Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information

Synthesis and combined Electrical-Magnetic and toxic dye sequestrating properties of a Cr(III)-Metallogel

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Synthesis of 5-Azidoisophthalic acid (N_3IPA):

To a mixture of 5-aminoisophthalic acid (2.00g,11 mmol) and 5ml concentrated HCl in 30 ml water was added drop wise a solution of $NaNO_2$(0.828g,12 mmol) in 5 ml water. The temperature was maintained between 0°-5°C. The solution was kept under stirring condition for 40 minutes until a pale yellow precipitate formed. Then ice cold aqueous solution of NaN_3 (0.780g, 12mmol) was added drop wise to this solution while the temperature was maintained below 5°C throughout the reaction. A white precipitate was started to develop and the resulting solution was stirred for overnight. The precipitate was filtered and washed with distilled water for several times to run out excess acid. Finally, the product thus obtained was dried under vacuum at 50°C and then recrystallized from absolute ethanol (Yield: 83% on the basis of 5-aminoisophthalic acid).

IR(4000-400cm-1) 3550s, 3464s, 3103s, 2121vs,1721vs, 1666m, 1603s, 1462m, 1406m, 1312s, 1218vs, 1171m, 1096m, 809w, 754w, 668m, 535w, 432w.

Elemental Anal: Calcd (found) C: 46.39 (45.71), H: 2.43 (2.21), N: 20.19 (19.52).

HRMS: Cald: 207.028, Found: 207.127

IR data:

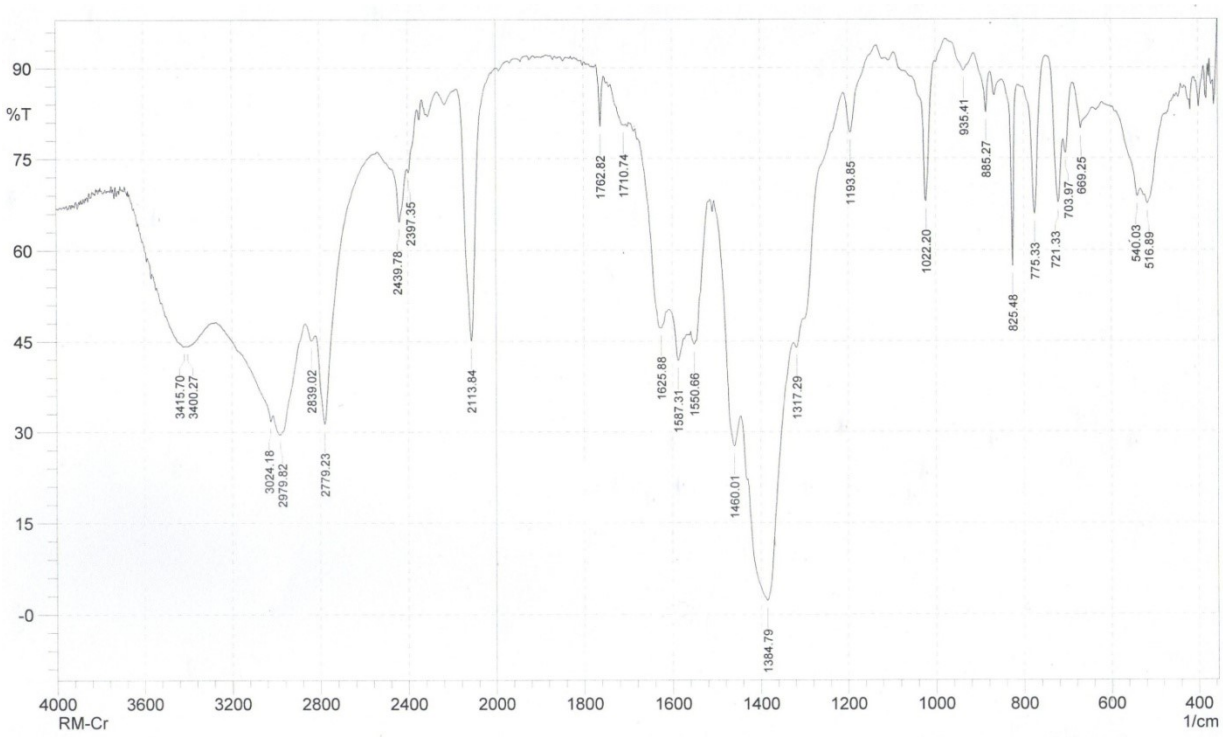


Figure S1: IR data of xerogel

UV-Vis data:

