Soft Matter



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Cite this: *Soft Matter*, 2023, **19**, 4926

Received 7th March 2023, Accepted 7th June 2023 DOI: 10.1039/d3sm00289f

rsc.li/soft-matter-iournal

Introduction

Heavy metal contamination in water is a severe environmental issue because it is non-biodegradable, persistent, and negatively affects health and the economy.¹ Among the highly abundant metal ions in the Earth sphere, iron is one of the most common metal elements that can be found in two cationic forms, *i.e.*, Fe(II) and Fe(III). The trivalent form is the most stable and easily targeted analyte for commonly detecting probe molecules. Even though both are essential for the health of plants, animals, and microbes, at larger concentrations, these microelements exert a variety of harmful effects.² For example, Fe^{3+} plays a crucial role in cellular processes such as oxygen transport, muscle functioning, DNA/RNA synthesis,

A coordination driven 'heat-set' Zr-gel: efficient fluorophore probe for selective detection of Fe³⁺ and nitrofuran-based antibiotics and smart approach for UV protection[†]

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Nature creates definite architecture with fluorescence capabilities and superior visual adaptation in many organisms, e.g., cephalopods, which differentiates them from their surroundings in the context of colour and texture that allows them to use this in defence, communication, and reproduction. Inspired by nature, we have designed a coordination polymer gel (CPG)-based luminescent soft material where the photophysical properties of the material can be tuned using a low molecular weight gelator (LMWG) with chromophoric functionalities. Herein, a water-stable coordination polymer gel-based luminescent sensor was created using zirconium oxychloride octahydrate as a metal source and H₃TATAB (4.4',4"-((1,3,5-triazine-2,4,6-triyl)tris(azanediyl))tribenzoic acid) as a LMWG. The tripodal carboxylic acid gelator H₃TATAB with a triazine backbone induces rigidity in the coordination polymer gel network structure along with the unique photoluminescent properties. The xerogel material can selectively detect Fe³⁺ and nitrofuran-based antibiotics (i.e., NFT) in aqueous medium through luminescent 'turn-off' phenomena. This material is a potent sensor because of the ultrafast detection of the targeted analytes (Fe^{3+} and NFT), with consistent efficacy in guenching activity up to five consecutive cycles. More interestingly, colorimetric, portable handy paper strip, thin film-based smart detection approaches (under an ultraviolet (UV) source) were introduced to make this material a viable sensor probe in real-time applications. In addition, we developed a facile method to synthesize CPG-polymer composite material that can be utilized as a transparent thin film to protect against UV radiation (200-360 nm), with approximately 99% absorption efficacy.

> metabolism, and electron transfer.³ However, excessive exposure or deficiency of iron can trigger several health issues such as Alzheimer's disease, insomnia, gastrointestinal disorders, anemia, and Parkinson's disease.⁴ The dissolution of rocks and minerals and their subsequent leaching into groundwater are the sources of geogenic Fe^{3+} contamination. Hence, it can affect the surface water and groundwater, depending upon the concentration.⁵ Fe^{3+} can alter the taste of water even when it is present at only 0.1 ppm concentration. Also, it can increase water turbidity and react with other compounds to accelerate the creation of oxygen radicals that damage DNA in cells. To this end, the development of efficient and cost-effective methods for detecting and distinguishing Fe^{3+} ions is essential because it mostly coexists with other interfering metal ions.⁶

> Antibiotics, which are widely used for treating bacterial illnesses in human health, agriculture, and animal farming, have been found to be one of the primary organic contaminants in water. Among various classes of antibiotics, nitrofurans (NFAs), a prevalent class of antibiotics containing 5-nitrofuran rings, have been widely used to treat bacterial and protozoal

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[†] Electronic supplementary information (ESI) available. See DOI: https://doi.org/ 10.1039/d3sm00289f

