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A "heat set" Zr-Diimide based Fibrous Metallogel: Multiresponsive Sensor, Column-based Dye Separation, and Iodine Sequestration



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ABSTRACT

Sensing and monitoring hazardous contaminants in water and radioactive iodine sequestration is pivotal due to their detrimental impact on biological ecosystems. In this context, herein, a water stable zirconium-diimide based metallogel (Zr@MG) with fibrous columnar morphology is accomplished through the "heat set" method. The presence of diimide linkage with long aromatic chain manifests active luminescence properties in the linker as well as in the supramolecular framework structure. The assynthesized Zr@MG xerogel can selectively detect $Cr_2O_7^{2-}$ (LOD = 0.52 ppm) and 2,4,6-trinitrophenol (TNP) (LOD = 80.2 ppb) in the aqueous medium. The Zr@MG paper strip-based detection for $Cr_2O_7^{2-}$ and nitro explosive makes this metallogel reliable and an attractive luminescent sensor for practical use. Moreover, a column-based dye separation experiment was performed to show selective capture of positively charged methylene blue (MB) dye with 98 % separation efficiency from the mixture of two dyes. Also, the Zr@MG xerogel showed effective iodine sequestration from the vapor phase (232 wt%). © 2022 Elsevier Inc. All rights reserved.

1. Introduction:

Rapid urbanization and industrialization are inevitable impacts of an ever-growing global population [1]. Industrial waste, such as heavy metal salts and toxic anions, have evolved into worldwide

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hazards, causing ecological imbalances via water and soil pollution [2]. Among various anionic species, a number of oxoanions such as $Cr_2O_7^{2-}$, AsO₄³⁻, TcO₄⁻, and SeO₃²⁻ have been designated as highly hazardous anionic contaminants by the United States Environmental Protection Agency [3]. Among them, dichromate ions can induce imbalance in human protein enzyme system even at very low concentrations [4,5]. The key sources of $Cr_2O_7^{2-}$ are paints, chromium electroplating, metallurgy, and leather tanning industries that can contaminate our ecosystem to lead to an unhealthy inhabitable environment [6,7]. Different techniques have been established for the detection and separation of above mentioned contaminants, such as ion exchange [8], inductively coupled plasma-mass spectrometry (ICP-MS) [9], electrochemistry [10], atomic absorption spectroscopy (AAS) [11], and resins [12]. Although these techniques are efficient but they are also time consuming [13], expensive, and involve tedious sample preparations [14]. On the other hand, the fluorescence sensing method gained widespread attention due to its easy detection ability in lower concentrations with selectivity [15,16]. In general, lanthanide based materials are used to detect $Cr_2O_7^{2-}$ due to their intense luminescence properties [17,18]. In this context, most of the fluorophores are unable to sense $Cr_2O_7^{2-}$ in aqueous medium due to their poor hydrolytic stability [19] or critical quenching effect in water medium [20]. Hence there are opportunities to synthesize a material that can be prepared easily and able to detect analyte selectively in aqueous medium [21]. Similarly, detecting nitro explosives for public safety, national security, and environmental protection using appropriate chemosensors has attracted much more attention [22-24]. 2,4,6trinitrophenol (TNP) is more potent explosives compared to other nitro aromatics [25]. It is often used in industrial processes, such as dye synthesis, ceramic industries, and fireworks production, which raises serious environmental and human health issues [26,27]. Till now, there have only been a few studies on luminescent based TNP detection using soft material as a sensor [28,29]. As a result, there is an urgent need to synthesize material for fast and selective detection of TNP in aqueous medium.

Dyes are an intrinsic part of many industries and are extensively utilized as colouring agents in the photography, paper printing, petroleum, leather, and pharmaceutical sectors [30,31]. In consequence, releasing these dyes as industrial waste can directly contaminate soil and water, which may adversely affect the ecological chain system of the respective [32,33]. There are various methods available to treat these pollutants; adsorption is the most common and straightforward. Although it is an easy technique, challenges may appear when separation from the mixture of dyes comes into the picture. So, there are opportunities to synthesize an efficient adsorbent that can selectively adsorb and separate the specific dye from the mixture of dyes for reutilization, which is environmentally and economically beneficial.

Continuous industrial growth and increasing global population have catapulted the energy demand to hit its highest peak. To meet the compulsion, fossil fuel burning is the general pathway; however, its future abundance and impact on global warming limit its potential use [34]. Nuclear energy is widely recognized as one of the most viable and important alternative energy sources [35]. After the fission process, residues such as ¹³¹I, ¹²⁹I, ⁹⁹Tc, ²³⁵U, etc., demand careful handling as they are extremely harmful [36-38]. Amongst them, ¹³¹I and ¹²⁹I are volatile and exhibit hazards to the ecosystem and bring direct threats to human physiology [39]. Accumulation of radioactive iodine in human organs leads to an increased risk of leukemia and metabolic disorders [40,41]. There are various materials that have been reported as iodine adsorbate, such as polymeric resins, silica, zeolite based materials, silver based high cost materials [42]. These materials have their limitation to use as a pioneer adsorbate. Recently metal sulfide based aerogels have been proven to be a very efficient material

for capturing iodine, but it involves tedious synthesis techniques [43]. There is an urgency to design and develop new materials to overcome above mentioned limitations.