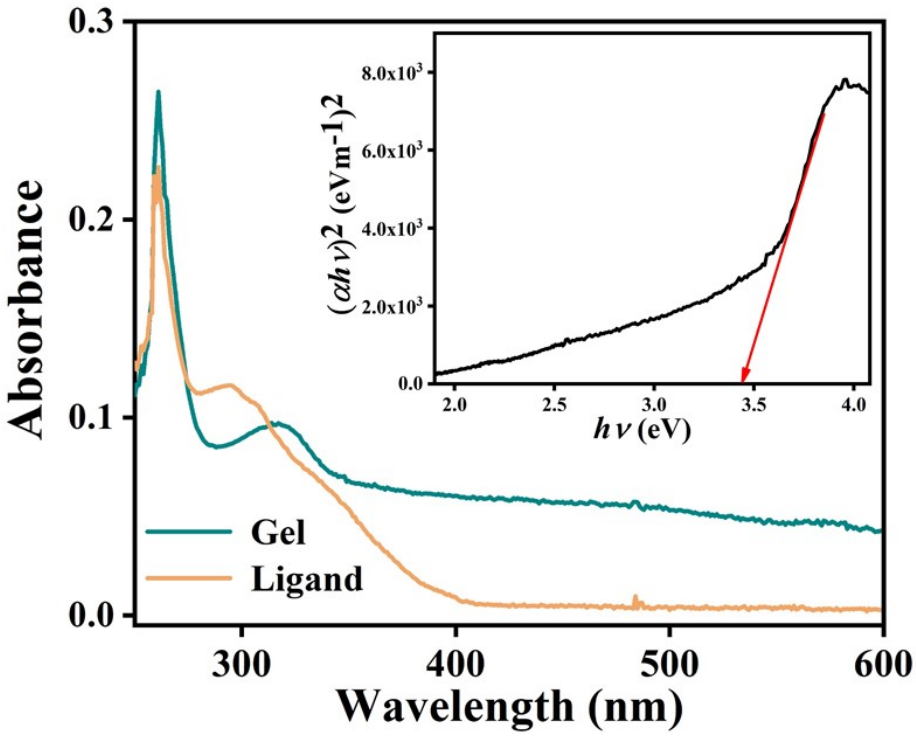
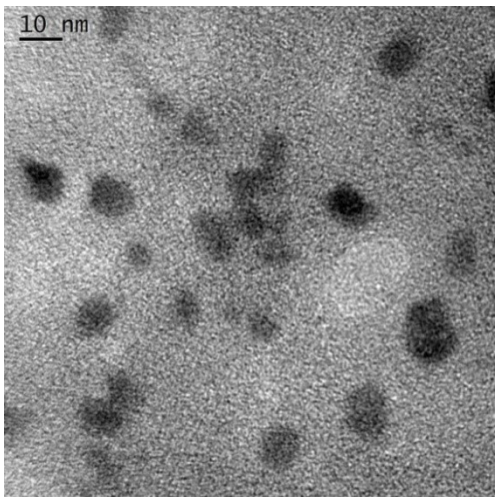
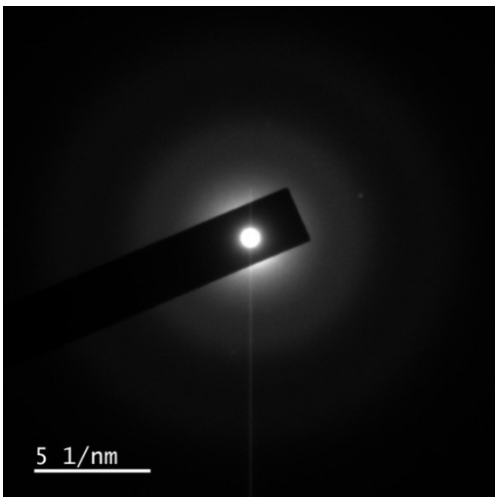


Figure S2: UV-Vis data of ligand and gel along with Tauc plot (inset).

Additional SEM and TEM images:

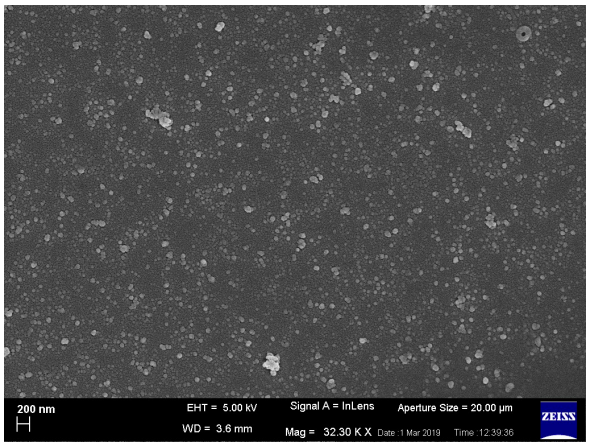
(a)





(b)

(c)



(d)

