Supplementary Information

A multi-stimuli responsive polyoxometalate-guanosine monophosphate hybrid chromogenic smart hydrogel

Amrita Chakraborty [a], Tanushree Ghosh [b] †, Suryakamal Sarma [a], Vidhi Agarwal [a], Rajesh Kumar*[b], and Tridib K Sarma*[a]

a Department of Chemistry, Indian Institute of Technology Indore, Simrol, Khandwa Road, Indore 453552, India.

b Department of Physics, Indian Institute of Technology Indore, Simrol, Khandwa Road, Indore 453552, India.

† Presently at the Department of Mechanical and Industrial Engineering, University of Toronto, 27 King's College Cir, Toronto, ON M5S 1A1, Canada

*Email id: Prof. Tridib K. Sarma: tridib@iiti.ac.in;

Prof. Rajesh Kumar: rajeshkumar@iiti.ac.in

Materials. Phosphomolybdic acid hydrate $H_3[P(Mo_3O_{10})_4]aq$ and 2,3-Dimercaptosuccinic acid was purchased from Sigma Aldrich. Guanosine-5′-monophosphate disodium salt hydrate (Na_2-GMP), Glutathione reduced ($C_{10}H_{17}N_3O_6S$), Sodium Iodide (NaI), and Sodium Chloride (NaCl) were purchased from Sisco Research Laboratory (SRL). Sodium Bromide (NaBr) was purchased from Alfa-Aesar. L-cysteine was purchased from HIMEDIA. Milli-Q was purchased from Merck, India. All the chemicals were used as purchased with no further purification.

Synthesis of the hydrogel. 60 mM phosphomolybdic acid (PMA) and 180 mM of guanosine monophosphate (GMP) were added to milli-Q in a vial while kept on continuous stirring for 2-5 minutes at 65 °C. The obtained clear yellow solution was allowed to rest and it spontaneously formed a hydrogel upon cooling to room temperature.

Instrumentation. UV-Vis and Circular Dichroism (CD) studies were recorded on a Perkin Elmer UV-Vis-NIR spectrophotometer (Model: Lambda 1050) and JASCO J-815 spectropolarimeter using a quartz cuvette of path length 1 mm respectively. Field emission scanning electron microscopy (FESEM) images were taken on Carl Zeiss Supra 55 instruments after Au coating. Transmission Electron microscope (TEM) images were taken from the electron microscope of model JEM-2100 at an accelerating voltage of 200 kV. Rheological studies were done using an Anton Paar Physica MCR 301 rheometer with parallel plate geometry (diameter 25 mm). A dynamic strain sweep experiment was performed using a constant frequency of 10 rad s^{-1}. The dynamic frequency sweep of the hydrogel was measured as a function of frequency in the range of 0.1−500 rad s^{-1} with a constant strain value of 1%. The thixotropic loop test was carried out at a constant frequency of 10 rad s^{-1}, and the applied strain was changed from 0.1% to 200%. Powder X-ray diffraction patterns (PXRD) of the xerogel were recorded on a Rigaku Smartlab, Automated Multipurpose X-ray diffractometer with Cu Kα source (the wavelength of the X-rays was 0.154 nm). FTIR study of xerogel was done on Bruker Alpha II Platinum ATR. ^{31}P NMR spectra were recorded using a 500 MHz

Bruker AV500 NMR instrument at 298 K using D_2O as solvent. X-ray photoelectron spectroscopy (XPS) study for the xerogels was carried out on Thermoscientific NEXA Surface analyser.

Characterization Methods.

Field Emission Scanning Electron Microscopy (FESEM). The hydrogels were diluted up to 250 times in milli Q water and 20 µl of it was drop-casted on a clean coverslip and left for air drying for 24 hours. The drop-casted samples were then coated with Au and imaged under the electron microscope.

UV-visible spectroscopy. UV-visible spectra of the hydrogel, PMA and GMP were recorded at a concentration of 0.025 mM each using a 1 cm path length cuvette. Titration spectra were performed upon successive addition of 0.025 mM GMP to a 0.025 mM aqueous solution of POM at a variable mole ratio.

Circular Dichroism (CD). The CD spectra of the hydrogels, POM, and GMP were recorded by diluting the samples up to 1 mM using a quartz cell of 1 mm path length with a scan range of 200-300 nm. The spectra were recorded with a slit width of 1 mm and a scan rate of 50 nm/s. Titration spectra were performed upon successive addition of 1 mM GMP to a 1 mM aqueous solution of PMA at a variable mole ratio.

NMR (^{1}H and ^{31}P). The NMR studies were performed for PMA, GMP, and PMA-GMP at similar concentrations as for hydrogel (PMA: 60 mM, GMP: 180 mM, and PMA-GMP 60:180 mM). To study the NMR of the hydrogel, it was converted to sol owing to its thermoreversible property and then transferred into the NMR tube.

Rheological Studies. Rheological studies were performed at room temperature (25 °C) using a parallel plate (25 mm diameter). A small amount of the gel was scooped out with the help of a spatula and kept on the plate for measurement. The strain sweep measurements of the hydrogels

were carried out at a constant frequency (10 $rads^{-1}$). The frequency sweep studies were performed in a 0.1−500 rad s^{-1} frequency range maintaining a constant strain of 1%. For the thixotropic loop studies, the strain was varied from 0.1% to 200% at an applied frequency of 10 rad s^{-1}. Successive low and high strains were applied at a period of 100 seconds.

Universal Testing Machine. The hydrogel was moulded into a rectangular shape. The gauge length was 3 mm and the width was 18 mm. The stretching speed was 15 mm/min.

UV-visible studies for chromism.