Gels are ubiquitous in our everyday lives [44]. A combination of the small fraction of gelators and large quantity of gelling solvent is required for supramolecular gel network [45]. Serendipity takes part in the creation of the semisolid gel materials [46]. Introducing metal ions into the gel matrices [47] not only stabilized the supramolecular gel network structure but also brought out the new field of applications such as redox activity [48,49], catalytic applications [50-54], conductivity [55,56], magnetism [57,58], luminescence sensors [59-62], etc. Metallogel (MOG) is gaining traction as a novel class of functional materials that involve metal ligand coordination or/and any other weak interactions to make supramolecular assemblies [63–66]. The low Molecular Weight Gelator (LMWG) [67] interacted with particular metal ion makes a stable supramolecular network that can be stabilized through various non-covalent interactions such as, hydrogen bonding, $\pi^{--}\pi\pi$ -stacking interactions [68–71].

Herein, we have synthesized a zirconium-diimide based metallogel using bifunctional (carboxylic acid/imide) tetrapodal based ligand (H₄L) [72]. The presence of diimide group with a long conjugated aromatic ring plays a vital role in forming metallogel via supramolecular interaction. A heat-set method [62] was used to synthesize the metallogel, which shows blue emitting color in the presence of a UV source (λ_{ex} = 365 nm). The material can detect $Cr_2O_7^{2-}$ and TNP selectively in aqueous medium using the fluorescence titration method with high Ksv values of 9760 M⁻¹ and 15295 M⁻¹ and low detection limit of 0.52 ppm and 80.2 ppb respectively [73,74]. More interestingly, a column-based dye separation technique was introduced to separate out one specific dye from the mixture of dyes. The xerogel material can selectively adsorb and separate methylene blue (MB) from the mixture of methylene blue (MB)/orange G (OG) dyes. It shows almost 98 % separation efficiency for MB from the mixture of two dyes. Furthermore, as synthesized Zr@MG was found to be an excellent host matrix for iodine sequestration from vapor phase. To become an efficient adsorbent of iodine, the material should show stability up to several cycles with good releasing capacity, and in this context, our material recyclability test was performed up to 3 cycles.

2. Experimental section:

2.1. Material used:

Sodium and potassium salts (NaBr, KI, KNO₃, K₂Cr₂O₇, NaCl, Na₂SeO₄, Na₃AsO₄, NaF, KNO₂, Na₂SO₄), zirconium oxychloride octahydrate, acetic acid, N,N'-dimethylformamide, dimethyl sulfoxide, iodine, methylene blue, orange G, TNP, toluene, aniline, benzoic acid, isophthalic acid, p-toluidine, phenol, 4-nitrophenol (4-NP) were purchased from Central Drug House (CDH). 5-aminoisophthalic acid and pyromellitic dianhydride were obtained from Alfa Aesar and Sigma Aldrich respectively. Nitrobenzene (NB) was purchased from Tokyo Chemical Industry (TCI). In the experiment, all compounds were used without further purification.

2.2. The synthesis procedure of H_4L ligand:

The ligand; N,N'-bis(5-isophthalic acid)-pyromellitic diimide was synthesized, followed by the reported procedure [72] with slight modifications. In a 100 mL round bottom flask, benzene-1,2,4,5-tetracarboxylic dianhydride (800 mg, 3.67 mmol) was mixed with 30 mL of glacial acetic acid. The mixture was kept for stirring at ambient temperature. After 15 min of stirring, 5-aminoisophthalic acid (1330 mg, 7.34 mmol) was added gently

to that mixture. After continuous stirring for 24 h, the white precipitate was obtained under a reflux condition at 120 °C temperature. After filtration, the obtained precipitate was washed with distilled water and chloroform five times, and then it was recrystallized in DMSO solvent. The obtained light yellow colored crystals were washed with distilled water followed by methanol and diethyl ether. Finally, it was kept in a vacuum oven at 70 °C temperature for drying. Yield: 1405 mg (25 mmol, 70.34 %). ¹H NMR (400 MHz, DMSO d_6): δ = 8.55–8.54 (t, *J* = 1.57 Hz, 2H, Ha), 8.46 (s, 2H, Hc), 8.38 (d, *J* = 1.57 Hz, 4H, Hb). ¹³C NMR (400 MHz, DMSO d_6): δ = 166.36, 165.66, 137.60, 132.84, 132.56, 132.30, 129.87, 118.50 (Figs. S1 and S2, see supporting information).

2.3. Metallogel synthesis:

A zirconium-diimide based metallogel was synthesized by the reaction of bifunctional tetrapodal ligand (H₄L) and zirconium oxychloride octahydrate through the heat set method. The ligand and metal salt were taken in 1:1 M ratio to form the metallogel. Typically, 0.1 M solution of $ZrOCl_2 \cdot 8H_2O$ was prepared in the solvent mixture of DMF: Water (3:2). Then, 0.1 M solution of H₄L was prepared in DMSO solvent. Finally, 5 mL solution of H₄L was directly poured into the glass vial containing 5 mL metal salt solution and kept in an oven at 90 °C for 30 min to get stable Zr@MG metallogel. The metallogel was dried through lyophilization process to get Zr@MG xerogel.