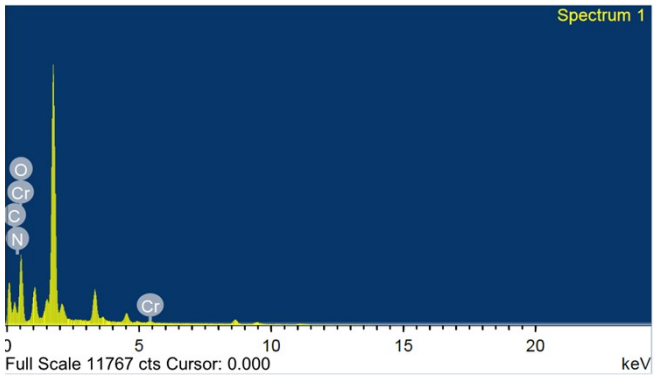
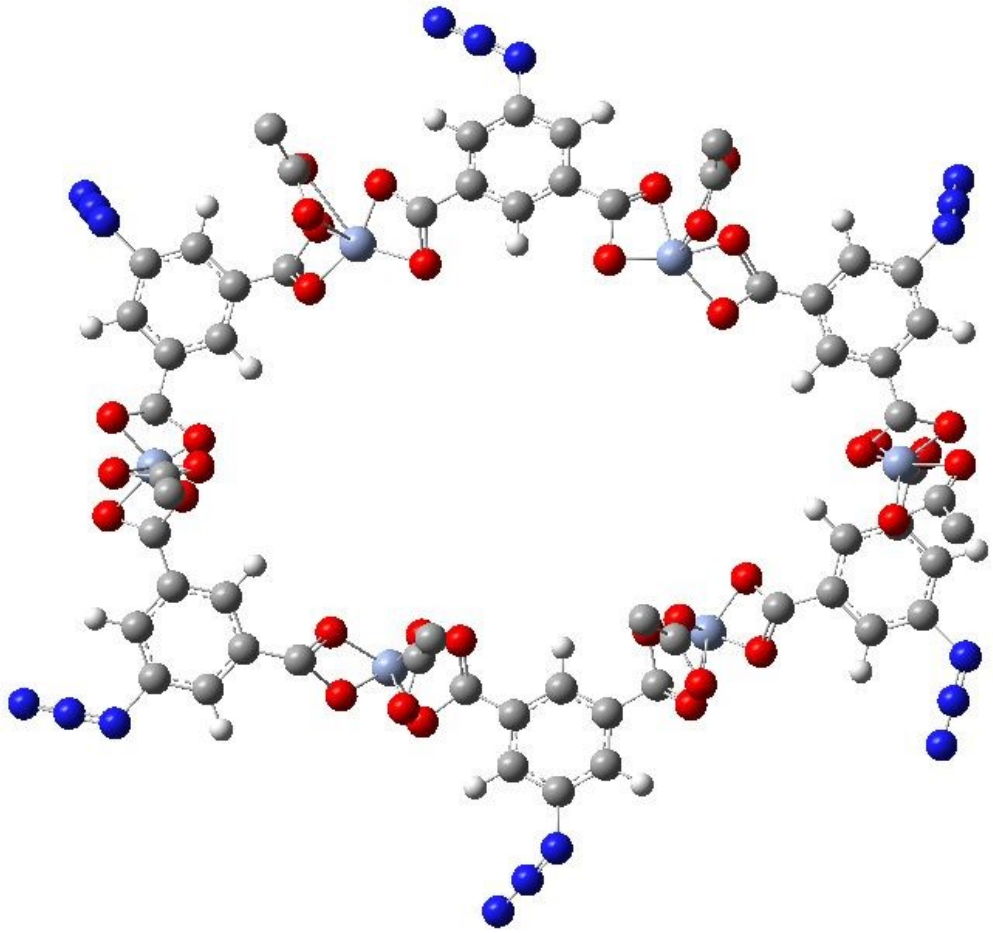


Table S1

(e)

Elements	Weight%	Atomic%
C	20.07	24.41
N	23.91	24.93
O	55.25	50.44
Cr	0.76	0.21

Figure S3: Microscopy analysis of gel showing (a) HRTEM image, (b) SAED pattern , (c) SEM image, (d) EDX spectrum and (e) composition of elements from EDX.



Scheme-SI: A schematic representation of possible self-assembly of the metallogel.

Rheology data:

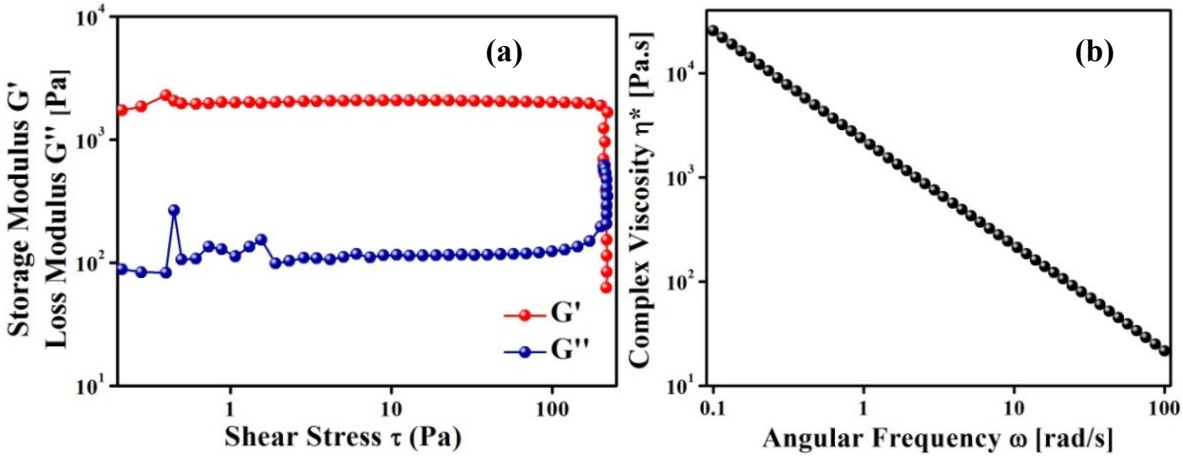


Figure S4: Rheology data of gel showing (a) stress sweep plot and (b) complex viscosity vs angular frequency plot.

Thermal Analysis(TGA):

The thermal stability of the compounds was studied by TGA. The experiment was performed on xerogel (dried under room temperature) sample under N_2 atmosphere with a heating rate of 10°C/min**.** First 7% weight loss is due to loss of methanol molecules. Subsequent weight loss upto 49% is associated with the combined loss of entrapped H_2O,DMF, and $–N_3$ molecules. The weight loss thereafter is basically due to disintegration of xerogel matrix with the increase in temperature.