The hydrogel was triggered by various stimuli such as mechanical stress (ground in mortar pestle for 10 mins), visible light (exposed to 3 white LEDs of 30 W in a dark box for 3 hrs), temperature (90 °C, 50 min), metals (various metal strips such as Fe, Cu, Zn, Pb, Sn, and Mg were dipped into the hydrogel for few minutes). Then UV-vis spectra of the hydrogel before any exposure to stimuli and after exposure to stimuli were recorded by sandwiching 125 µl of the hydrogel in between two quartz glasses with the help of double-sided adhesive.

To prepare an electrochromic device, a thin layer of hydrogel was prepared by pouring 200 µl (in liquid state) onto a mould of dimension 1.5 cm x 3 cm. Then the layer of hydrogel was simply layered on an ITO plate from one end and was supported over a glass slide over the other end (the non-conductive side of the ITO adhered to the glass slide using an adhesive) such that the hydrogel itself acted as an electrode now.

The hydrogel was oxidised back to a yellow colour by adding H_2O_2 to the blue hydrogel except in the case of electrochromism where a reversible cycle was obtained by providing reverse bias.

Cyclic Voltammetry.

The cyclic voltammogram was recorded using a Swagelok cell with two parallel stainless-steel electrodes. The data was recorded on Metrohm Autolab potentiostat (PGSTAT302 N) within a range of -1.5 V to +1.5 V at a scan rate of 50 mV s^{-1}.

Conductivity Measurement.

The conductivity of synthesized PMA-GMP hydrogel was measured by the electrochemical impedance spectroscopy (EIS) method using a Swagelok cell with two parallel stainless-steel electrodes. The EIS data were recorded on Metrohm Autolab potentiostat (PGSTAT302 N) within the 0.1 Hz to 10 kHz frequency range at room temperature. The conductivity of hydrogel was calculated using the following Equation:

$$\sigma = L / (R_{ct}*A)$$

Where σ is the conductivity, A is the area, L stands for the height of the gel in the cell, and R_{CT} is the resistance of the gel.

X-ray photoelectron spectroscopy (XPS).

XPS was recorded for Mo in the case of pre-stimuli xerogel and xerogel after exposure to stress, light, temperature, electricity, and metal (Cu). The percentage for reduced Mo^{V} was calculated by the ratio of the area under the curve due to Mo^{V} to the area under the curve for total Mo present.

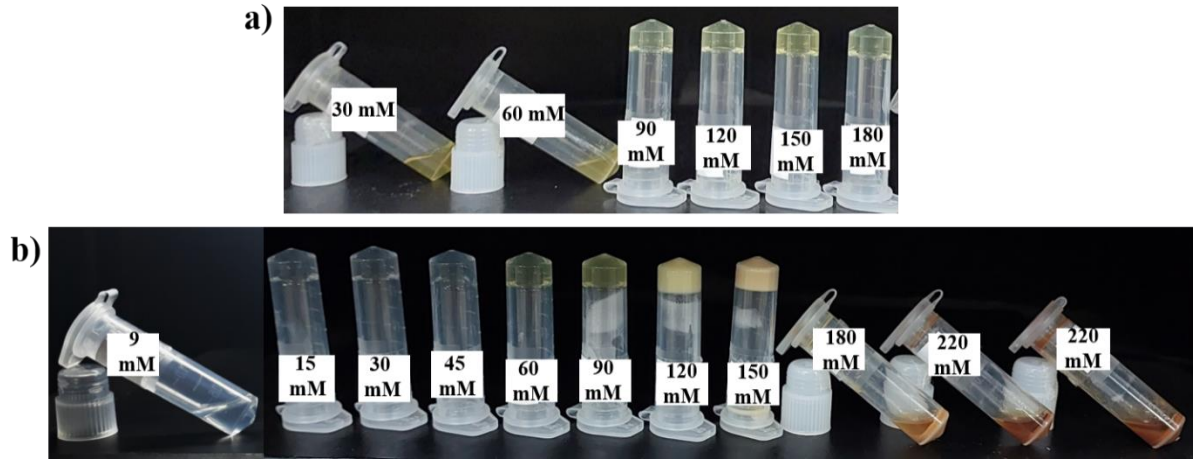

Figure S1. Digital images of PMA-GMP system (a) varying the concentration of GMP while keeping the concentration of PMA constant at 60 mM, (c) varying the concentration of PMA while keeping GMP concentration constant at 180 mM.