2.4. The methodology for $Cr_2O_7^{2-}$ and TNP sensing:

The fluorescence titration experiment was carried out by taking 4 mg of Zr@MG xerogel dispersed in 2 mL of water. After dispersing into the water, the xerogel suspension was sonicated for 30 min for further photoluminescence (PL) study. A prominent emission peak was recorded at 440 nm when the suspension was excited at 335 nm. Sensing experiments were performed using 10 mM aqueous solution of sodium and potassium salts. On the other hand, 10 mM aqueous solution of each organic analyte was prepared for further sensing study. In every experiment, each analyte was added up to 200 μ L in Zr@MG suspension, and emission spectra were recorded. The same excitation wavelength (335 nm) and emission wavelength (440 nm) were monitored throughout the PL study except for TNP. A bathochromic shift in the characteristic emission peak was observed after gradual adding of it up to 200 μ L (440 nm to 485 nm).

Quenching efficiency for each analyte was calculated using the equation expressed by,

$$(1 - I/I_0) \times 100\%$$
 (1)

 I_0 is the fluorescence intensity before adding analytes, and I is the fluorescence intensity after adding analytes.

2.5. Paper strips technique for $Cr_2O_7^{2-}$ and TNP detection:

Whatman filter paper was cut down in a rectangular shape (2 cm \times 3 cm) for the fluorescence paper strips test. These were immersed into 30 mL of xerogel water suspension and kept in ultra-sonification for 30 min. After that, these were dried in a vacuum oven at 60 °C for 3 h. The paper strips were ready to use for Cr₂O₇² and TNP detection.

2.6. Column-based dye separation/kinetics study:

The selective dye separation efficiency for this xerogel material was investigated using a column-based technique. Two columns were packed with the xerogel material (40 mg of the compound in each column). An aqueous solution of MB dye (30 mg/L) was

used for a single adsorption experiment, and in another column, a binary mixture of two dyes, i.e., MB/OG (30 mg/L + 30 mg/L) was passed to observe separation phenomena. UV–Vis spectroscopic study was performed after taking the effluent to correlate with the naked eye test. A separate kinetic study was performed for the MB, OG, as well as for a mixture of MB/OG dye using UV–Vis spectroscopy. 10 mg of xerogel material was taken in 20 mg/L dye solution, and dye adsorption performance was observed up to 60 min for each experiment.

2.7. Iodine sequestration experiments:

A gravimetric approach was implied to examine the iodine uptake process in vapor phase. One small glass bottle containing 200 mg of xerogel was connected through another container where iodine pellets were placed. The complete system was maintained under atmospheric pressure at a constant temperature of around 75 °C. After cooling down to room temperature, iodine loaded xerogel was weighed at various time intervals in order to determine the iodine adsorption capacity of the xerogel. The following equation was used to evaluate the iodine loading capacity

$$x = (\frac{M_2 - M_1}{M_1}) \times 100wt\%$$
⁽²⁾

lodine adsorption capacity is denoted by x; M_2 and M_1 are the weight of the xerogel after and before iodine adsorption, respectively.

3. Result and discussion:

The presence of imide linkage with aromatic ring triggers the hydrogen bonding as well as π - π stacking interactions, resulting in the formation of supramolecular 3D gel network structure through self-assembly (Fig. 1a). A temperature dependent gelation study was accomplished to investigate the gelation behavior. From room temperature to 50 °C, it was in a sol state, and the changes in gelation behaviour were observed afterwards. Finally, it formed a stable gel at 90 °C (Fig. 1b-e). The carboxylic acid groups are coordinating sites to bind with Zr (IV). The as synthesized metallogel was transparent enough (Fig. 1f and g) to see the 'IITP' logo from the top of the vial (thickness around 1 cm). More interestingly, shape mediated different structures such as 'heart' and 'star' like shapes were made to show utility the metallogel as soft material (Fig. 1h and i).

The viscoelastic nature of the metallogel was examined through rheological study. Zr@MG metallogel showed higher $G'(\omega)$ value than $G''(\omega)$ in the entire tested frequency range confirming gel behavior of the material, where $G'(\omega)$ and $G''(\omega)$ can be expressed as follows

$$\mathbf{G}^{'} = \left(\frac{\mathbf{\sigma}_{0}}{\gamma_{0}}\right) \cos\left(\delta\right) and \mathbf{G}^{''} = \left(\frac{\mathbf{\sigma}_{0}}{\gamma_{0}}\right) \sin\left(\delta\right)$$

Here, ω is the angular frequency (G') is the storage modulus and (G'') is the loss modulus. The value of the G'-G'' difference for Zr@MG xerogel was found to be 106598 Pa at 0.1 Hz frequency (Fig. S3, see supporting information). In addition, strain sweep measurement revealed gel to the sol transition point of the material. Zr@MG metallogel showed solid like behavior at lower strain value, and with increasing strain, storage modulus crossed over loss modulus (at shear strain 0.41 %), and gel to sol transition occurred (Fig. S4, see supporting information).