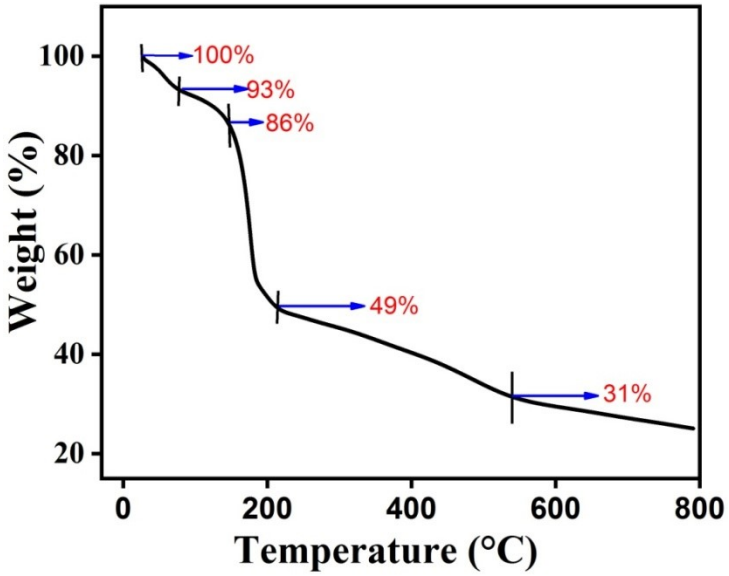


Figure S5: TGA of xerogel

Electrical Characterization:

The Thermionic Emission (TE) theory is adopted to get more insights of the charge transport mechanism in the devices.[1] The current of a diode can be expressed as the following equations according to TE theory.[2]

$$I = I_0 \exp\left(\frac{qV}{\eta kT}\right)\left[1 - \exp\left(-\frac{qV}{\eta kT}\right)\right] \qquad \ldots\ldots(S1)$$

Where,

$$I_0 = AA^{*}T^2 \exp\left(-\frac{q\phi_B}{kT}\right) \qquad \ldots\ldots(S2)$$

$$\phi_B = \frac{kT}{q} \ln\left(\frac{AA^*T^2}{I_0}\right) \qquad \text{……(S3)}$$

Where, I_0 indicates the saturation current, q represents the electronic charge, k is the Boltzmann constant, T is the temperature in Kelvin, V is the forward bias voltage, η is the ideality factor, ϕ_B is the effective barrier height at zero bias, A is the diode area (7.065×10^{-6} m^2), A^* is the effective Richardson constant (1.20×10^6 $Am^{-2}K^{-2}$). From Cheung, the forward bias I-V characteristics in term of series resistance can be expressed as.[3]

$$I = I_0 \exp\left[\frac{q(V - IR_S)}{\eta kT}\right] \qquad \text{…….(S4)}$$

Where, the IR_S term represents the voltage drop across series resistance of device. In this circumstance, the values of the series resistance can be determined from following functions using equation (7).[4]

According to Cheung's model:

$$\frac{dV}{d\ln(J)} = \left(\frac{\eta kT}{q}\right) + R_S AJ \qquad \text{…….(S5)}$$

$$H(J) = R_S AJ + \eta\phi_B \qquad \text{……(S6)}$$

and H(J) can be expressed as:

$$H(J) = V - \left(\frac{\eta kT}{q}\right)\ln\left(\frac{J}{A^*T^2}\right) \qquad \text{…….(S7)}$$

Stability for nanocomposite gel/Al structured thin film:

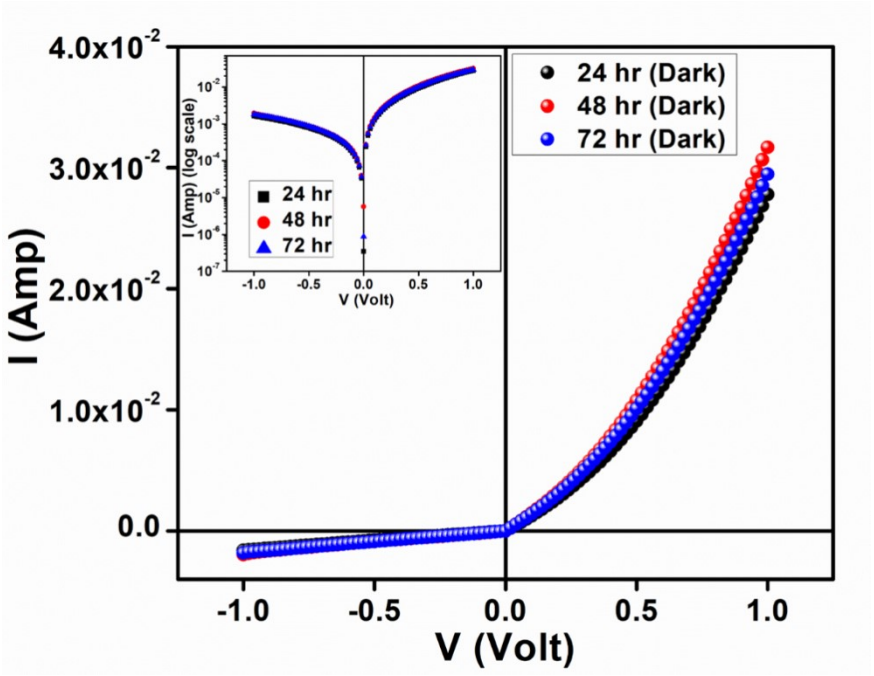


Figure S6: I-V curve with a time interval of 24hr, 48 hr and 72 hrs.

