Electronic Supporting Information

Light Responsive Two-Component Supramolecular Hydrogel: A Sensitive Platform for Humidity Sensors

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Contents

Experimental Details

Materials

Azobenzene-4,4'-dicarboxylic acid (95 %, TCI Chemical Company), Hexadecyltrimethylammonium bromide (CTAB) (99 %, Sigma Aldrich) and Sodium Hydroxide (97 %, Sigma Aldrich) were used as received. Disodium salt of azobenzene-4, 4'-dicarboxylic acid (AZNa) was prepared by dissolving the corresponding acid; azobenzene-4, 4'-dicarboxylic acid (0.5 g, 1.85 mmol) in 250 mL aqueous sodium hydroxide solution (pH 11) at 60 °C, then filtered the insoluble portion. Evaporation of filtrate portion produced bright red color powder of disodium salt of azobenzene-4, 4'-dicarboxylic acid, AZNa. Yield: 0.52 g (89 %).

Gel formation Method

For a typical gel formation reaction, AZNa (10.0 mg, 0.03 mmol) was dissolved in 500 µl of distilled water in a glass vial with gentle heating. To this solution while hot, aqueous solution (500 µl) of CTAB (23 mg, 0.06 mmol) has been added and mixed thoroughly. Within 2-3 min thick orange color gel formed which is stable in inverted vial.

Instrumentation

^{1}H NMR spectra were performed on a 600 MHz Avance III Bruker Corporation instrument using D_2O as solvent. Variable temperature ^{1}H NMR spectra were recorded with two gel samples (1.6 wt%, 0.33 wt%) from 25 °C to 50 °C with every 2 °C (± 1 °C) intervals and stabilization time was 10 min in each step. UV-vis spectra were recorded with Varian Carry 5000 UV-vis NIR spectrophotometer. Irradiation of UV light (365 nm) was carried out with OmniCure Series 2000 instrument.

The gel melting temperature (T_{gel} ± 1°C) was determined by placing the gel containing screw caped glass vials in a temperature controlled water bath (Buchi, Model B-491) and visually observing the flow upon tilt for every degree rise in temperature.

Scanning Electron Microscope

The morphological study of the fibers was done on an FEI Quanta 600 (USA) scanning electron microscope (SEM). The gel solution was dropped casted on aluminum tape and was coated with a thin layer of gold (5 nm).

Transmission Electron Microscope

Transmission electron microscopy (TEM) measurement of the gel sample was performed on a Tecnai T12 instrument at an acceleration voltage of 120 kV at room temperature. The sample was prepared by placing a drop of diluted gel on a carbon-coated copper grid followed by drying overnight.

Atomic Force Microscope

Atomic Force Microscopy (AFM) data were acquired using an Agilent 5400 SPM instrument (USA) in the tapping mode. The samples were deposited on a freshly cleaved Mica surface and left to dry for 12 hours in a vacuum desiccator.

Confocal Laser Scanning Microscopy (CLSM)

Confocal laser scanning microscopy (CLSM) images were obtained on FV1000, Olympus Co.