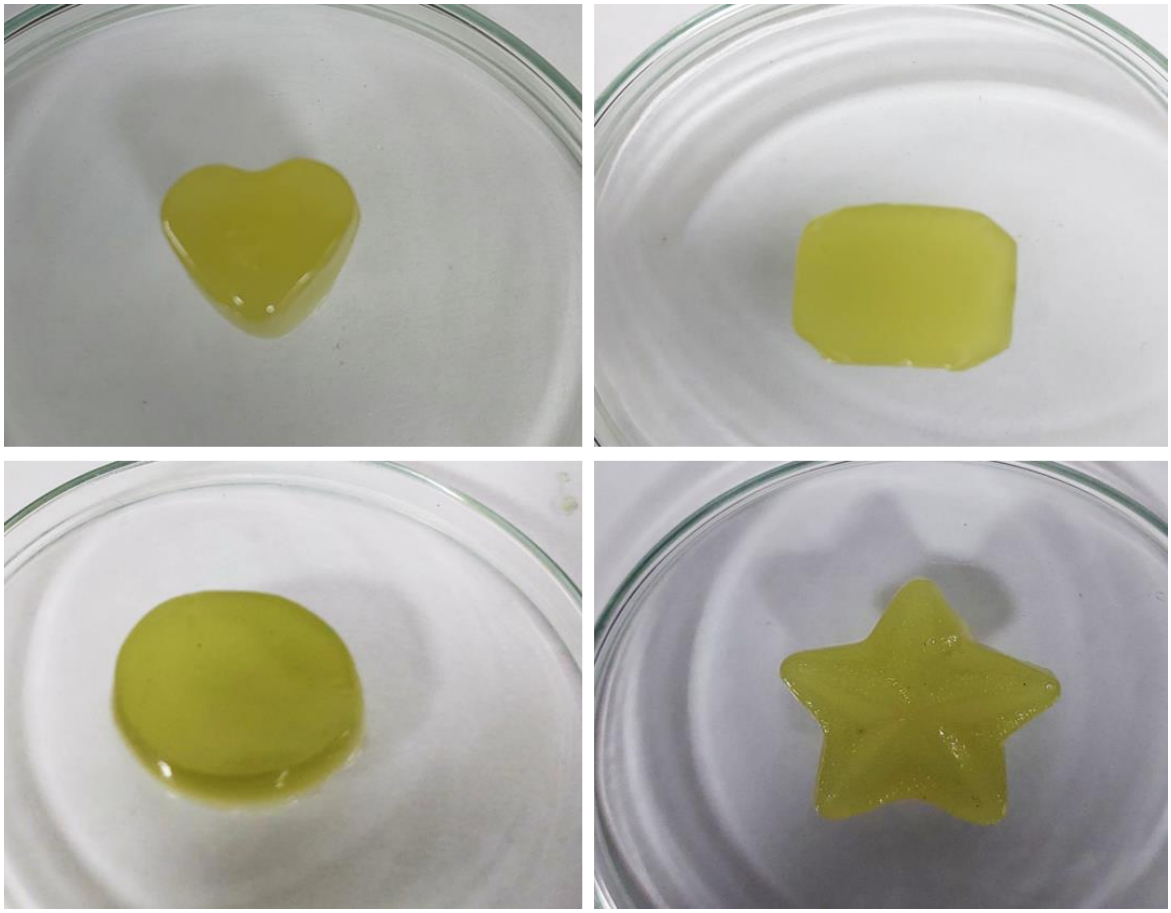

Figure S2. Digital images depicting the shape moulding ability of PMA-GMP hydrogel owing to its thermo-reversible property.

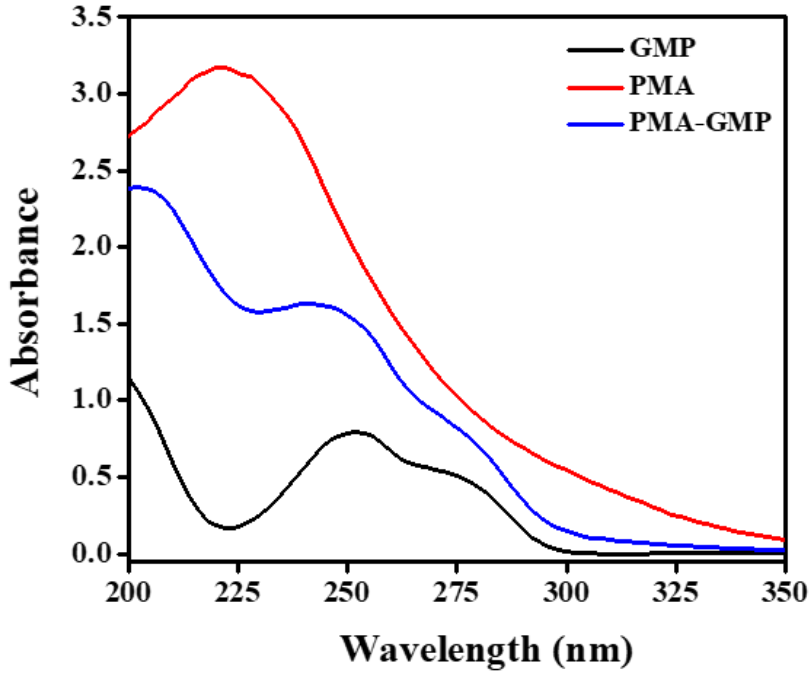

Figure S3. UV-visible spectra of GMP, PMA, and PMA-GMP solution.

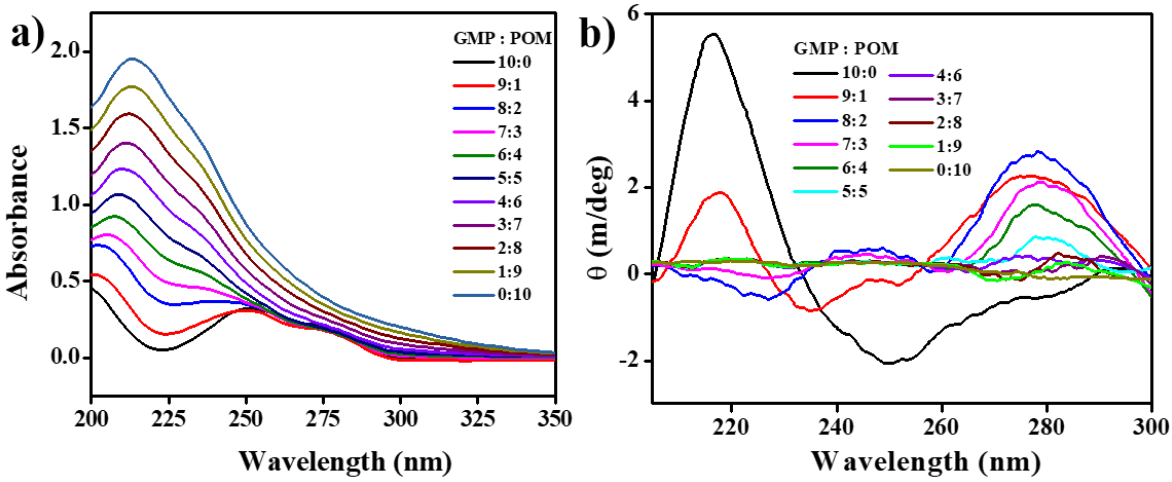

Figure S4. (a) UV-visible and (b) circular dichroism spectra of PMA-GMP recorded with decreasing mole fraction of GMP.