Integrity of sample through IR:

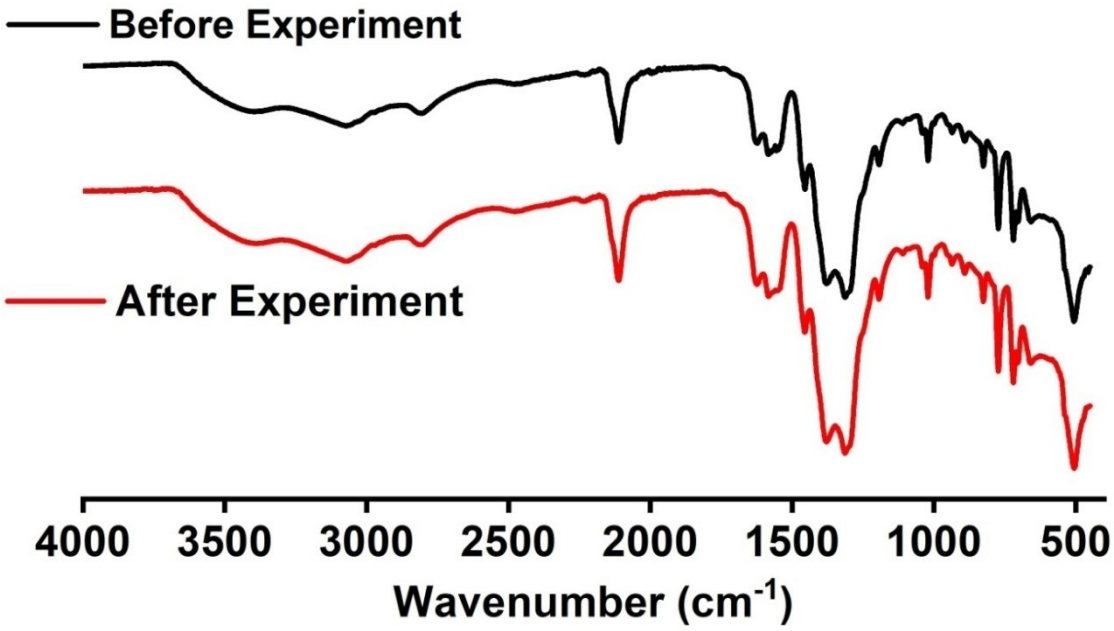


Figure S7: Comparison of FTIR spectra of the xerogel before and after the proton conductivity experiments.

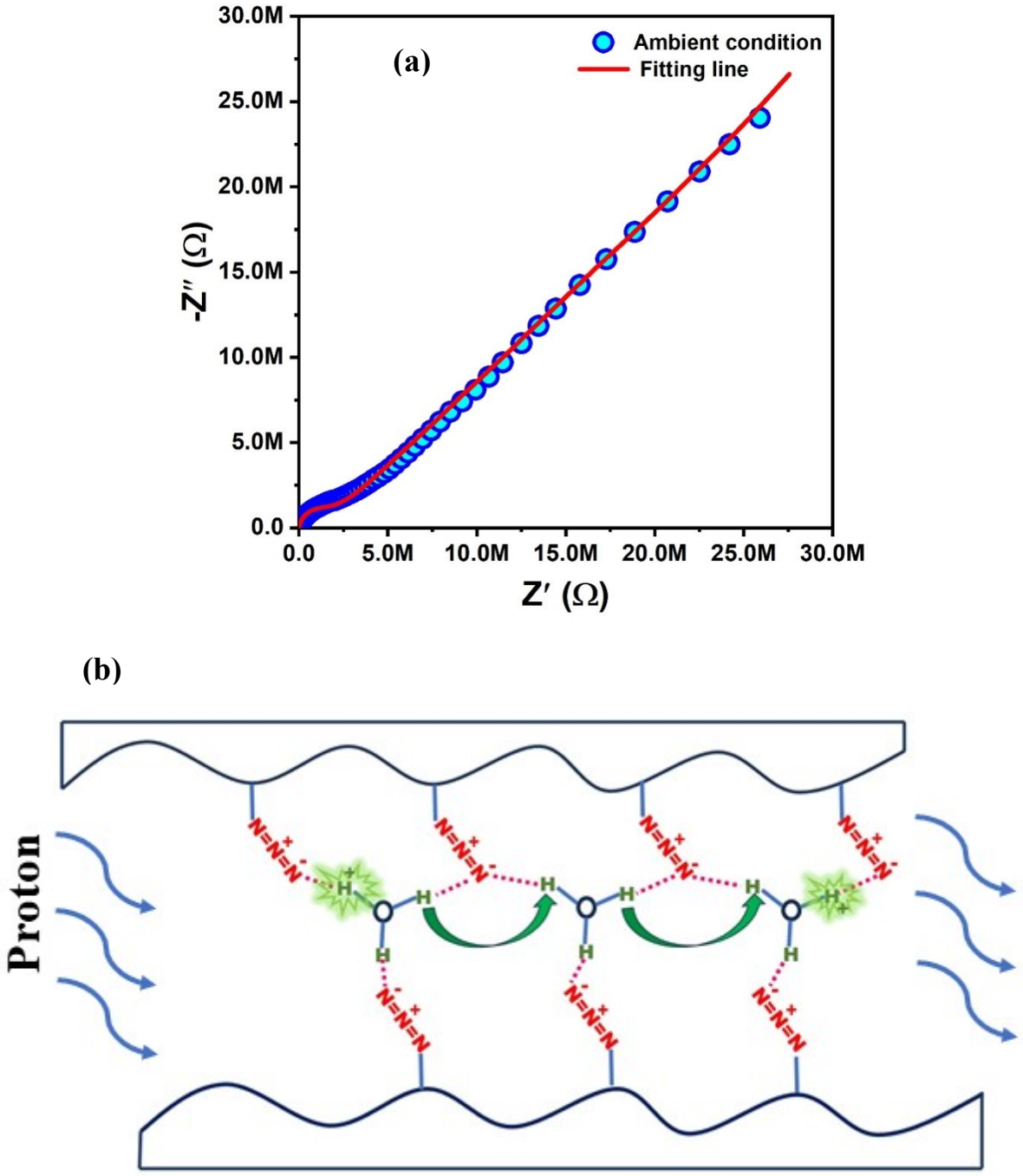


Figure S8: (a) Nyquist plots of the activated xerogel and (b) Possible proton conduction path.