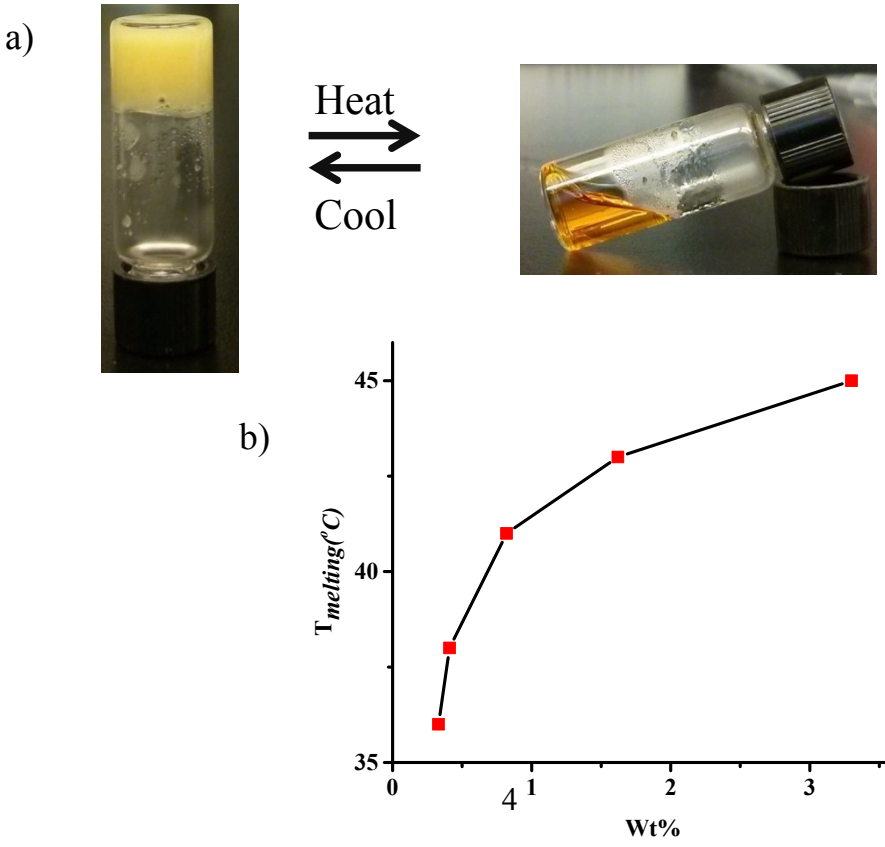
Rheology

For all the samples, rheological measurements were performed on Anton Parr, MCR 302 rheometer using 25 mm diameter parallel plate geometry with a constant tool gap of 1 mm. The gel sample was placed on the lower plate, and frequency sweep experiments were carried out at a constant frequency of 1 rad/s at 25 °C to obtain storage or elastic modulus, G', and loss or viscous modulus, G''. The amplitude sweep measurements were carried out at a constant stress in the linear viscoelastic range. For each gel, the experiments were carried out three times and average values were plotted. The elastic modulus values were taken in the linear viscoelastic region (LVR), which are independent of the applied strain.The storage modulus (G') and loss modulus (G'') with respect to applied stress (amplitude sweep) and

applied frequency (frequency sweep) has been measured for 1.65 wt%, 2.47 wt% and 3.3 wt% hydrogel samples.

Humidity Experiment

Forhumidity testing, two different experimental approaches were conducted, the purge and ramp experiment, as described in literature.[13] The temperature of the chiller bath was maintained at 17 °C while the ambient temperature was measured at 20 °C. We found similar results from both experiments and sensing films. The presented results in the manuscript are for the ramp experiment since it provides more data points compared to the purge and achieving the same response.