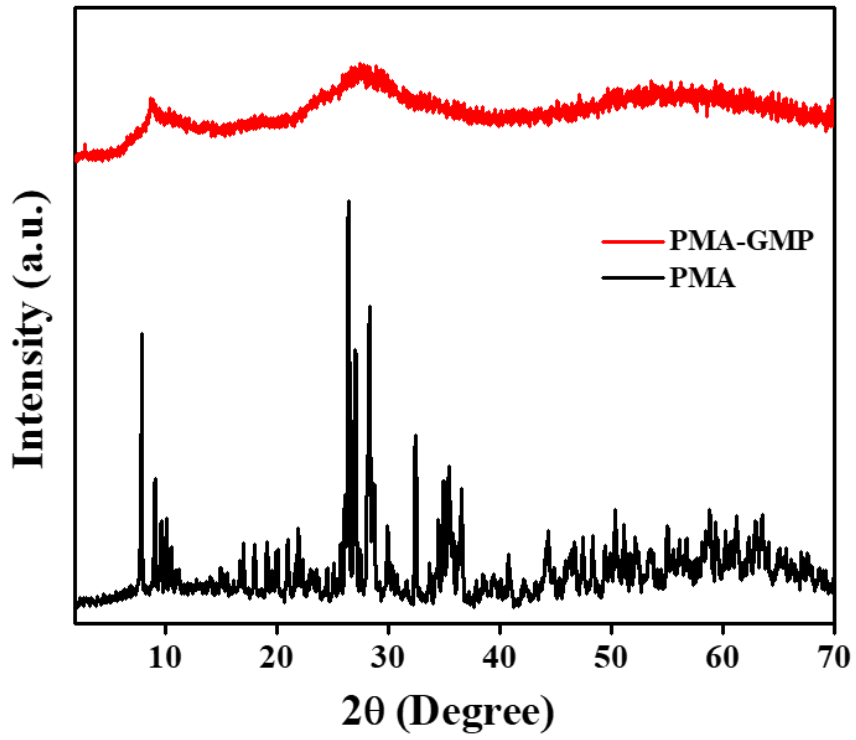

Figure S5. Powder XRD spectra for PMA and PMA-GMP.

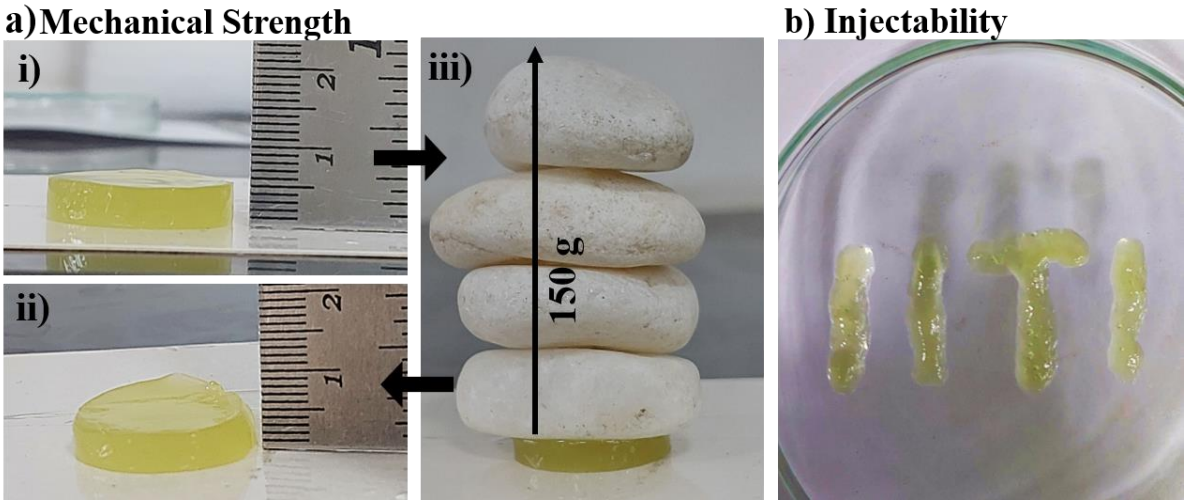

Figure S6. Digital images showing (a) the mechanical strength and (b) the injectability of the hydrogel.