Gas Adsorption studies:

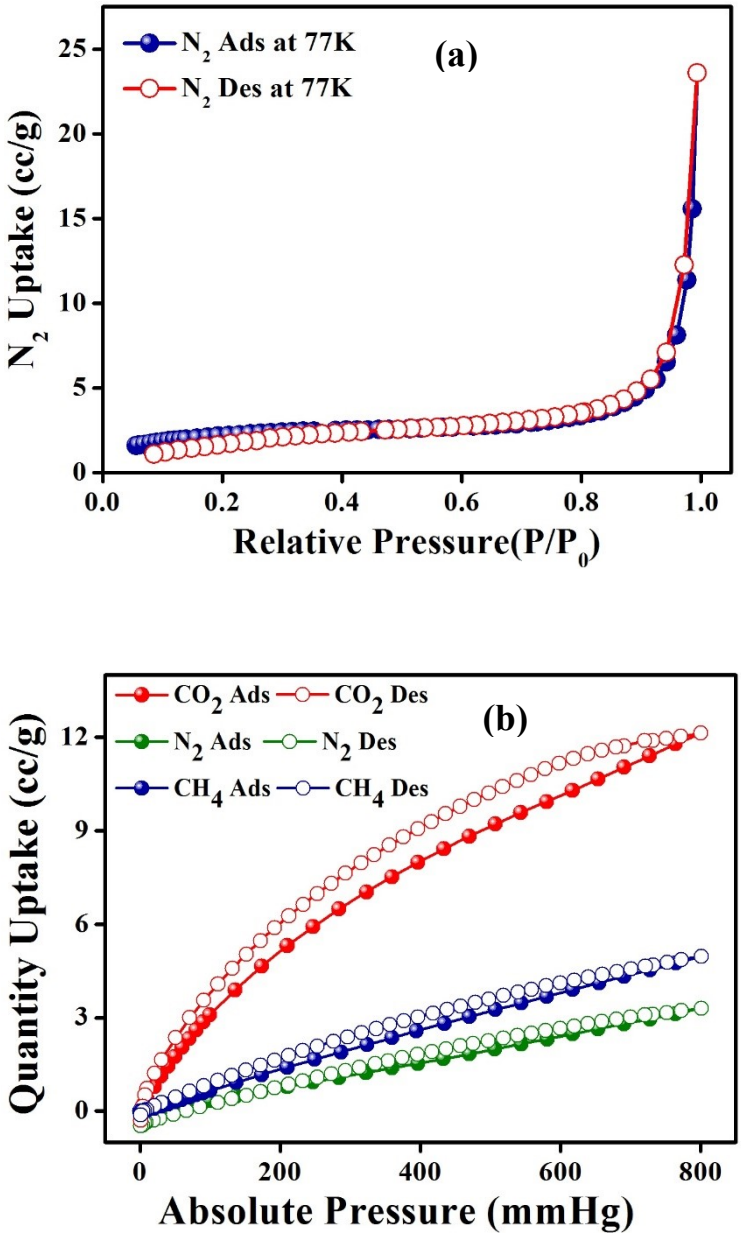


Figure S9: Gas adsorption data of the xerogel showing (a) N_2 adsorption at 77K and (b) Selective CO_2 adsorption over N_2 and CH_4 at room temperature.