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infections in humans and animals.⁷ Nitrofurantoin (NFT), nitrofurazone (NFZ), and furazolidone (FZD) are the most commonly used NFAs for treating a wide variety of bacterial infections. Due to the widespread practice of discharging livestock manure into rivers or utilizing it as fertilizer on agricultural land, these antibiotics may be commonly found in the environment, leading to detrimental effects on soil and water.8 Most importantly, these antibiotic residues in the environment may cause antimicrobial resistance that affects non-target organisms in living systems, especially in the human body, causing numerous unwanted health issues.^{9,10} As a result, many developed countries have implemented prohibition on the use of numerous classes of antibiotics. Regrettably, NFAs continue to be found in various agricultural goods, groundwater, and food materials.¹¹ Therefore, developing rapid and convenient approaches to detect antibiotics in water is of the utmost importance.

In recent years, coordination polymer gels have been applied to catalysis, sensing, tissue engineering, drug delivery, and adsorption studies.¹²⁻¹⁷ Beyond the realm of serendipity, there have been significant efforts in this research area to develop new gels. The development of preparatory methods for gelation has progressed so that different strategies can be implemented that can tune various interesting properties, such as thixotropic and self-healing properties.¹⁸ Interestingly, there are advantages to 'heat-set' gels over other soft material ranging from mechanical to photophysical stabilities.¹⁹ In an early study in terms of this 'heat-set' gelation process, a cobalt-based triazole complex with a long lipophilic group was reported by Kuroiwa et al.20 An amide-based tripodal carboxylic acid-based linker was used by Zhu et al. to form a dinuclear Rh-based supramolecular gel through thermal agitation. The aerogel was used as a catalyst for different organic transformations.²¹ In a recent study, Zhang et al. reported Tb-mediated metal organic gels that exhibited stable luminescent behaviour in the presence of multiple stimuli-responsive effects.²² In addition, there is versatile applicability of luminescent-based coordination polymer gels in the field of optical sensors. Lanthanide-based materials are well known for their interesting photophysical behaviour.^{23,24} For example, Chen et al. tuned white light emission using europium and terbium metal salts with different stoichiometric ratios to form gels with a terpyridine-based linker.²⁵ Maji and co-workers reported photochromic material with a photo-switching emission.²⁶ In addition to these lanthanide-based materials, luminescent coordination polymer gel (CPG) was also synthesised by introducing a low-molecular weight gelator (LMWG) and transition metal ions. Sebastian et al. utilized copper-based gels for lethal cyanide ion detection in water medium.²⁷

Luminescence-based detection method has received significant interest due to its easy sample preparation technique with high selective sensing of analytes from their respective mediums. Lanthanide-based materials (such as lanthanide metalorganic frameworks (Ln MOFs)) are most commonly used as optical sensors for monitoring environmental pollutants, but they are limited by multiple factors, most notably costeffectiveness and water stability.^{28,29} Hence, there is a pressing need to fabricate a sensor material that is inexpensive and stable in aqueous medium. Likewise, CPGs, which are similar to MOFs, are composed of organic linkers and metal nodes. In comparison to MOFs, there is relatively easier synthesis and scalability with CPGs, and thus, these 'soft' CPGs are ideal materials for optical sensors.³⁰ Using the 'heat-set' phenomena to introduce a strategy to develop luminescent coordination polymer gels would be a fascinating approach for the detection of pollutants in aqueous medium.