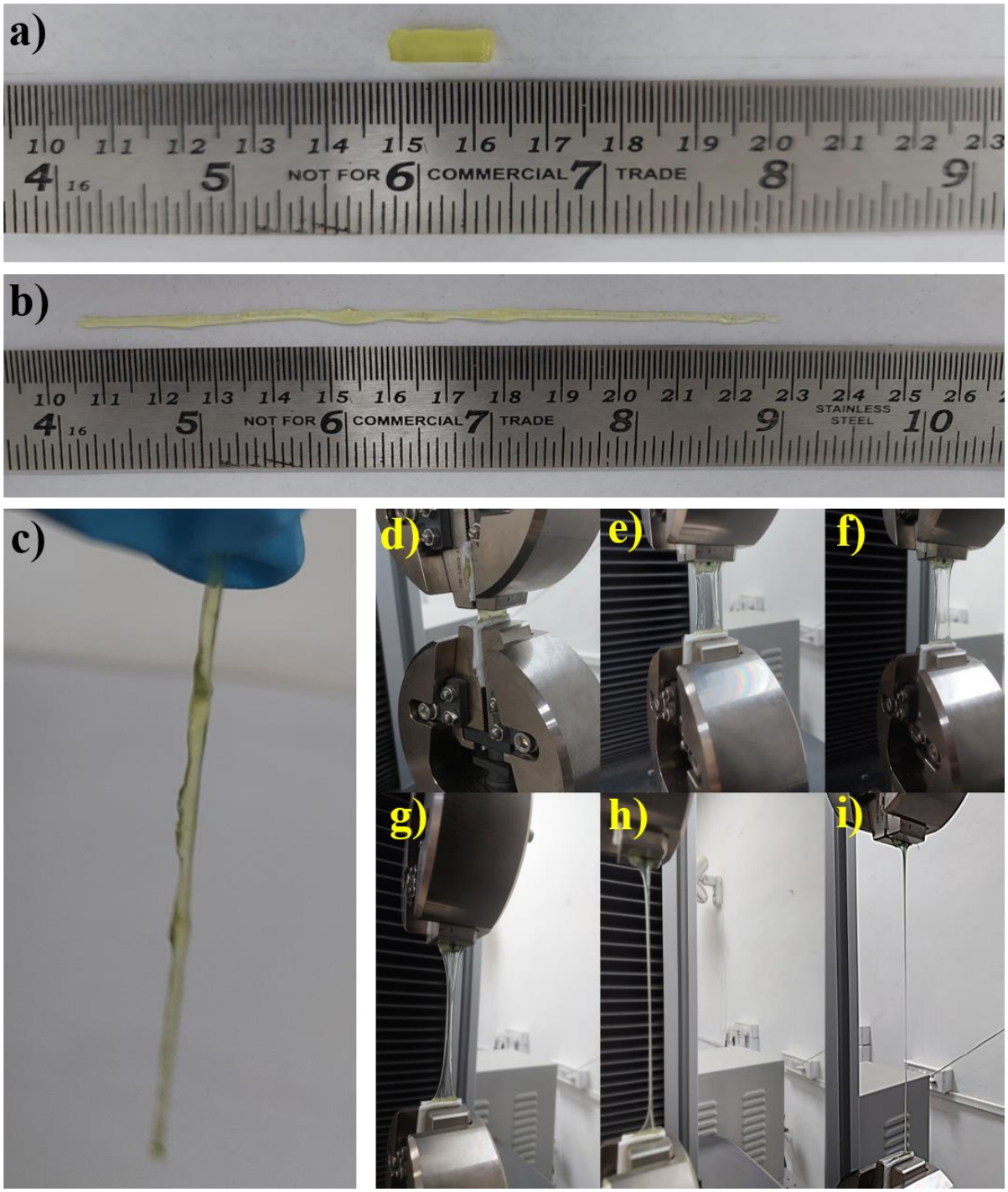

Figure S7. (a-b) Digital image displaying the tensile strength (a 1 cm long piece of gel is stretched to 12 cm) of PMA-GMP hydrogel, (c) elongated hydrogel lifted to show its stability, (d-i) digital images taken during gel being stretched by the universal testing machine to quantify the tensility of the hydrogel.

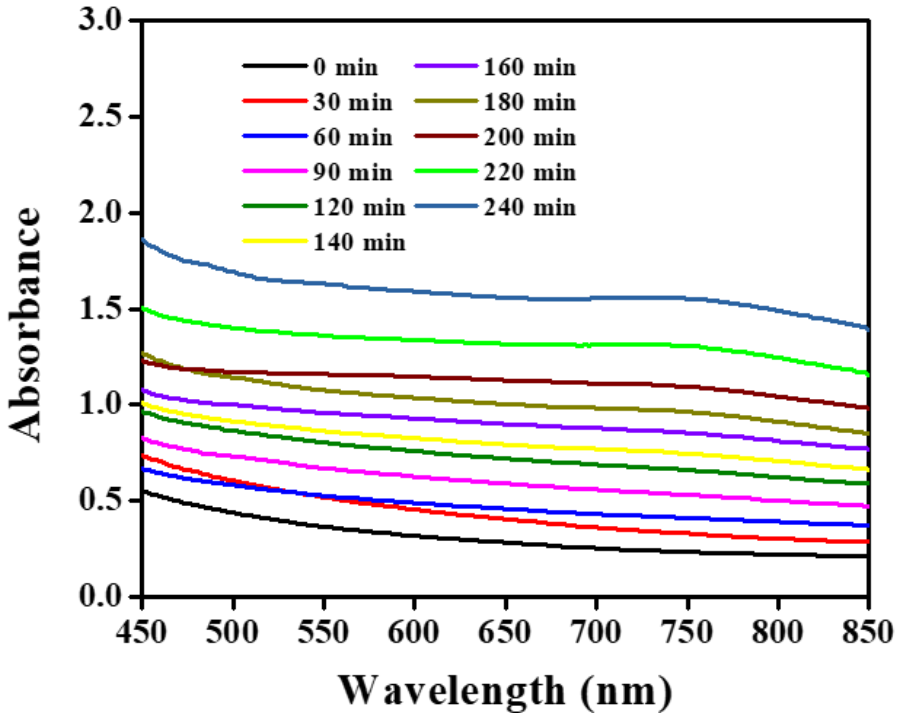

Figure S8. Time-dependent UV-visible spectra of the hydrogel after exposure to light.