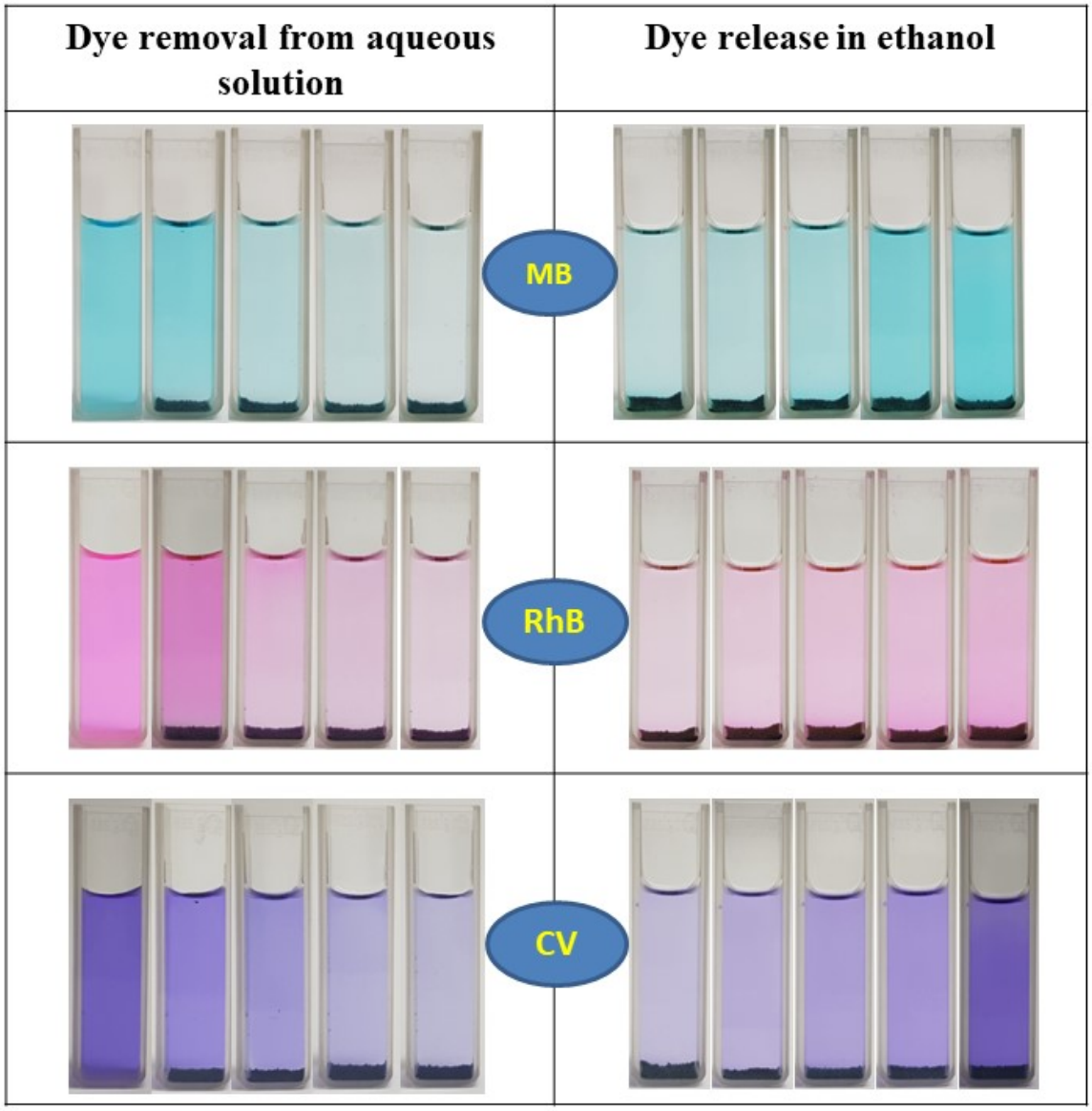


Figure S10: Gradual change in colour intensity due to adsorption and the corresponding release event.

Table S2

Organic Dyes	Methelene Blue (MB)	Rhodamine B (RhB)	Crystal Violet (CV)
% Removal (from aqueous solution)	**82.25**	**82.17**	**76.45**
% Release (in ethanol)	**76.74**	**45.36**	**93.18**

