

## Metallogels Through Glyme Coordination – Supplementary Information

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### Materials

All chemicals were obtained from commercial suppliers and used without further purification unless otherwise noted. Copper(II) chloride dihydrate (ACS Reagent,  $\geq 99.0\%$ ), thiomalic acid (*ReagentPlus*,  $\geq 99.0\%$ ), diethylene glycol dimethyl ether (*ReagentPlus*, 99%), tetraethylene glycol dimethyl ether ( $\geq 99\%$ ), and poly(ethylene glycol) dimethyl ether (average  $M_n \sim 250$ ) were obtained from Sigma-Aldrich. 1,2-dimethoxy ethane (99+% stab. with BHT) and triethylene glycol dimethyl ether (99%) were obtained from Alfa Aesar. Filters used were VWR syringe filters, 0.2  $\mu\text{M}$  cellulose acetate.

### Cu-TM/G1 Synthesis

A 100 mM solution of thiomalic acid (1.2 mmol, 3 eq., in 12 mL 0.3 M NaOH) and 100 mM solution of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.4 mmol, 1 eq., in 4 mL  $\text{H}_2\text{O}$ ) were filtered. The thiol solution was added to the blue copper chloride solution in a 50-mL polypropylene centrifugation tube and turned the solution black. 1,2-dimethoxyethane (G1, 12 mL) was immediately added, and the resulting cloudy white suspension shook at 4 °C for 45 min or until a dense yellow phase was apparent. After centrifugation at 3220 g for 10 min at 4 °C the clear, colorless supernatant was siphoned off of the viscous yellow liquid. Only the bottom portion of the liquid was used in experimentation to be sure no residual solvent was brought over into the final product.

All glymes studied (G1-G~5) are capable of substituting G1 in the above synthesis. Other metal salts and thiolates (examples found in Table S1) are replaceable with one minor alteration to the synthetic method: 18 mL of glyme should be added when using glutathione or cysteine in place of thiomalic acid.

It is important to note that a 1:3 metal:thiol ratio is necessary to form the material regardless of the metal oxidation state (*i.e.*, 3 equivalents of  $\text{AgNO}_3$  are necessary to form Ag-SR/Gn despite Ag(I) already in the necessary +1 oxidation state).

### Instrumentation

Oscillatory shear measurements were performed on a TA Instruments ARES rheometer. Dynamic frequency sweeps were performed for each sample using a 0.1% shear strain (verified linear viscoelastic region) over a frequency range of 0.05 to 1000  $\text{rad s}^{-1}$ . Strain sweeps were performed for each sample at 1  $\text{rad s}^{-1}$  over a range of 0.01 to 90%.

Small angle X-ray scattering (SAXS) data were collected on a Rigaku S-Max 3000 High Brilliance 3 Pinhole SAXS system outfitted with a MicroMax-007HFM Rotating Anode ( $\text{CuK}\alpha$ ), Confocal Max-Flux™ Optic, Gabriel Multiwire Area Detector and a Linkham thermal stage. The feature at  $q=0.25$  is an artifact at the edge of the detector.

X-ray diffraction (XRD) was performed on a Scintag X-2 Advanced Diffraction system equipped with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ).

Scanning electron microscopy (SEM) was performed on a JEOL JSM-6500F microscope operating at an accelerating voltage of 15 kV.

UV-Visible spectroscopy (UV-Vis) was performed on a Nanocrop 2000c Spectrophotometer on a 1-mm path length pedestal. Data were smoothed under

Savitzky-Golay method with a 10-point window to make trends more apparent (raw data available in Fig. S4).