In FT-IR, the two characteristic peaks at 1775 cm^{-1} and 1718 cm^{-1} were observed due to the presence of an imide bond in the framework, and a new peak was generated at 1558 cm^{-1}



Fig. 1. (a) Metallogel synthesis scheme, (b-e) temperature dependent gelation study, (f-g) transparency test of the metallogel, and (h-i) different shape mediated structure.

due to the formation of carboxylate linkage for metal ion coordination (Fig. S5, see supporting information). Furthermore, ¹³C NMR spectra (solid state) were recorded for both ligand (H₄L) and Zr@MG xerogel to know about metal–ligand coordination. The downfield shifts (~ 0.9 ppm) in characteristic carbonyl peaks suggest the interaction between the metal ion and –COOH group of the linker moiety (Fig. S6, see supporting information) [75].

Thermogravimetric analysis was performed to check the thermal stability of the Zr@MG xerogel. First weight loss of ~ 10 % occurred below 150 °C, which may be due to the liberation of coordinated solvent molecules and physiosorbed moisture. After that, two-step weight loss happened with increasing temperature. One was observed around 27 % weight loss due to an increase in the temperature from 155 °C to 316 °C, and another one of ~ 28 % up to 587 °C suggests decomposition of the Zr@MG xerogel (Fig. S7, see supporting information).

The powder X-ray diffraction study was performed to check the crystallinity of the synthesized material, a broad peak in the spectrum confirms the amorphous nature of the compound (Fig. S8, see supporting information). EDX analysis affirmed the presence of Zr, C, N, and O elements. In addition, elemental mapping analysis suggests the homogenous distribution of those elements in the xerogel material (Figure S9a-S9f, see supporting information).

To get a more profound idea of the surface morphology of the xerogel, FESEM was carried out to take images in various resolutions and magnifications, revealing the presence of columnar structure throughout the surface of the material (Fig. 2a–c).

The TEM micrographs display fibrous structure, which constitutes the columnar structure shown by the FESEM images of that xerogel (Fig. 2d–e). The amorphous nature of the material was also confirmed by Selected Area Electron Diffraction (SAED) (Fig. 2f).

3.1. Photophysical properties:

H₄L ligand showed two absorbance peaks in the solid UV-Vis spectrum; one was around 355 nm, and another was 281 nm (Fig. S10a, see supporting information). These absorbance peaks were observed due to intraligand π - π * transition and, or π *-n transition. On the other hand, Zr@MG showed only one absorbance peak around 326 nm. The band gap (2.88 eV) of the xerogel was determined from the solid-state UV-Vis spectrum (Fig. S10b and equation S1, see supporting information). The metallogel showed blue luminescence under a UV lamp (λ_{ex} = 365 nm), and CIE (1976) Chromaticity diagram[76] supports this result (Fig. 3a and b). In addition, the photoluminescence behavior of the xerogel was studied in solid as well as in the dispersion phase. In solid state, the emission peak of Zr@MG was observed at 469 nm $(\lambda_{ex} = 335 \text{ nm})$ and in dispersion phase (aqueous medium) at around 440 nm (λ_{ex} = 335 nm) with a blue shift[77] (Fig. S11a and b, see supporting information). The PL experiment was carried out in different solvents also. In water, the peak showed the highest intensity compared to other organic solvents (DMF, DMSO, ethanol, THF, acetone, DMA) [78]. The high dielectric constant of water may be the reason for the high PL intensity [79]. This phenomenon was enough to make Zr@MG xerogel a promising candidate for $Cr_2O_7^{2-}$ sensing in the aqueous medium (Fig. S12, see supporting information). In addition, water is the best solvent as a sensing medium when it counts for real time application.

To know about leaching, the PL experiment was performed after filtering the dispersed sample. No characteristic emission peak was observed with the filtrate solution, which indicates the solid particles (in dispersion phase) were only responsible for giving such an intense peak. Then, the possibility of leaching was completely ruled out (Fig. S13, see supporting information).



Fig. 2. (a-c) FE-SEM micrographs (d-e) TEM images, (f) SAED pattern of the Zr@MG xerogel.

3.2. $Cr_2O_7^{2-}$ sensing study in aqueous medium and portable paper test:

All anions were gradually added up to 200 µL into the suspension of Zr@MG xerogel. The reading of blank xerogel suspension and after adding each analyte (from 10 µL to 200 µL) was monitored individually. A pronounced quenching in the PL peak occurred only in the presence of $Cr_2O_7^{2-}$ (Fig. S14a–i, see supporting information). Adding 10 μ L Cr₂O₇²⁻ solution at a specific time interval into the suspension resulted in quenching of the emission peak at 440 nm. A decrement in emission peak was observed with an increasing volume of dichromate in the suspension (Fig. 3c). In addition, quenching efficiency was calculated using Eq. (1). Apart from dichromate ion, all interfering anions showed negligible quenching efficiency (in the range of \sim 5–25 %); almost 91 % quenching efficiency was observed in the case of $Cr_2O_7^{2-}$ (Fig. 3d). On the other hand, quantitative analysis was carried out for the fluorescence quenching study, and this can be explained through the S-V equation (Stern-Volmer equation) [80], which is expressed as,

$$I_0/I = K_{sv}[Q] + 1 (3)$$

where K_{sv} is the Stern-Volmer (S-V) constant or quenching effect coefficient (M⁻¹), and molar concentration of the quencher is denoted by Q. The S-V plot shows linear behavior in the lower concentration region, and with increasing the analyte concentration, linearity decreases (Fig. 4a). So, the quenching mechanism may follow either dynamic and static concomitantly or certain kinds of competitive absorption phenomena (like the *Inner Filter Effect*). [81–83] The K_{sv} value of 9760 M⁻¹ was calculated from S-V plot and which is comparable with other known reported dichromate sensors (Table S1, see supporting information). The low detection of limit (0.52 ppm) was calculated using 3 σ/k equation (where σ = standard deviation of repetitive blank measurements and k is the slope of the line) (Fig. S15, see supporting information). These two results dictate high selectivity towards dichromate sensing of the xerogel. An efficient sensor is one that can detect $Cr_2O_7^{2-}$ in presence of other interfering anions in water.