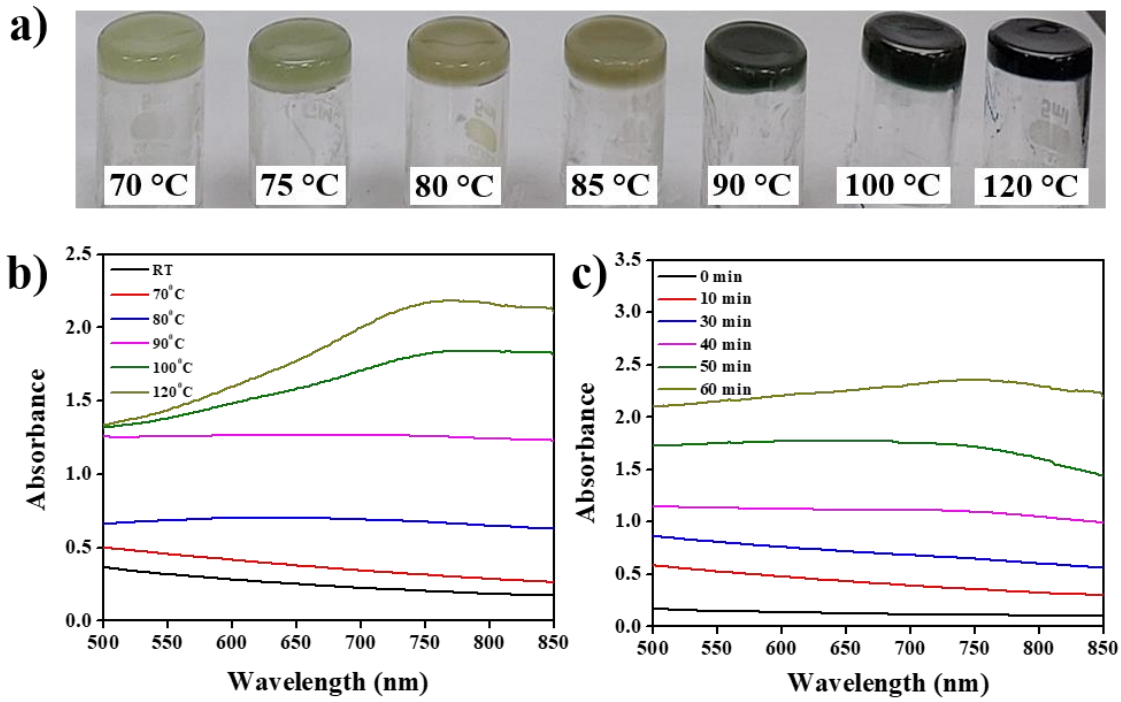

Figure S9. (a) digital image of PMA-GMP hydrogel exposed to different temperatures for 40 mins, (b) UV-visible absorbance spectra of the hydrogel heated at different temperatures for 40 mins, and (c) Time-dependent UV-visible spectra of PMA-GMP hydrogel exposed to 90 °C for 60 mins.

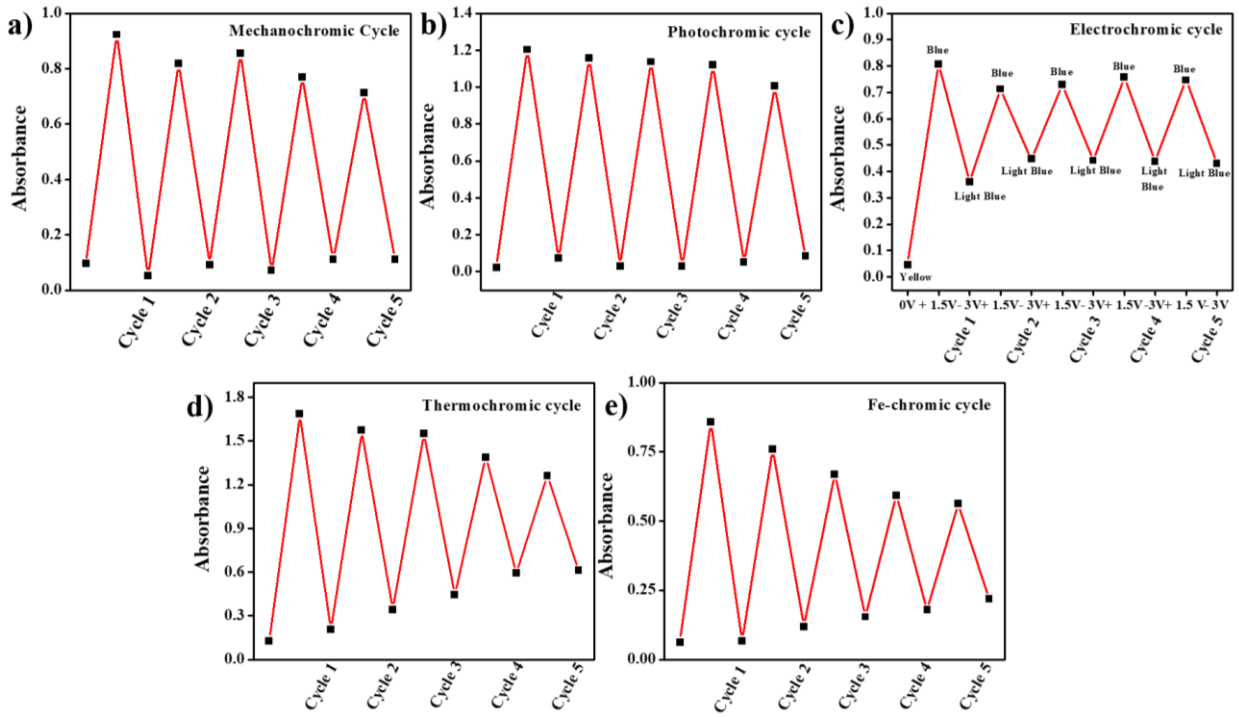

Figure S10. Reversibility cycle for chromism induced by various stimuli (a) mechanical stress, (b) visible light, (c) electricity, (d) temperature, and (e) metal (Fe).