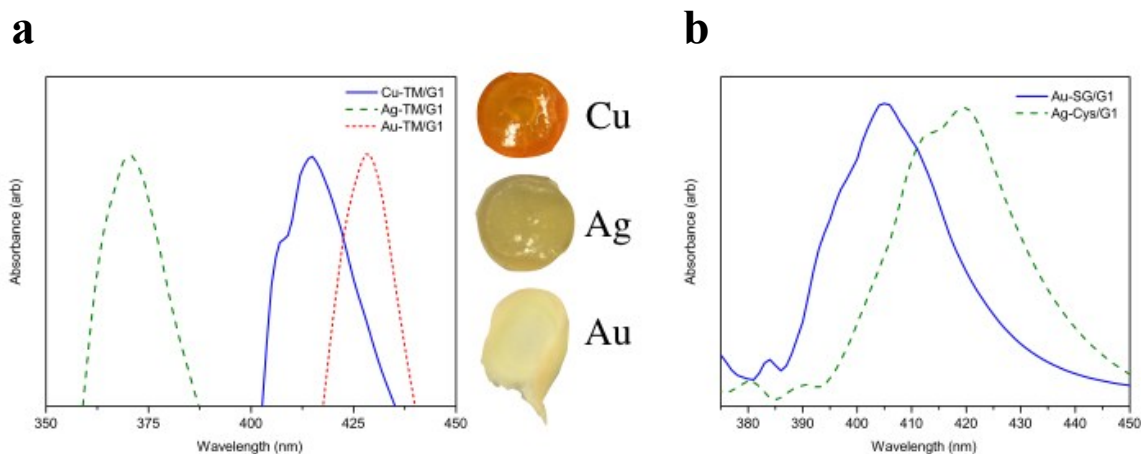
### Rheometry Sample Preparation

Immediately after its synthesis, 150  $\mu\text{L}$  of the viscous liquid was transferred into an 8-mm diameter rubber mold on parafilm. After drying for 24 h in ambient laboratory conditions it was transferred to a dessicator (RH = 0%) and dried for another 24 h at ambient temperature and pressure. This method allowed water to slowly diffuse out of the gel to evaporate and prevented the material from cracking. The resulting puck fits perfectly under the 8-mm top plate on the rheometer. This method provided reproducible and accurate rheological measurement of the material.

