ^c	Vol. ^d	Gelation Time ^e	Gel-Phase Colour ^f	Picture
1.	 Xylene	I	500	1	-	-	
2.	 D MSO	S	500	1	15min	Blue	
3.	 1-Propanol	I	1200	1	-	-	
4.	 n-Octanol	I	500	1	-	-	
5.	 A cetone	S	500	1	15min	Blue	
6.	 MeOH	S	500	1	15min	Blue	





7.	 C H ₃ CN	S	500	1	15min	Blue	
8.	 C cyclohexane	I	500	1	-	-	

^aGelation tests were performed as discussed in the Experimental Section: Cu(NO₃)₂·3H₂O (0.241 g, 1 mmol) in DMF (500 μl) and tartaric acid (0.300 g, 2 mmol) in DMF (500 μl). The temperature of the ultrasonic bath was 30 ± 2 during the sonication.

^bSolvent abbreviations: CH₃CN = Acetonitrile, DMSO = Dimethyl sulfoxide, MeOH = Methanol. ^cMinimum Gelation Concentration (MGC) of CuA-Tar metallo gel is 500 mg mL⁻¹. ^dTotal volume of the solvents. ^eAll gels were completely opaque. ^fAbbreviations: S = Solution; I = insoluble; P = precipitate.



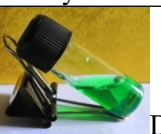






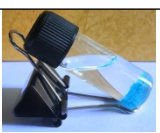


Table S5. Gelation process of CuA-Tar metallo gel^a with CuCl₂·2H₂O in various solvents^b





Entry	Solvent ^b	Phase	Conc. ^c	Vol. ^d	Gelation Time ^e	Gel-Phase Colour ^f	Picture
1.	 D Xylene	I	500	1	-	-	
2.	 D MSO	S	500	1	15min	Blue	
3.	 A 1-Propanol	I	1200	1	-	-	
4.	 A n-Octanol	I	500	1	-	-	
5.	 A cetone	S	500	1	15min	Blue	
6.	 A MeOH	S	500	1	15min	Blue	

7.	 CH ₃ CN	P	500	1	15min	Blue	
8.	 Cyclohexane	S	500	1	15min	Blue	

^aGelation tests were performed as discussed in the Experimental Section: CuCl₂·2H₂O (~0.171 g, 1 mmol) in DMF (500 μl) and tartaric acid (0.300 g, 2 mmol) in DMF (500 μl). The temperature of the ultrasonic bath was 30 ± 2 during the sonication. ^bSolvent abbreviations: CH₃CN = Acetonitrile, DMSO = Dimethyl sulfoxide, MeOH = Methanol. ^cMinimum Gelation Concentration (MGC) of CuA-Tar metallogel is 500 mg mL⁻¹. ^dTotal volume of the solvents. ^eAll gels were completely opaque. ^fAbbreviations: S = Solution; I = insoluble; P = precipitate.



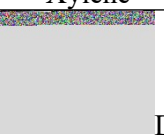

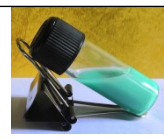






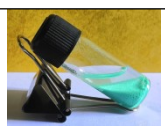
Table S6. Gelation process of CuA-Tar metallogel^a with CuSO₄·5H₂O in various solvents^b





Entry	Solvent ^b	Phase	Conc. ^c	Vol. ^d	Gelation Time ^e	Gel-Phase Colour ^f	Picture
1.	 Xylene	I	500	1	-	-	
2.	 MSO	S	500	1	15min	Blue	
3.	 1-Propanol	I	1200	1	-	-	
4.	 n-Octanol	I	500	1	-	-	
5.	 cetone	S	500	1	15min	Blue	
6.	 MeOH	S	500	1	15min	Blue	

7.	 CH ₃ CN	P	500	1	15min	Blue	
8.	 cyclohexane	S	500	1	15min	Blue	

^aGelation tests were performed as discussed in the Experimental Section: CuSO₄·5H₂O (0.159 g, 1 mmol) in DMF (500 μl) and tartaric acid (0.300 g, 2 mmol) in DMF (500 μl). The temperature of the ultrasonic bath was 30 ± 2 during the sonication.
^bSolvent abbreviations: CH₃CN = Acetonitrile, DMSO = Dimethyl sulfoxide, MeOH = Methanol. ^cMinimum Gelation Concentration (MGC) of CuA-Tar metallogel is 500 mg mL⁻¹. ^dTotal volume of the solvents. ^eAll gels were completely opaque.
^fAbbreviations: S = Solution; I = insoluble; P = precipitate.