The PL spectra were checked after adding each analyte (70 μ L) to the xerogel suspension. Noticeable changes in quenching of emission peak were missing for all cases, but there was a sudden drop in emission peak while adding 70 μ L of Cr₂O₇⁻ into that suspension (Fig. S16a-S16i, see supporting information). The selective sensing of Cr₂O₇⁻ in presence of all interfering anions with almost similar efficiency suggests the applicability of Zr@MG xerogels as a promising sensor material for Cr₂O₇⁻ detection in aqueous medium (Figs. 4b and S17, see supporting information). The optical images of blank dispersion of Zr@MG xerogel alone and after adding 100 μ L and 200 μ L of Cr₂O₇⁻ (10 mM solution) into that suspension under UV light (365 nm) gave visual evidence of blue light quenching after adding dichromate ions (Fig. 4c).

A portable handy paper strips test was performed to correlate this experiment with real time application. Dried paper strips (coated with Zr@MG xerogel) were taken to follow further procedure.10 μ L of Cr₂O₇²⁻ solution for each concentration (i.e., 10^{-3} M and 10^{-2} M) was drop casted into the paper strips using a micropipette. Under UV light source (λ_{ex} = 365 nm), a dark spot was observed in higher concentration, and a comparatively lighter spot was found in lower concentration due to quenching of the blue fluorescence (Fig. 4d–f).

3.3. Plausible mechanism behind $Cr_2O_7^{2-}$ sensing:

Quenching phenomena may occur through various mechanistic pathways, such as static or dynamic quenching, or typically through competitive absorption mechanisms. Static quenching



Fig. 3. (a) Blue luminescence of Zr@MG metallogel under UV source (λ_{ex} = 365 nm), (b) CIE (1976) Chromaticity diagram of the Zr@MG xerogel plotted from PL intensity, (c) dichromate ion sensing through fluorescence titration method, (d) quenching efficiency for different anions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

may occur due to ground state complex formation. On the other hand, dynamic quenching may involve through excited state collision process. Apart from these two static and dynamic quenching, competitive absorption phenomena may also be the reason behind quenching.

Specific experiments were carried out for a better understanding of this sensing mechanism. In EDX analysis, no noticeable peak was observed for the Cr atom (Fig. S18, see supporting information), that revealed quenching is not happened due to the replacement of Zr atoms with Cr atoms in the networking structure. In addition, the FT-IR spectrum (in ATR mode) before and after the experiment showed an almost superimposable spectrum that also ruled out the possibility of quenching that happened through changes in the local chemical environment of the Zr@MG framework (Fig. S19, see supporting information). No appreciable difference was observed in the average excited state lifetime value for pristine Zr@MG and after adding Cr₂O₇²⁻ into Zr@MG suspension (Fig. S20, see supporting information). This rules out the possibilities of PET (Photoinduced Electron Transfer) [84], FRET (Forster Resonance Energy Transfer) [85], or any kind of collision process between quencher and fluorophore in the excited state.

Furthermore, temperature dependent fluorescence experiment was studied to gain more resounding evidence about the quenching mechanism. Generally, with rising temperature disorderness in ground state molecules increases which restricts molecular interactions [86,87]. Quenching efficiency of 88 %, 87 %, and 85 % were observed after adding 200 μ L of Cr₂O₇² into the pristine xerogel (dispersed into aqueous solution) at three variable temperatures, i.e., 20° C, 40° C, and 60° C respectively (Fig. 5a–d). The observed results are quite similar to the room temperature quenching study, so the plausibility of quenching through ground state complex formation between fluorophore and quencher molecule seems improbable.

On the other hand, any weak interactions are influenced by varying the ionic strength of the solution, and it also affects ground state complex formation [88]. Consubstantial results in quenching efficiency by using 1 M NaCl solution excluded the possibility of such a mechanism (Fig. 5e–f). However, after adding 10 mg of Zr@MG xerogel into 100 ppm of $Cr_2O_7^{7-}$ solution (in water), almost imperceptible changes were observed in the UV–Vis spectra ($Cr_2-O_7^{7-}$ characteristic absorbance peak; from 0 min to 360 min), and it can also confirm by the naked eye (Figs. S21a and S21b, see supporting information). So, quenching through surface adsorption can also be ruled out.

Finally, in an aqueous medium, UV–Vis spectroscopy was carried out for all anions. $Cr_2O_7^2$ shows a strong absorbance in the range of 250–500 nm. On the other hand, no interfering anions absorb in this range. So, negligible changes in average fluorescence lifetime value before and after adding $Cr_2O_7^{2-}$ anion into the system and considerable spectral overlap between the absorbance band of $Cr_2O_7^{2-}$ (absorber) and the excitation and/or emission spectrum of the fluorophore (Fig. S22, see supporting information) confirms the *Inner Filter Effect* (IFE) quenching mechanism.[89].