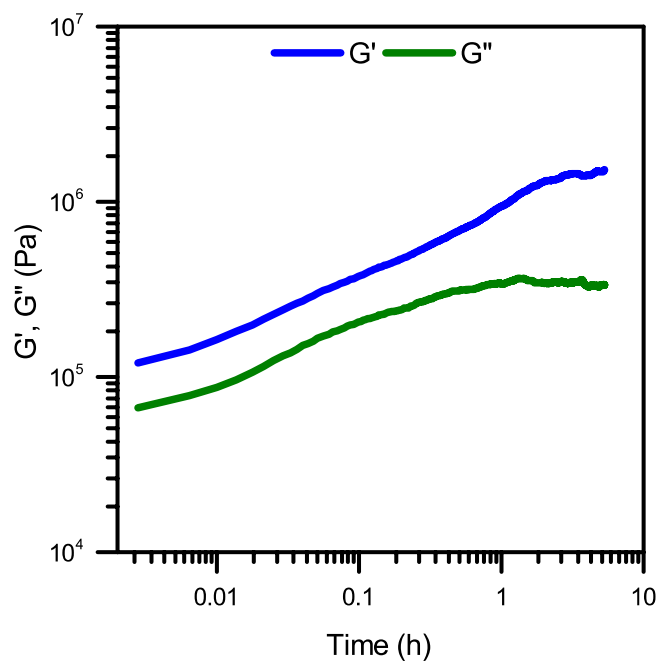
### Supplementary Figures

**Table S1** Reagents capable of forming the reported metallogel

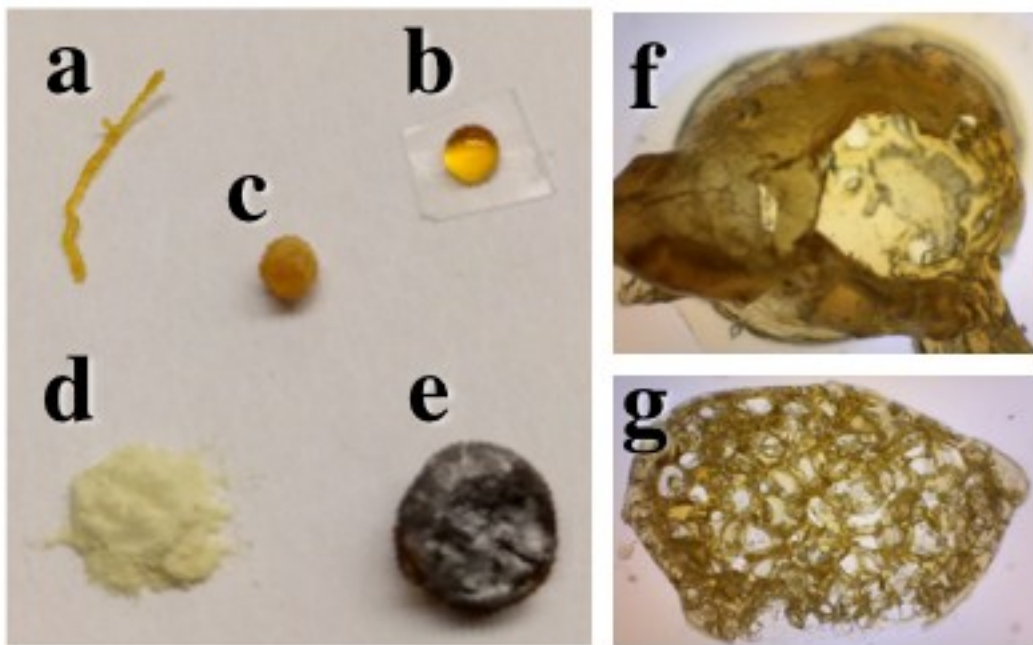
Metal Salt	Thiol	Glyme
copper(II) chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ )	glutathione (GSH)	1,2-dimethoxyethane (G1)
silver(I) nitrate ( $\text{AgNO}_3$ )	thiomalic acid (TM)	diethylene glycol dimethyl ether (G2)
gold(III) chloride trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ )	L-cysteine (Cys)	triethylene glycol dimethyl ether (G3)
		tetraethylene glycol dimethyl ether (G4)
		dimethyl polyethylene glycol $M_n \sim 250$ (G $\sim$ 5)