Herein, a carboxylic acid-based tripodal linker containing a triazine moiety in its backbone was used to synthesize a coordination polymer gel, where zirconium oxychloride octahydrate was used as a metal source. In general, zirconiumbased MOFs are water stable.^{31,32} In this context, we synthesized a luminescent probe that can act as a stable optical sensor in aqueous medium, where a triazine backbone-based carboxylic linker creates a rigid structure and also assists in the generation of distinct photoluminescent (PL) characteristics. The triazine core enhances the hydrogen bonding and π - π stacking ability that acts as a driving force to form a supramolecular network structure.³³ These non-covalent forces also play an essential role in small organic molecule sensing.³⁴ The free nitrogen donor of the linker moiety eases the pathway of electron transfer to electron-deficient centres. The xerogel material was utilized as a luminescent-based sensor for selective detection of Fe³⁺ and nitrofurans (NFAs) antibiotics. In the context of selective detection, the K_{SV} and limit of detection (LOD) are the important parameters for novel optical chemosensors. Recently, Mitra and co-workers reported amine-grafted zinc-based supramolecular gels that are capable of detecting Fe³⁺ ions and NFT antibiotics at the ppm level in aqueous medium (the LOD values for Fe³⁺ and NFT were 6.13 ppm and 4.62 ppm, respectively, with high K_{SV} values).³⁵ Jiang *et al.* used a naphthalimide-based gel to selectively detect Fe³⁺ ions with LOD value of 6.96 \times 10⁻⁸ M.³⁶ A pillar[5]arene-based CPG material was reported by Zhang et al. for nanomolar detection of Fe³⁺ (0.102 nM).³⁷ Gupta and co-workers reported numerous LMWGs, one of which was able to detect antibiotics at the nanomolar level (150 nM for NFT antibiotics with a high K_{SV} value of 2.3 \times 10⁻⁴ M).³⁸ Apart from these CPGs, there have been several reports related to MOFs and MOF-based composite materials for selective detection of antibiotics. Interestingly, a fluorescence 'on-off-on' method was investigated by Pal and co-workers for detection of antibiotics through a MOFgel composite material.³⁹ Zhu et al. synthesized a terbiumbased MOF for detection of NFA-based antibiotics with a high K_{SV} value.¹¹ The LOD of Zr–CPG was found to be 68 ppb for Fe³⁺ and 50 ppb for NFT, which is comparable with other reported materials. The K_{SV} values of 7.16 \times 10³ M⁻¹ and 1.53 \times 10⁴ M⁻¹ were found for Fe³⁺ and NFT, respectively. These low detection limits and high K_{SV} values for both analytes demonstrate the efficiency of the sensor. Moreover, the sensing mechanism was investigated in depth, using experimental and theoretical methods. This material is more suited for real-time application when it can be used with paper strip and thin film-based smart detector probes.

Even though exposure of the skin to ultraviolet (UV) rays is beneficial (*e.g.*, for vitamin D generation), regular exposure to

UV radiation, especially UVB rays (280–320 nm), can result in detrimental effects on the skin through DNA damage.^{40,41} However, the most harmful radiation is the short-wavelength UVC (<280 nm), which is greatly reduced by the atmosphere.⁴² Similarly, UVA is equally responsible for its harmful effects such as skin tanning and wrinkles.⁴³ Thus, there has been extensive study on transparent UV-shielding materials for use in UV-protective coatings, optical filters, and other products.^{44–46} Herein, xerogel material was used to form an optically transparent thin film as a potent UV blocker in the presence of poly(methyl methacrylate) (PMMA) that may be used in sunprotective glass, light-sensitive materials in pharmaceutical and chemical industries, and packaging for electronic equipment.

Experimental section

Materials used

Nitrate salts of metal ions (Fe^{3+} , Zn^{2+} , Na^+ , Al^{3+} , Co^{2+} , Cu^{2+} , Cr^{3+} , Hg^{2+} , K^+ , Ca^{2+} , Ni^{2+} , and Cd^{2+}) and sulphate salts (for Fe^{2+}) were used for making metal ion solutions. All of these metal salts, and zirconium oxychloride octahydrate, 1,4-dioxane, cyanuric chloride, sodium bicarbonate, sodium hydroxide, and *N*,*N'*-dimethylformamide were purchased from Central Drug House (CDH). 4-Aminobenzoic acid was obtained from Sigma-Aldrich. Sulfadiazine (SDZ), sulfamethazine (SMZ), nitrofurantoin (NFT), nitrofurazone (NFZ), furazolidone (FZD), chloramphenicol (CAP), dimetridazole (DTZ), ornidazole (ODZ), and ronidazole (RDZ) were purchased from various commercial sources. In the reactions, all chemicals were used without further purification. Milli-Q water was used for all photophysical studies.