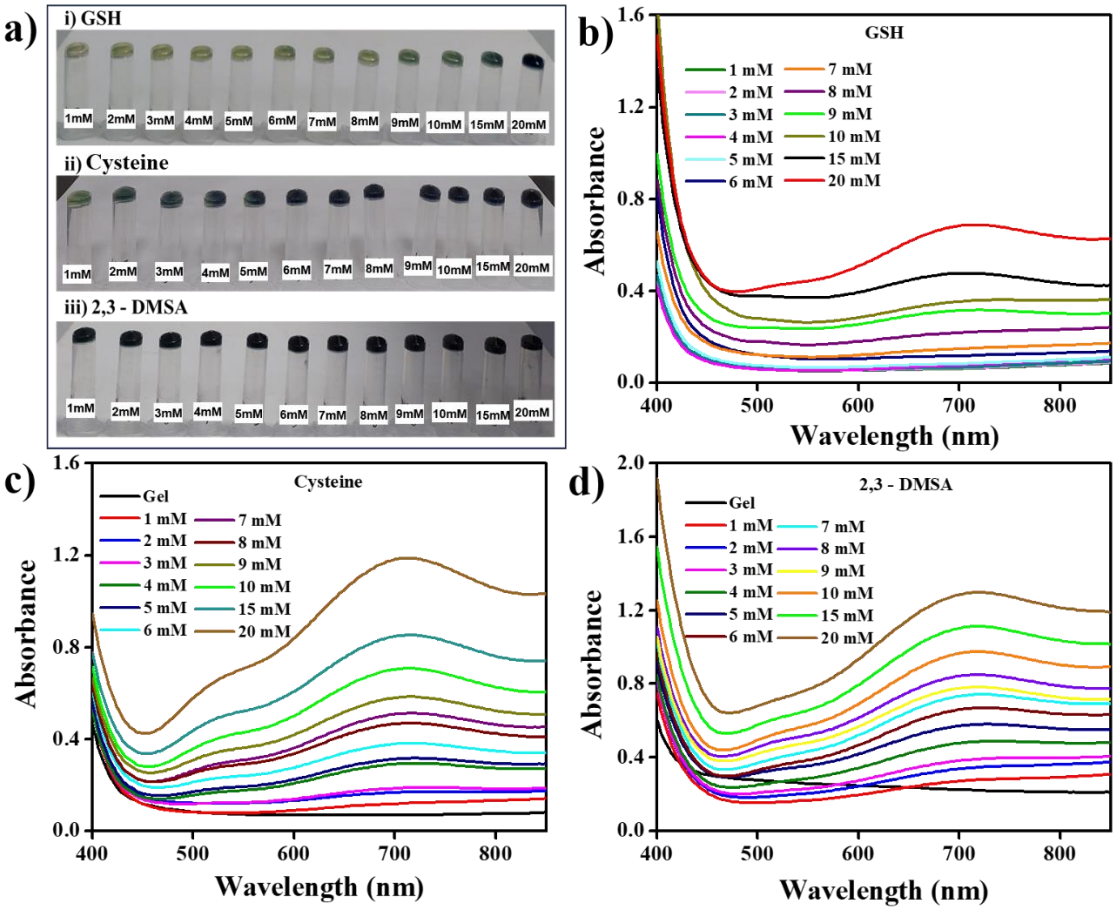

Figure S11. (a) Digital image of hydrogel when exposed to various concentrations of (i) Glutathione (GSH), (ii) Cysteine, and (iii) 2,3- dimercaptosuccinic acid (2,3-DMSA), (b,c,d) concentration-dependent absorption spectra of the hydrogel when treated with GSH, cysteine, 2,3-DMSA respectively.