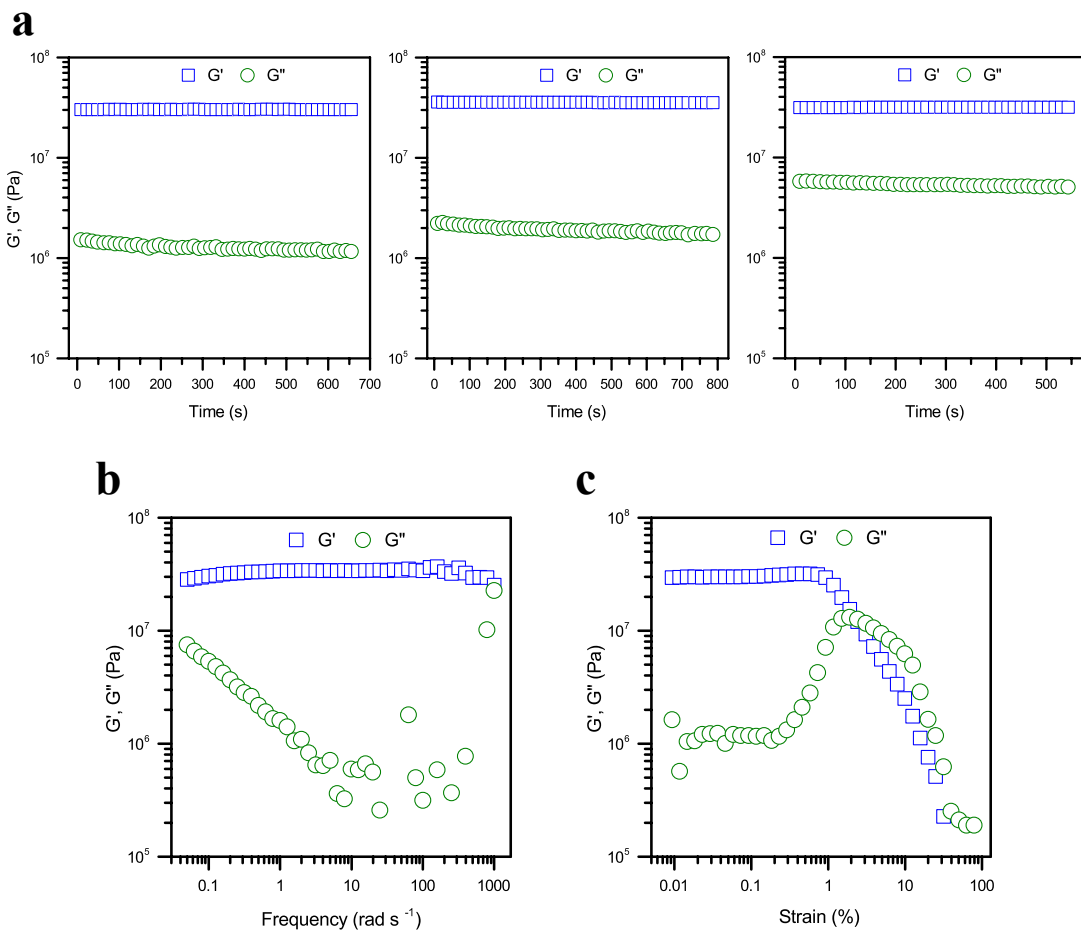
**Fig. S1** Linear absorption of samples prepared from reagents listed in Table S1: (a) Comparison of peak absorbance between materials made with Cu, Ag, and Au, along with pictures of each material; (b) gold-glutathione (Au-SG) and silver-cysteine (Ag-Cys) as examples of materials made with other thiols. Data presented were smoothed under Savitzky-Golay method with a 10-point window.