3.4. Recyclability test:

While talking about any material's potential application value towards its respective field, reusability is a big concerning factor that should be noticed. After each cycle of the sensing experiment, the material was washed several times with deionized water, fol-



Fig. 4. (a) The S-V plot of Zr@MG xerogel for $Cr_2O_7^{2-}$ quenching in aqueous medium, (b) quenching study of Zr@MG xerogel for $Cr_2O_7^{2-}$ (up to 70 μ L) in presence of different anion in aqueous medium, (c) optical images of quenching in presence of different volume of dichromate ion in the presence of UV source ($\lambda ex = 365 \text{ nm}$), (d–f) portable test for easy detection of dichromate.

lowed by acetone to remove the dichromate ions from the dispersed solution. The xerogel material was collected through filtration. After that, it was dried in a vacuum oven (~ 50 °C) for 12 h before being used in the next cycle. Zr@MG xerogel showed efficient quenching phenomena in presence of $Cr_2O_7^{2-}$ up to 5 cycles, and no significant changes in quenching behavior were observed during the completion of each cycle (Fig. S23, see supporting information). The FT-IR spectrum data after the 5th cycle also revealed the retention of the local chemical environment. So, Zr@MG xerogel can be used as a stable sensor for deftly sensing $Cr_2O_7^{2-}$ in aqueous system.

To check the sensing efficiency of the material for $Cr_2O_7^{2-}$, a kinetic study through PL experiment was performed. After adding different volumes (10 µL, 50 µL, 100 µL, and 200 µL of 10 mM dichromate solution) into the Zr@MG suspension, an immediate equilibrium was established, which shows the efficiency of the material for detection of $Cr_2O_7^{2-}$ in aqueous medium (Fig. S24, see supporting information).

3.5. Detection of TNP:

For the TNP sensing, all organic analytes were gradually added up to 200 μ L into the suspension of Zr@MG xerogel. The emission peak of blank xerogel suspension and suspension after adding each analyte was monitored individually. Apart from nitroaromatic compounds, a very negligible change in intensity of the characteristic emission peak of Zr@MG suspension was observed for common organic compounds (quenching efficiency in the range of ~ 2-10%). A relatively smaller change was observed for nitrobenzene (quenching efficiency of 28 %), and approx. 65 % of quenching efficiency showed for 4-nitrophenol. In comparison, a significant 'turn-off' phenomenon was noticed for TNP with a 99 % quenching efficiency (Fig. 6a). The fluorescence quenching phenomena were quantified using the Stern-Volmer equation (Eq. (3)). The K_{sv} value of 15295 M⁻¹ was calculated from the S-V plot, with a linear fit correlation coefficient of 0.9832, the S-V quenching curve exhibits a good linear relationship. However, a deviation in linearity was observed with increasing concentration of the analytes, which may indicate the energy transfer mechanism behind this quenching effect (Fig. 6b). The low detection of limit (80.2 ppb) was calculated using 3 σ/k equation (Fig. S25, see supporting information). The high K_{sv} value and a very low detection limit dictate high selectivity towards TNP sensing of the xerogel, which is comparable with other known reported TNP sensors (Table S2, see supporting information). Furthermore, TNP detection studies were carried out to check selectivity in presence of each individual organic molecule. After adding 200 µL of TNP into the system, rigorous quenching was observed with a bathochromic shift suggesting strong interaction between the fluorophore probe and quencher molecule (Fig. S26a-S26h, see supporting information). A kinetic study of the PL quenching effect was performed to check the material's efficiency for TNP detection. A fast equilibrium was established after adding different volumes (i.e., 10 μL , 50 μL , 100 μL , and 200 μL of 10 mM TNP solution into the Zr@MG suspension) of analytes in the same concentration (Fig. S27, see supporting information). It clearly shows quick detection of TNP with Zr@MG material.



Fig. 5. (a–c) Temperature dependent (at 20 °C, 40 °C, and 60 °C) quenching study for Zr@MG xerogel towards $Cr_2O_7^{2-}(d)$ quenching efficiency for same in 3-D bar diagram, (e) quenching study with increasing ionic strength of the medium (1 M NaCl) for Zr@MG xerogel towards $Cr_2O_7^{2-}$, (f) quenching efficiency for same in 3-D bar diagram.

A portable paper strips model was fabricated to detect TNP as an easy detection technique. All analytes (10 mM) were drop casted (up to 10 μ L) into the dried paper strips (coated with Zr@MG xerogel) using a micropipette for further detection. The darkest spot was observed only for TNP, followed by 4nitrophenol in presence of a UV source (λ ex = 365 nm). The rest of the analytes show negligible effect, which dictates similar results as seen in PL quenching study (Fig. 6c).