Table S7. Gelation process of CuA-Tar metallogel^a with Cu(OH)₂ in various solvents^b

Entry	Solvent ^b	Phase	Conc. ^c	Vol. ^d	Gelation Time ^e	Gel-Phase Colour ^f	Picture
1.	 Xylene	I	500	1	-	-	
2.	 MSO	S	500	1	15min	Blue	
3.	 1-Propanol	I	1200	1	-	-	
4.	 n-Octanol	I	500	1	-	-	
5.	 acetone	I	500	1	-	-	
6.	 MeOH	I	500	1	-	-	

7.	 CH ₃ CN	P	500	1	15min	Blue	
8.	 C cyclohexane	I	500	1	-	-	

^aGelation tests were performed as discussed in the Experimental Section: Cu(OH)₂ (0.097g, 1 mmol) in DMF (500 μl) and tartaric acid (0.300 g, 2 mmol) in DMF (500 μl). The temperature of the ultrasonic bath was 30 ± 2 during the sonication. ^bSolvent abbreviations: CH₃CN = Acetonitrile, DMSO = Dimethyl sulfoxide, MeOH = Methanol. ^cMinimum Gelation Concentration (MGC) of CuA-Tar metallogel is 500 mg mL⁻¹. ^dTotal volume of the solvents. ^eAll gels were completely opaque. ^fAbbreviations: S = Solution; I = insoluble; P = precipitate.

pH dependent CuA-Tar metallogel formation strategy

pH dependent CuA-Tar metallogel formation strategy with DMF solution of Cu(OAc)₂·H₂O salt and Tartaric acid clearly shows that the CuA-Tar metallogel is formed at pH = 3.90. The variation of pH is maintained by Cu(OAc)₂·H₂O and Tartaric acid and it also supports minimum critical gelation concentration (MGC) where it is clearly show that the CuA-Tar metallogel only formed with 500 mg mL⁻¹ of Cu(OAc)₂·H₂O salt and Tartaric acid (where, [Cu(CH₃COO)₂·H₂O]:[tartaric acid] = 1:2, (w/w)).

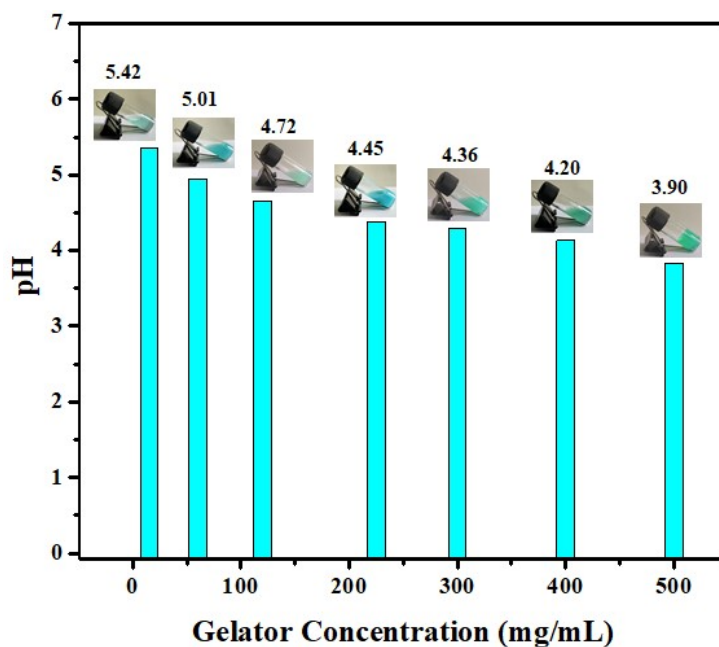


Fig. S1. pH dependent CuA-Tar metallogel formation strategy with DMF solution of Cu(OAc)₂·H₂O salt and Tartaric acid.