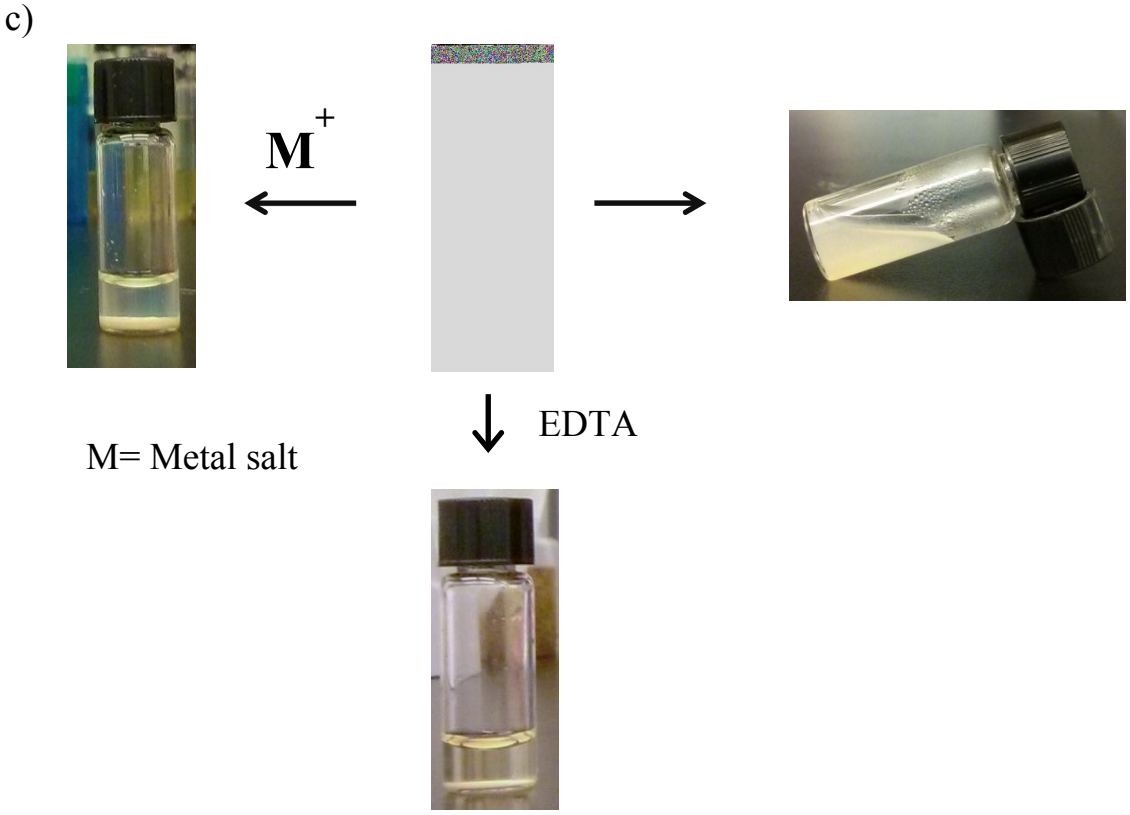


Fig. S1 a) Thermo-reversibility of the hydrogel; b) gel melting temperature with different gelator concentrations; c) responsiveness of the hydrogel to different chemical stimuli

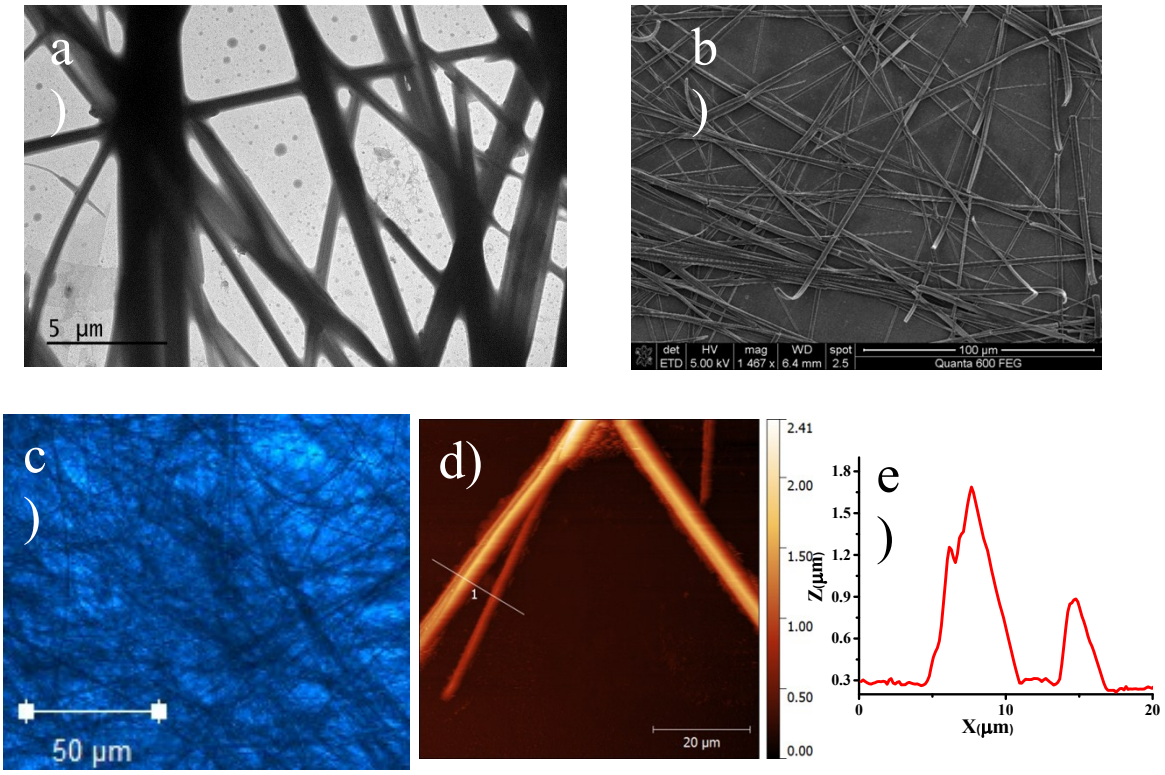


Fig. S2 Microscopic images of hydrogel; a) TEM, b) SEM , c) CLSM, d) AFM height profile image, e) cross-section analysis along the gray line in panel d.