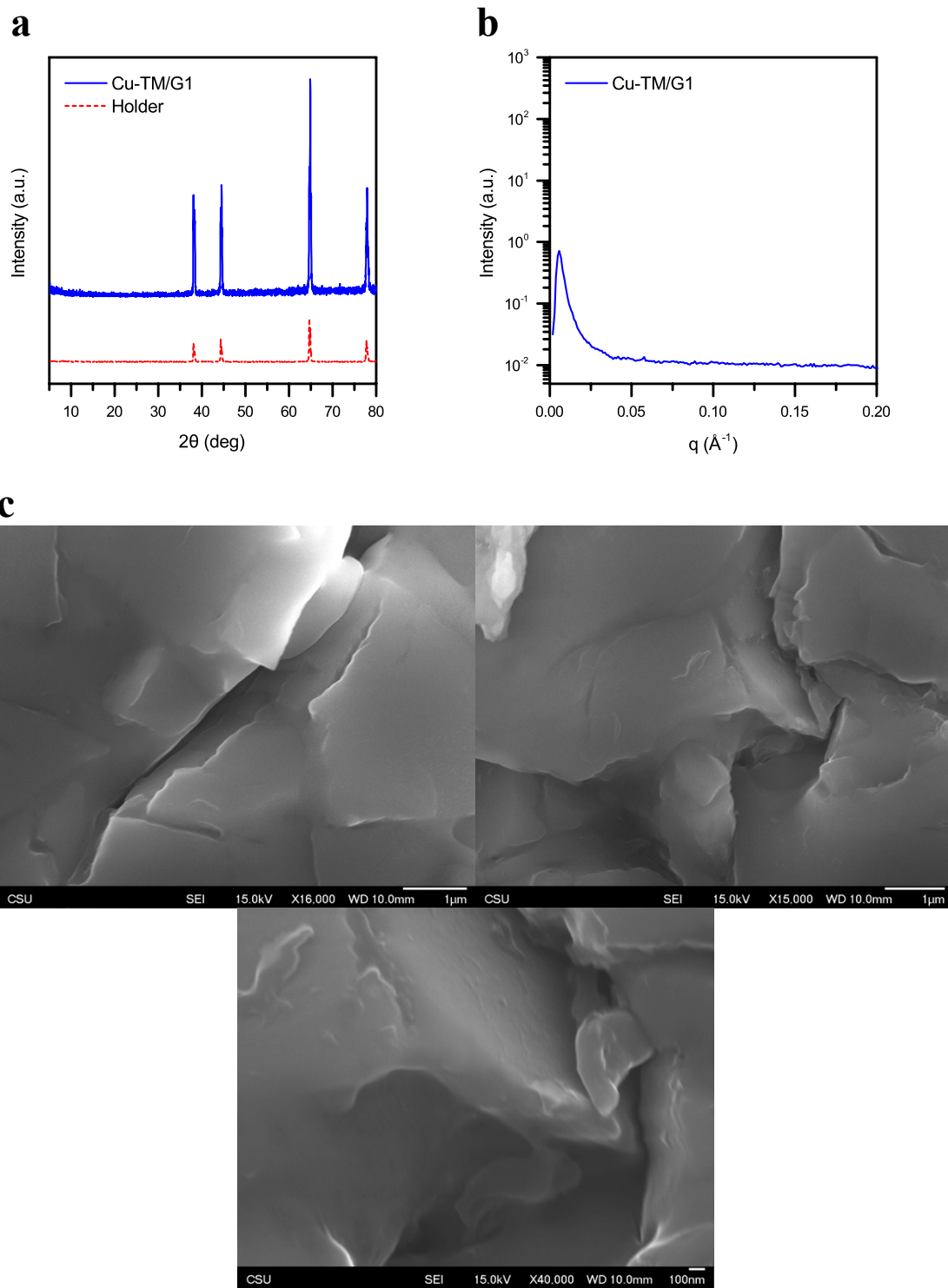
**Fig. S2** Time sweep rheometry of Cu-TM/G1 shows elasticity increase as the sample dries in ambient conditions.



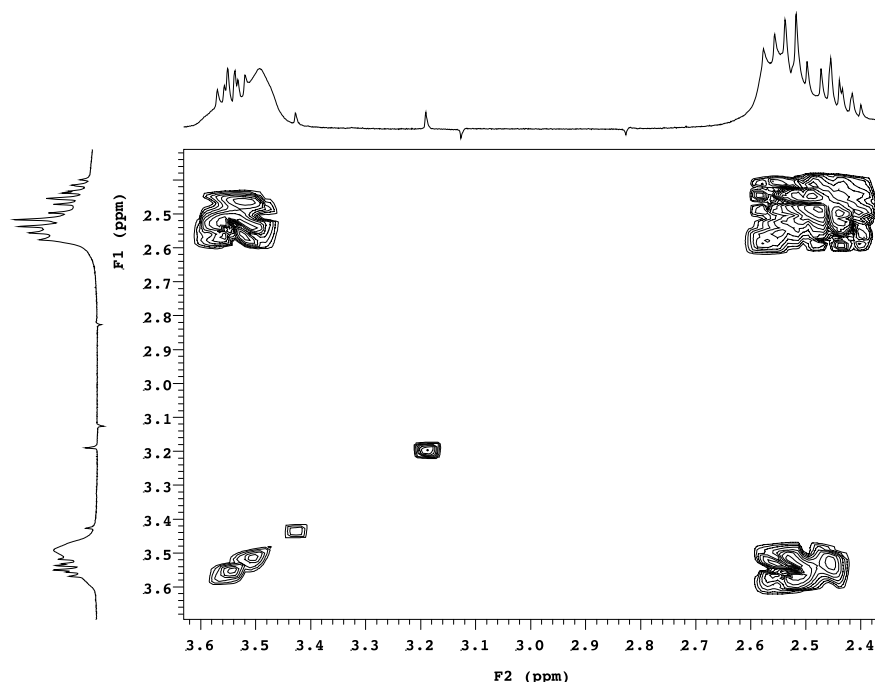
**Fig. S3** Pictures of Cu-TM/G1 in various solid forms: (a) wire, (b) gel, (c) hard sphere, (d) powder, (e) rigid puck, (f) hollow sphere, and (g) foam.