3.6. Plausible mechanism for TNP detection and recyclability test:

In order to understand the mechanism of luminescence quenching (static or dynamic) a fluorescence, UV–Vis, and lifetime experiments were performed. There was rigorous quenching of the pristine emission peak of Zr@MG suspension observed after adding TNP into the system (Fig. 6d). The peak was not only quenched but also red-shifted, which may be attributed to strong π - π stacking interaction or/and hydrogen bonding with the hydroxyl group of the TNP and diimide functionalized long aromatic linker. This manifests a photoinduced electron transfer process between the electron donor (herein, organic linker) to an electron acceptor (TNP). A change in average lifetime value in time-resolved photoluminescence (TRPL) decay experiments after adding TNP into the system ruled out the possibility of static quenching through ground state complex formation (Table S3, see supporting information). So, it may involve a long-range energy transfer mechanism or



Fig. 6. (a) Quenching efficiency for different analytes, (b) The S-V plot of Zr@MG xerogel for TNP quenching in aqueous medium, blue luminescence of Zr@MG metallogel under UV source ($\lambda_{ex} = 365 \text{ nm}$) (c) Portable paper strips test (d) TNP sensing through fluorescence titration method. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

short-range electron transfer process. Furthermore, UV -Vis spectroscopic analysis for all respective analytes and PL study of the fluorophore probe revealed an explicit overlapping zone between the absorbance band of TNP (acceptor excitation) and emission spectrum of Zr@MG (donor emission), indicating resonance energy transfer may be a reason behind this quenching effect (Fig. S28, see supporting information). The high selective sensing behavior towards TNP for Zr@MG can be described by density functional theory (DFT) at the B3LYP/6-31G** level. [90,91] The photophysical study of the Zr@MG material reveals ligand centered luminescent, so electrons can easily be transferred from the high energy LUMO of diimide based ligand (H₄L) to the lower energy LUMO of an electron deficient group. The presence of nitro groups with their strong electron withdrawing effect stabilizes their lowest unoccupied MOs (LUMOs) in comparison to other non-nitro groups containing organic compounds, which manifests electron transfer phenomena more rigorously from the higher energy LUMO of the organic linker to lower energy LUMO of a nitro group containing organic moiety. In TNP, a hydroxyl group with three nitro groups enhances the intermolecular electron transfer process through π - π stacking and hydrogen bonding interaction that may lead to a selective high quenching effect. The DFT study of all organic molecules revealed that only the TNP molecule has lower energy LUMO (-4.02 eV) than the linker (H_4L) LUMO (-3.83 eV) (Fig. 7). That facilitates electron transfer phenomena more easily compared with others. So,

both FRET and PET may be possible pathways in the photoluminescence quenching process.

The recyclability test (up to five cycles) was performed to check the material efficiency as a TNP sensor. After the completion of each cycle, the dispersed solution (Zr@MG dispersed in 2 mL water and 200 μ L of TNP) was filtered off by washing through deionized water and acetone. The xerogel material was dried under a vacuum oven (~ 50 °C) for 12 h and collected for the next cycle. No apparent changes were observed in sensing activity after the fifth cycle, and quenching efficiency was almost shown a similar result with consecutive cycles (Fig. S29a-29b, see supporting information). The FT-IR spectra were performed before and after the sensing experiment. The main characteristic peaks were unchanged, which suggests retention of the local chemical environment of the Zr@MG xerogel after the sensing experiment (Fig. S30, see supporting information).

3.7. Selective capture and column-based separation of MB dye:

Compared to a conventional dye adsorption study, selective adsorption of a specific dye from two differently charged dye mixtures is more enchanting because it decreases industrial waste via reutilization of the dye. Herein, column-based dye adsorption experiments were carried out to separate MB dye from MB/OG mixture. Two separate columns were packed with Zr@MG xerogel

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Fig. 7. HOMO and LUMO energy diagram for the organic analytes and the H₄L ligand.

(40 mg in each column). MB dye (30 mg/L) was passed through one column to observe the dye adsorption ability. The naked eye test confirms no dye is coming out from the column (Fig. 8a and SV1, see supporting information). Furthermore, the UV–Vis study of the pristine dye solution and the effluent supports the naked eye observation. The characteristic absorbance peak for MB dye (at 664 nm) was not observed in the effluent solution (Fig. 8b). Simi-

larly, a mixture of anionic and cationic dye solution (30 mg/L of MB + 30 mg/L of OG; green colored solution) was passed through another column to check selectivity toward dye adsorption; an orange colored solution was separated out as effluent (Fig. 8c and SV2, see supporting information). The characteristic peak (at 664 nm) for MB was fully diminished with a narrow change in absorbance value for OG (at 486 nm) dictates high selective



Fig. 8. (a) Separation of MB from dye solution, (b) absorbance value before (only MB) and after separation (effluent) of the MB dye, (c) selective capture of MB dye from the mixture of MB/OG dyes (d) absorbance value before (dye mixture) and after separation (effluent) of the MB/OG dye mixture.

adsorption toward positively charged dye (Fig. 8d). In addition, kinetic study was carried out for individuals as well as for mixture of dye solutions (20 mg/L). No appreciable change was observed in the absorbance value for OG dye, but the characteristic peak for MB was extensively decreased with increasing time, showing the selectivity for MB over OG. The xerogel material shows 98 % separation efficiency for MB dye from the mixture of MB/OG (Fig. S31a-31c, see supporting information). MB dye adsorption on the Zr@MG xerogel is more akin to the pseudo-first order model (Fig. S32 and Table S4, see supporting information). Furthermore, ζ potential studies revealed the negative charge distribution (-23.0 mV) on the overall surface of the material that may be the reason behind strong electrostatic interactions between positively charged MB dye with material which may lead to selective adsorption behavior (Fig. S33, see supporting information).