Table S1: *G*' – *G*" and Yield Stress value for hydrogels with three different gelator concentrations

Gel wt %	(*G*' – *G*") (Pa)	Yield stress (σ_y) (Pa)
1.65	2861	2.76
2.47	8949	3.57
3.3	10147	4.41

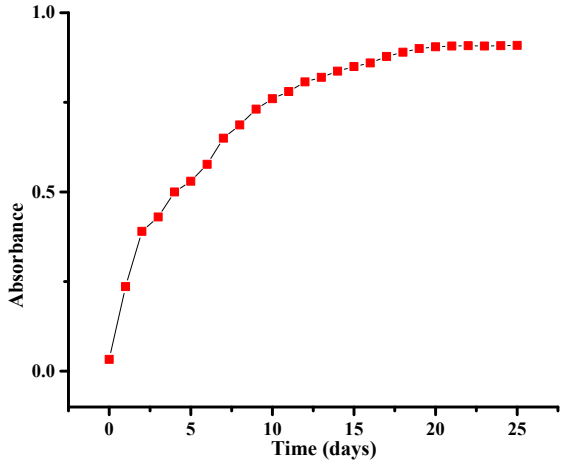


Fig. S3 Gel erosion kinetics over 25 days time under water at room temperature.

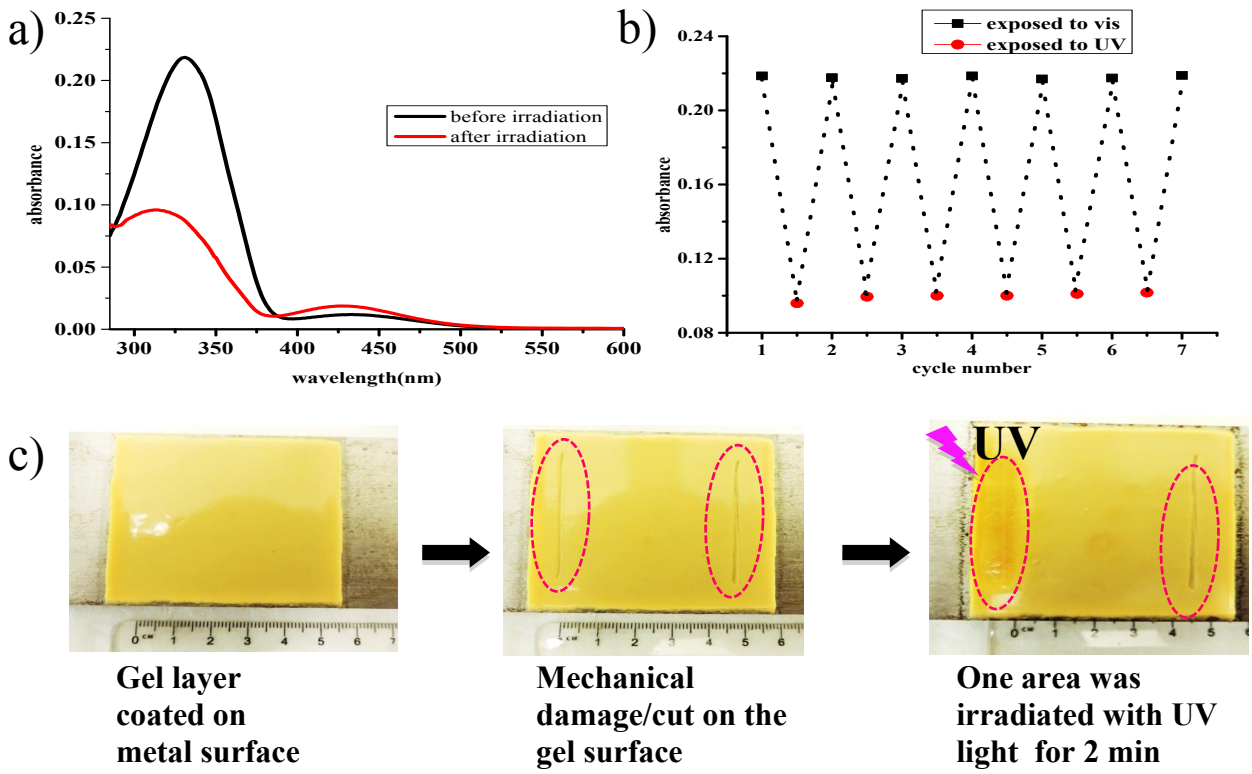


Fig. S4 a) Uv/vis spectra before and after irradiation of dilute gel (1 X 10 $^{-5}$ M); b) the absorbance at 347 nm of sample by alternate irradiation at UV and visible light, respectively; c) UV-induced self-repairing of a gel coating on metal surface.