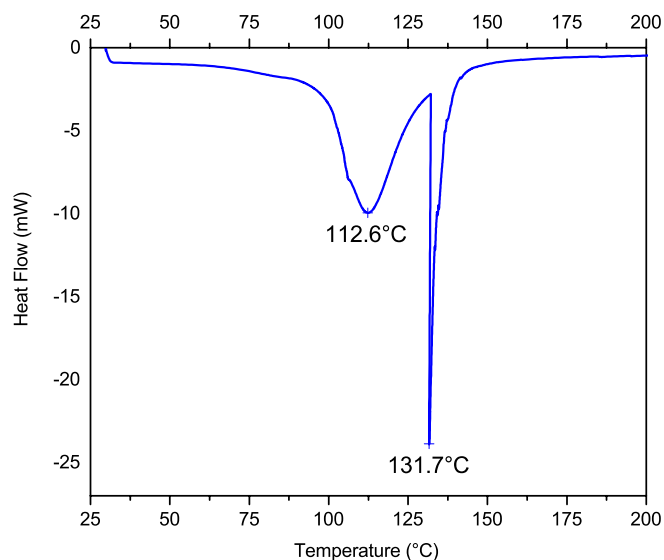
**Fig. S4** Representative Cu-TM/G1 curves used to obtain data in Table 1. (a) Time sweep on three separate samples prepared simultaneously. (b) Frequency sweep run at fixed strain ( $\gamma = 0.1\%$ ). (c) Strain sweep run at fixed frequency ( $\omega = 1$  Hz).



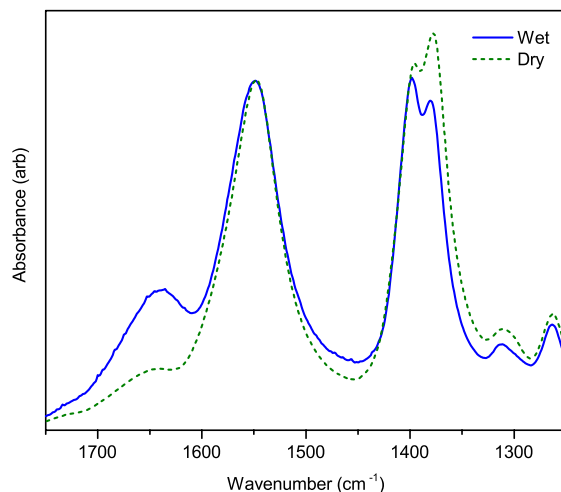
**Fig. S5** (a) XRD of the sample (solid blue line) only shows diffraction peaks attributed to the sample holder (dashed red line). (b) SAXS displays one feature ( $q = 0.25$ ) that is an artifact at the edge of the detector; no other diffraction peaks are apparent. (c) SEM micrographs of Cu-TM/G1 display a uniform surface around cracks that formed as the sample dried. Scale bar is  $1\ \mu\text{m}$  for the top two images and  $100\ \text{nm}$  for the bottom image.