The LMWG (H₃TATAB) synthesis

The LMWG was synthesized with slight modifications to the reported procedure.⁴⁷ In a 25 mL beaker, a mixture of cyanuric chloride (0.73 g, 4 mmol) was prepared with 8 mL of 1,4-dioxane and stirred for 30 min at 0 °C. A separate 100 mL round bottom (RB) flask was used to prepare a solution of 4-aminobenzoic acid (2.18 g, 16 mmol) in 25 mL of water. Next, 4 ml of 5 N NaOH and NaHCO₃ (1.1 g, 13.2 mmol) were added to the RB flask, and the liquids were mixed well and then stirred at 0 °C for 30 min. After that, the mixture from the beaker was gently transferred (drop by drop) into the RB flask, and the liquid was stirred at 0 $^\circ C$ for 1 h. It was then refluxed overnight at 110 °C. The clear solution was cooled to room temperature and acidified with 10% HCL to maintain the pH level at approximately 2. A white suspension was obtained, and it was washed several times with deionized water. The solid residue was dried in a vacuum oven at 80 °C for 12 h. Yield: 1.37 g (2.82 mmol, 70.57%). ¹H NMR (400 MHz, DMSO-d₆): δ = 7.86 (d, 6H), 7.97 (d, 6H), 9.81 (s, 3H). ¹³C NMR (400 MHz, DMSO-d₆): δ = 167.60, 164.33, 144.46, 130.55, 124.37, 119.75 (Fig. S1 and S2, see the ESI[†]).

Synthesis of the supramolecular gel

A tripodal carboxylic acid-based LMWG (H_3 TATAB) with a triazine backbone was used for synthesis of the CPG, where zirconium acts as the metal node. The linker and zirconium oxychloride octahydrate were mixed in a 1:1 molar ratio to form the coordination polymer gel. Typically, a solvent mixture of DMF : water (3:2) was prepared to make a 0.1 M solution of ZrOCl₂·8H₂O. In a separate glass vial, a 0.1 M solution of the linker was prepared using DMF as a solvent. Finally, the individual solution was mixed in a similar volume ratio in a 20 mL glass vial and kept in an oven. It formed a stable gel at 90 °C. The Zr–CPG xerogel was prepared after freeze-drying of the as-synthesized CPG.

The photophysical study for Fe³⁺ and nitrofuran sensing

Preparation of 10^{-2} M fresh solutions proceeded for each analyte for further photophysical studies. First, 4 mg of xerogel material was dispersed into 2 mL of water for the fluorescence titration experiment. The suspension was used for the PL study after 1 h of ultrasonication, and it exhibited an explicit luminescence peak at 421 nm when excited at 328 nm. The photoluminescence quenching behaviour of the characteristic peak of the xerogel suspension was monitored for each analyte after increasing the volume from 0 μ L to 200 μ L. Eqn (1) was used to calculate the quenching efficiency expressed by:

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

where I_0 and I denote the luminescent intensities of the xerogel material before and after adding the analytes, respectively.

Results and discussion

Synthesis and characterization of the CPG

A zirconium-based supramolecular gel was formed using a tripodal carboxylic acid linker containing a triazine backbone that created a rigid network structure and induced H-bonding possibilities. The carboxylic acid acted as coordinating sites for zirconium metal ions to form a supramolecular gel structure (Fig. 1(a)). A 'heat-set' method was used to synthesize the gel.²² At room temperature, the homogenous mixture of linker and metal salts was more or less transparent, and the sol-to-gel transition was observed through variations in temperature. In the temperature range of 25–40 °C, it was in a sol state, and after increasing the temperature, changes in gelation behaviour were observed until, finally, a stable gel (Zr–CPG) was formed at 90 °C (Fig. 1(b)).