3.8. Iodine capture and storage:

The nitrogen-rich diimide linkage with the extended conjugative aromatic framework in the material prompted us to study iodine adsorption. We studied iodine adsorption phenomena in vapor phase. The gravimetric method was used to examine vapor phase iodine adsorption. The xerogel showed adsorption capacity of around 108 wt% after 24 h, and this experiment was monitored for up to seven days. The adsorption capacity after seven days.

reaches an equilibrium uptake capacity of 232 wt% (Fig. S34a, see supporting information). PXRD was performed before and after the adsorption study, and it does not show the formation of any new phases (Fig. S34b, see supporting information).

3.9. Plausible mechanism for iodine sequestration:

Adsorption is a surface phenomenon, and adsorbate's structure, functionality and surface properties can be considered driving factors that affect the adsorption capability of an adsorbate. Hydrogen bonding, electrostatic interactions, and various π - π interactions between absorber and adsorbate are the main reasons behind adsorption.

In the FT-IR spectrum, the intensity of $\nu_{\text{C=C(str)}}$ band (at 1462 cm⁻¹) increased in I₂ loaded Zr@MG compared to the pristine xerogel, suggests I^m π interaction between iodine and C=C bond in xerogel framework (Fig. S35, see supporting information). To get a more detailed understanding from a mechanistic standpoint, Raman spectroscopy was performed. No pronounced peak was observed in comparatively lower wavenumber for I₂ loaded xerogel. So, polyhalide species $([I_3]^-, [I_5]^-)$ may not form during adsorption. On the other hand, a single strong peak around 208 cm⁻¹ was confirmed about the homogeneous adsorption environment around Zr@MG xerogel and depicted the binding mode of the iodine molecule onto that xerogel (Figure S36, see supporting information). In general, in Raman spectroscopy, a peak around 213 cm⁻¹ comes due to I-I bond stretching in I₂-hexane, while in I_2 benzene it comes around 205 cm⁻¹. Stronger (I^{...} π) interaction in I₂ benzene is the reason behind this red shift in stretching frequency which is absent in I₂-hexane[92]. While relating to the above fact, in our case, it showed a peak around 208 cm⁻¹ that may be due to presence of strong $(I^{\dots}\pi)$ interactions between iodine and conjugated aromatic framework.[93].

3.10. Release capacity and recyclability test:

lodine desorption of I₂ loaded Zr@MG in vapor phase was studied *via* a gravimetric method. 30 mg of I₂ loaded Zr@MG xerogel kept in heating condition at 120 °C for 90 min. The loss in wt% was calculated within a time interval. The result showed around 90 % of adsorbed iodine was desorbed from I₂ loaded Zr@MG xero-

gel within 90 min (Fig. S37, see supporting information). It suggests effective iodine releasing efficiency of the adsorbate.

The recyclability test was performed for up to 3 cycles. After the first cycle, I₂ loaded xerogel was washed with ethanol multiple times and kept in with a similar setup for the next cycle. The photographs (0 min, 60 min, 90 min) indicate releasing of iodine from adsorbed material in ethanolic solution (Fig. 38a-38c, see supporting information). The light yellow color of the xerogel was completely changed into dark brown color after iodine adsorption and showed light brown color after washing in ethanolic solution (Fig. 38d-38 g, see supporting information). After completion of the second and third cycle, the material showed adsorption capacity up to \sim 184 wt% and \sim 170 wt%, respectively (Fig. S39, see supporting information), which indicates some iodine molecule gets trapped in the host matrix and shows decrement in capacity. Furthermore, the jodine peak observed in EDX analysis (after washing with ethanol) supports the above result (Fig. S40, see supporting information).

4. Conclusion:

In conclusion, an agua stable luminescent Zr-diimide based supramolecular metallogel is accomplished by the heat set method. FESEM and TEM micrograph images revealed the fibrous like columnar morphology of Zr@MG xerogel, and SAED and PXRD apprise its amorphous nature. Detection of $Cr_2O_7^{2-}$ in presence of other interfering anions in aqueous medium with high K_{sv} suggests selectivity and sensitivity of the material. Experimental evidences show that Inner Filter Effect (IFE) is the most probable quenching mechanism. The material also exhibits high quenching efficiency with a very low detection limit for TNP in aqueous medium. The negative charge distribution on the surface of the material manifests selective capture of positive dye from a mixture of cationic and anionic dye. The recyclability test confirms the reusability and real-time application for both dichromate sensing and also in iodine sequestration. The presence of diimide linkage with long conjugative aromatic chain prompts I $\cdots \pi$ interaction, which makes this material a suitable iodine adsorbate. Moreover, a handy paper strips test was developed to detect dichromate ions on-site basis. These findings suggest that Zr@MG xerogel might be an excellent host matrix for iodine and a viable sensor for $Cr_2O_7^{2-}$ and TNP.

Data availability

Data will be made available on request.

Declaration of Competing Interest:

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/i.icis.2022.11.111.

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