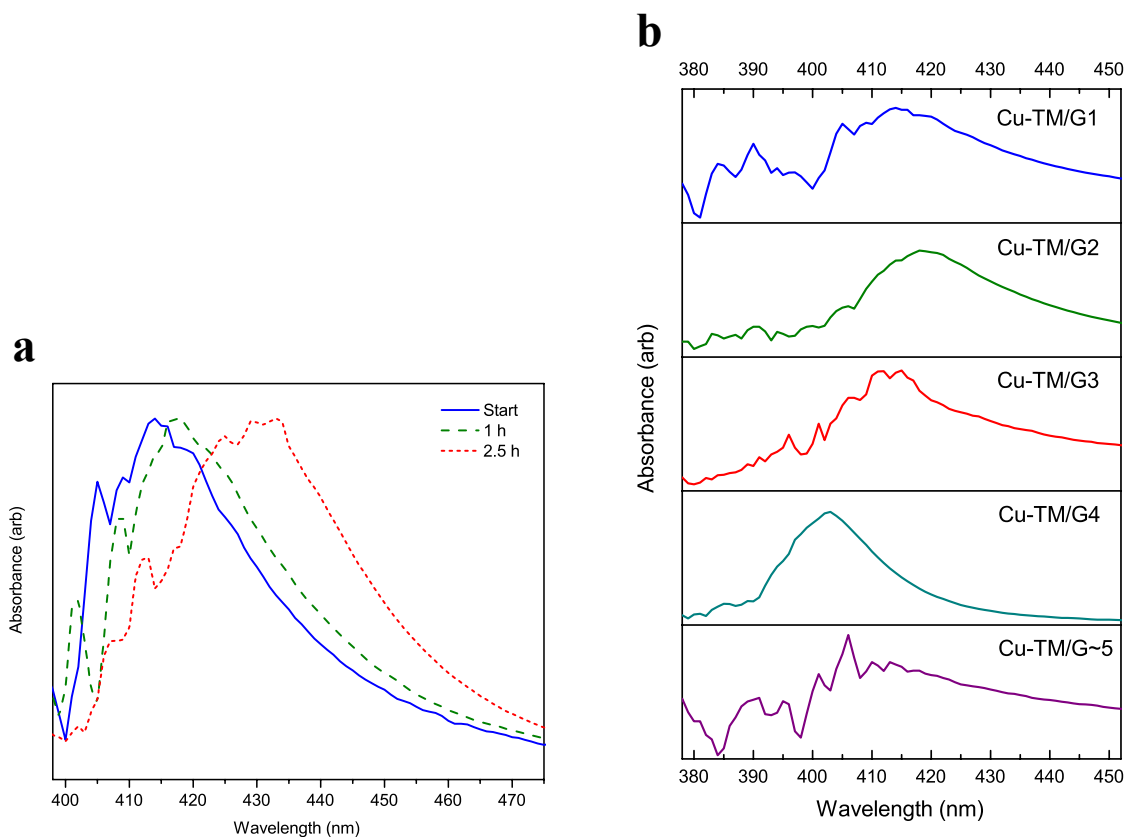
**Fig. S6**  $^1\text{H}$ - $^1\text{H}$  correlation spectroscopy of Cu-TM/G1 synthesized in  $\text{D}_2\text{O}$ . The peaks at 3.2 and 3.4 ppm correspond to G1 and all other peaks correspond to metallopolymer. The absence of off-diagonal peaks between G1 and metallopolymer suggests that G1 interacts non-covalently with the metallopolymer.



**Fig. S7** Differential scanning calorimetry of freshly synthesized Cu-TM/G1 differentiates between free solvent water (low temperature) and water trapped in the molecular network (high temperature). These peaks are attributed to water loss because they are irreversible and are not apparent in desiccated material. The sample pan was reweighed after the run to determine 3.7 mg of water (59 wt%) was lost during the experiment.



**Fig. S8** Infrared spectroscopy of freshly synthesized Cu-TM/G1 (solid blue line) and after drying for 12 h (dashed green line). The peak at 1548 cm<sup>-1</sup> (carbonyl stretch) does not shift in energy while the sample dries and implies that the carboxylate environment remains unchanged. The peaks at ~1380 cm<sup>-1</sup> (glyme ether stretch) display a shift in relative intensity, which indicate the local environment of glyme ether changes while the sample dries.



**Fig. S9** Raw linear absorption (a) of Cu-TM/G $n$  while drying and (b) comparison between Cu-TM/G $n$ . Data presented in the main text (Fig. 3) were smoothed under Savitzky-Golay method with a 10-point window.