The linker solubility was confirmed in different solvents. It was fully soluble in DMF and DMSO, but solubility was decreased in other common organic solvents. Therefore, gel formation was investigated using different solvents as well as solvent mixtures. Control experiments revealed the importance of water in this gelation process. The gel-forming nature was tested using DMF/water, DMF/MeOH, DMF/EtOH, DMSO/water, DMSO/MeOH, and DMSO/EtOH combinations. Among these, gel formation only occurred in DMF/water and DMSO/water.



Importantly, a strong gel was formed in the DMF/water combination, while a white precipitate was formed in the DMF/MeOH and DMSO/MeOH combinations. In DMSO/EtOH, a clear solution was observed, and in DMF/EtOH, little turbidity was observed after heating at 90 °C for a prolonged time period (Table S1, see the ESI†). Hence, water plays an important role in the gelation process. The degree of hydrogen bonding ability in different solvents regulates the gel formation.²¹

To investigate the mechanism behind 'heat-set' gel formation, turbidity tests were performed. During different time intervals, the transmittance of the mixture was measured using a UV-Vis spectrophotometer. The decrease in light transmittance of the reaction mixture with increasing time at 90 $^{\circ}$ C indicated heating phenomena that induced aggregation, and led to the formation of the gel (Fig. S3, see the ESI†).

Fourier transform-infrared (FT-IR) analyses (ATR mode) were performed for the linker and reaction mixture (containing the metal salt and linker) at different time intervals of heating at 90 °C. A clear shift to a lower wavenumber of O–H stretching vibration was observed from 3510 cm⁻¹ to 3450 cm⁻¹, suggesting an increase in the hydrogen bonding ability of the gelling mixture with increasing time. Additionally, a shift of carbonyl stretching frequency to a lower wavenumber (from 1660 cm⁻¹ to 1647 cm⁻¹) occurred, indicating metal–ligand coordination (Fig. S4, see the ESI†).⁴⁸

Furthermore, diffuse-reflectance spectra (DRS) were used to explore the π - π stacking interactions that may influence the gelation process. To guide the self-assembly process followed by aggregation (through heating), the samples were prepared at different time intervals. Each sample was freeze-dried, and powdered samples were characterised with DRS. A clear redshift (328 nm to 340 nm) was observed for various time-dependent reaction mixtures (sols to gels), suggesting imperceptible aggregation

via π - π stacking (Fig. S5, see the ESI[†]).^{49,50} The tripodal carboxylic acid linker with its triazine core plays an important role in generating this interaction, which basically promotes the overall gel formation. To this end, the obtained results dictate that various non-covalent interactions, such as hydrogen bonding and π - π interactions, as well as metal ligand coordination, were involved in this 'heat-set' gel formation.

To understand the mechanical strength of the metallogel, frequency sweep and strain sweep experiments were performed using a rheometer. The viscoelastic nature of the Zr–CPG was observed through the variation of storage modulus (G') and loss modulus (G'), which are expressed as follows:

$$G' = (\sigma_0 / \gamma_0) \cos(\delta)$$
 and $G'' = (\sigma_0 / \gamma_0) \sin(\delta)$

Freshly prepared CPG was used to obtain $G'(\omega)$ and $G''(\omega)$ values in the frequency range of 1–100 Hz. In the entire frequency range, the storage modulus was higher than the loss modulus (*i.e.*, $G'(\omega) > 10^3$ Pa and $G''(\omega) < 10^3$ Pa), exhibiting solid-like behaviour (Fig. S6, see the ESI†). In the lower strain region, it showed solid-like behaviour, and at 0.129% strain, the magnitude of G' was equal to that of G''. After this point, the storage modulus became lower than the loss modulus, which indicated a gel-to-sol transition (Fig. S7, see the ESI†).