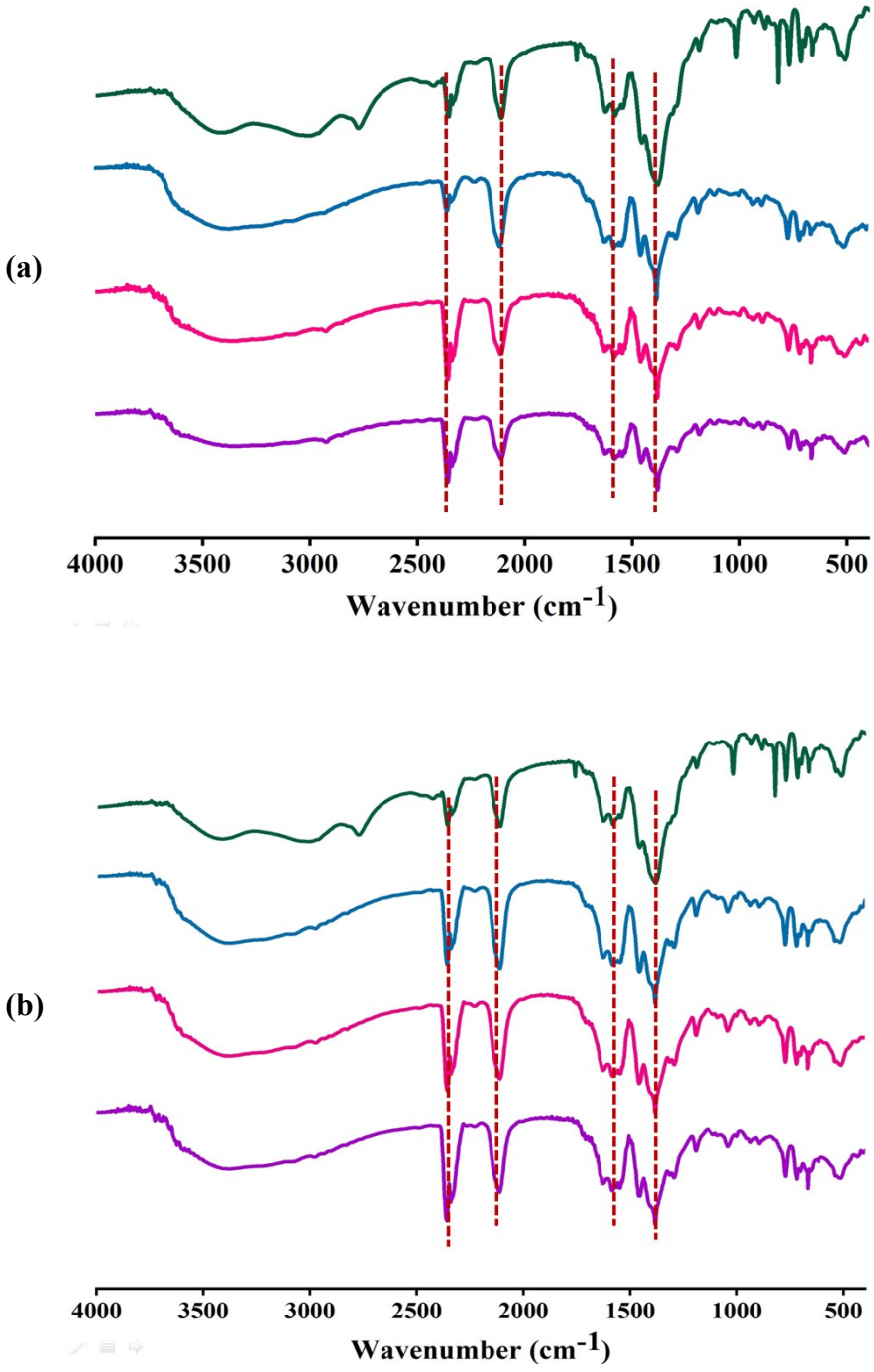


Figure S11: Merged plot of IR of xerogel (green) after (a) adsorbing different dyes (blue: MB, pink: RhB & violet: CV) and (b) releasing those dyes.

Images of adsorption and desorption:

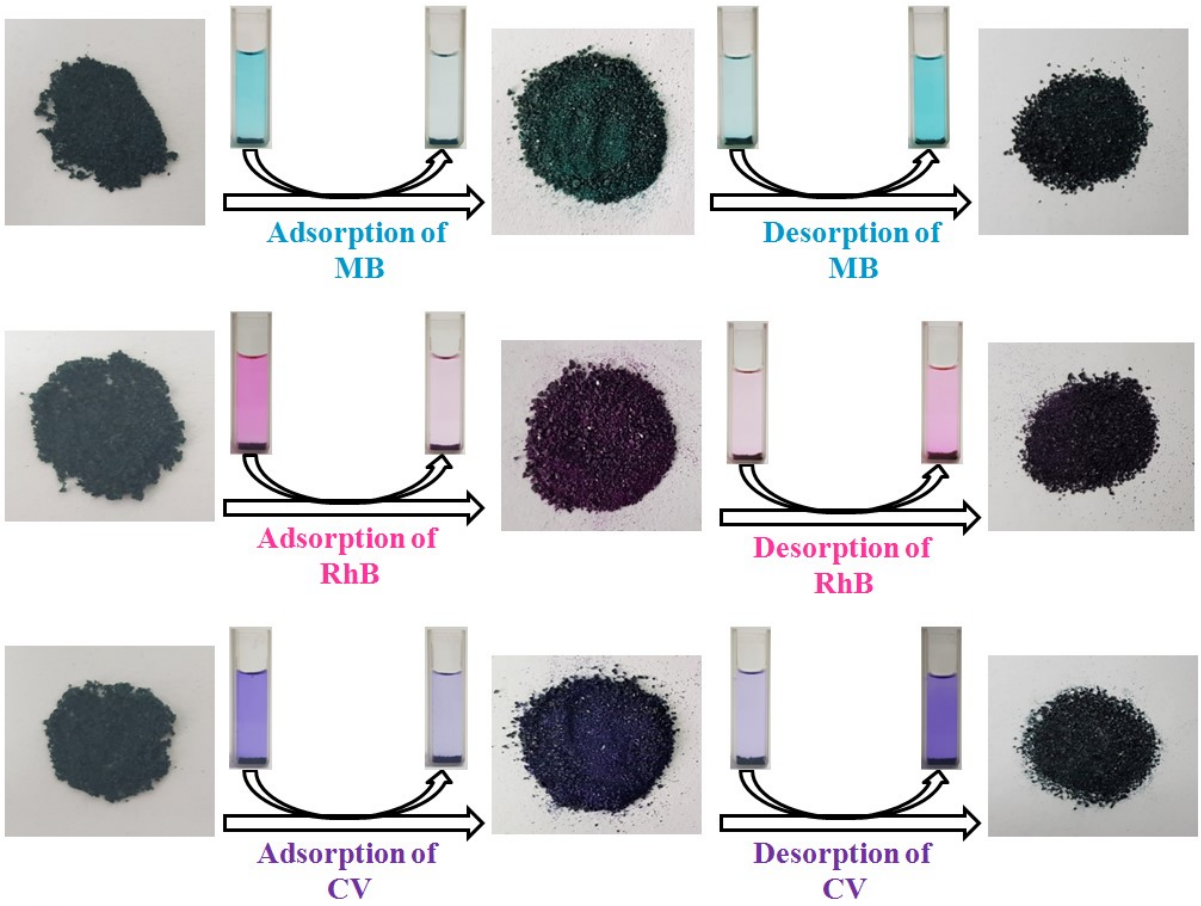


Figure S12: Images of xerogel after adsorption (from aqueous solution)and desorption (release in ethanol) of various dyes

References:

1. E. H. Rhoderick and R. H. Williams, Metal-Semiconductor Contacts, Clarendon Press, Oxford, 2nd edn, 1988.

2. S. M. Sze, Physics of Semiconductor Devices, Wiley, New York., 1981.

3. S. Sil, R. Jana, A. Biswas, D. Das, A. Dey, J. Datta, D. Sanyal and P. P. Ray, *IEEE Trans. Electron Devices*, 2020, **67**, 2082-2087.

4. M. Das, J. Datta, A. Dey, R. Jana, A. Layek, S. Middya and P. P. Ray, *RSC Adv.*, 2015, **5**, 101582-101592.