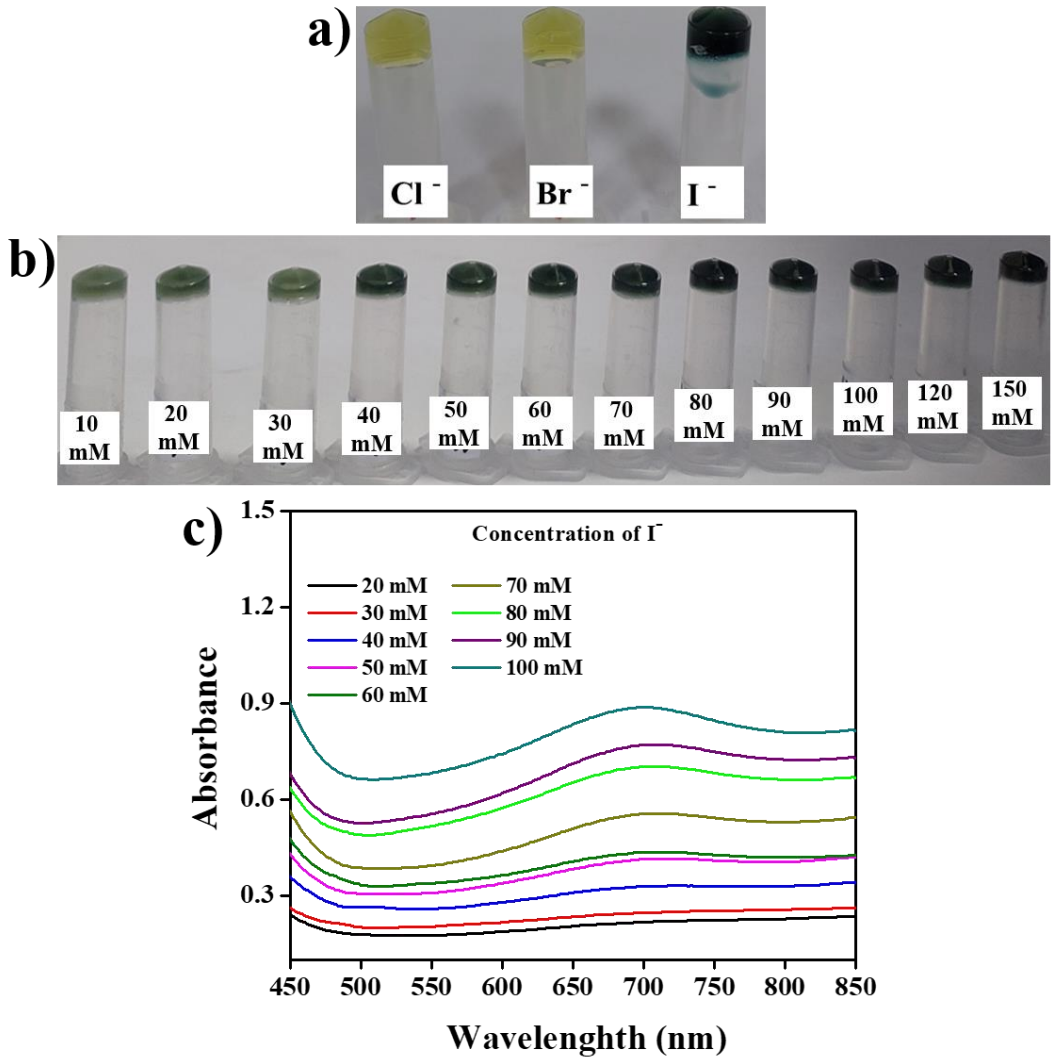

Figure S12. (a) Digital image of the hydrogel when treated with NaCl, NaBr, and NaI, (b) digital image of the hydrogel when treated with varying concentrations of iodide, (c) absorption spectra of the hydrogel when treated with varying concentrations of iodide.

Figure S13. (a) Hydrogel before exposure to pH change, (b) increasing pH by adding base leading to gel to sol transition of the hydrogel with bluish colour, and (c) acid added to the previous system to lower pH leading to restoration of the gel.

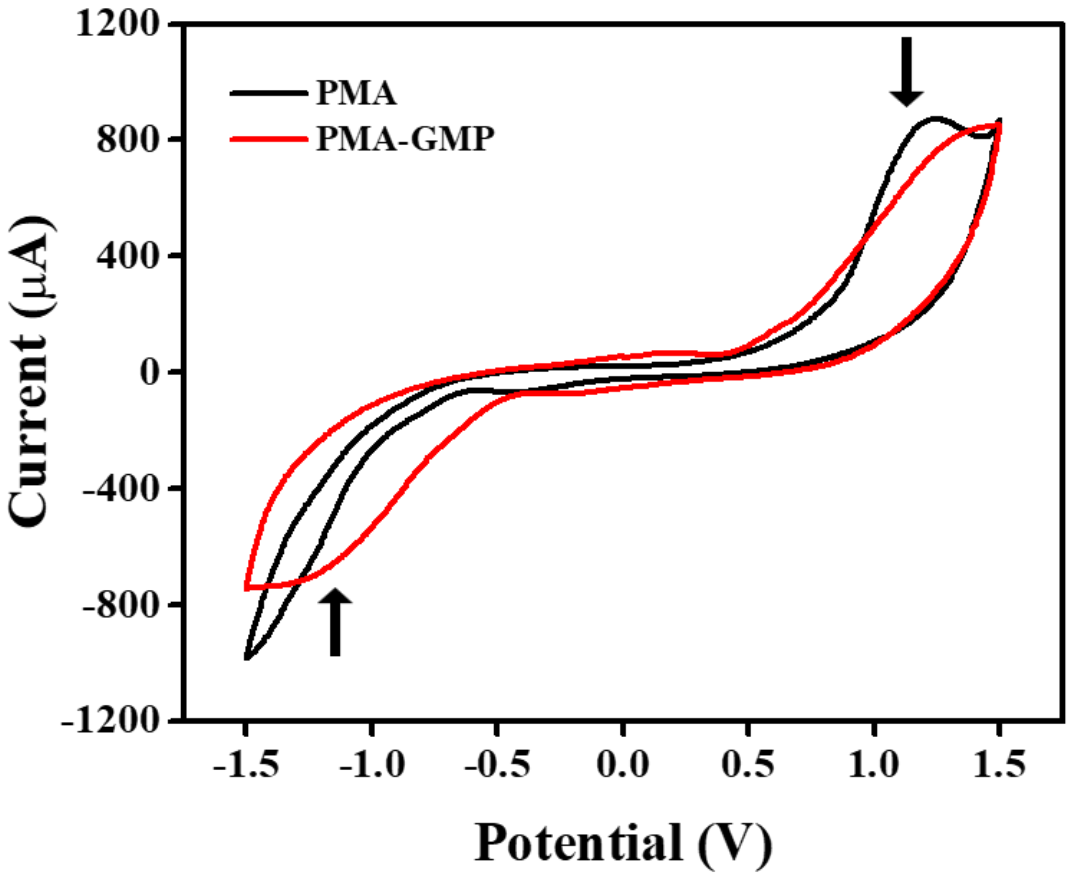

Figure S14. Cyclic voltammogram of bare PMA solution and PMA-GMP hydrogel at the scan rate of 50 mV s^{-1}.