A broad peak in the powder X-ray diffraction pattern exhibits the amorphous behaviour of the xerogel material (Fig. S8, see the ESI†). Thermogravimetric analysis shows continuous weight loss with increasing temperature (Fig. S9, see the ESI†).

To understand the surface morphology of the xerogel material, images were captured through FESEM and TEM. FESEM images (Fig. 2(a)-(c)) show a vertically grown fibre-like morphology, while TEM images reveal that these fibres were composed of a highly agglomerated network structure (Fig. 2(d)-(f)). The thermal



Fig. 2 (a)-(c) FESEM images, (d)-(f) TEM micrographs, and (g)-(k) elemental mapping of Zr-CPG.

agitation during the 'heat-set' gelation process promotes aggregation, which results in gel formation. Micrographic analysis of xerogel material indicated that this aggregation induced the gel phenomenon. Energy-dispersive X-ray study provided conclusive evidence of zirconium, carbon, nitrogen, and oxygen in the material (Fig. S10, see the ESI†). In addition to this, the elemental mapping study indicated that these elements are consistently and homogenously distributed throughout the xerogel substance (Fig. 2(g)–(k)).

Photophysical study

A solid-state UV-Vis study revealed an absorbance band at approximately 330 nm for the H₃TATAB linker that may involve intraligand π - π * and n- π * transitions. The xerogel material showed a prominent absorbance band at 328 nm, which resembled the linker absorbance band and suggested linkerinduced UV absorbance in the xerogel material (Fig. S11a and b, see the ESI†). The photoluminescence behaviour also indicates ligand centre luminescence of the xerogel material. The linker and xerogel material exhibited explicit luminescent peaks at 435 nm and 447 nm, respectively (same excitation at 328 nm) (Fig. S12a and b, see the ESI†). Relatively higher intensity of characteristic photoluminescence peaks of the xerogel material was observed in the case of DMF, DMSO, and water compared

to other solvents. Their high dielectric constant may be the cause of the high intensity in the observed PL spectra.⁵¹ Compared to DMF, DMSO, THF, and acetone, the peak in ethanol and water was being shifted towards longer wavelengths. Intermolecular proton transfer may be the reason for this redshift, as these are polar protic solvents,⁵² and, most importantly, it exhibited the most stable and intense peak in the presence of water (Fig. S13, see the ESI[†]). For real-time application of a material, it is more optimal to utilize water as a sensing medium than other organic solvents, especially under physiological conditions. A leaching test was also used to understand sensor stability. The PL spectra were recorded of the xerogel material dispersed in water and after filtration of the suspension. The pronounced characteristic emission peak of the xerogel material was absent for the filtrate solution, which suggests that the peak was generated due to the solid particles dispersed in the water medium, and no leaching was observed (Fig. S14, see the ESI⁺).

Metal ion sensing

The supramolecular gel network structure was composed of a tripodal carboxylic acid-based linker with an electron-rich triazine backbone to facilitate interactions with Lewis acidic metal centers that generally ease the pathway of electron transfer. To this end, we strived to prepare a luminescent probe

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for selective detection of metal ions. The photoluminescence behaviour of the xerogel material in the presence of different metal ions was investigated at room temperature. Individual metal ions (10 mM) were added (up to 200 μ L) to the aqueous suspension of xerogel material. Intriguingly, an effective quenching of the characteristic luminescence peak of the xerogel material was observed while Fe³⁺ ions were added to the suspension. The peak was quenched (Fig. 3(a)). Apart from the ferric ions, no obvious photoluminescence quenching phenomena were observed for the remainder of the metal ions (Fig. S15a–l, see the ESI†). This result can be correlated with the quenching efficiency for all metal ions. There was an impetuous increase in the efficiency (approximately 90%) of quenching the luminescence of the pristine material after the addition of Fe³⁺. However, negligible effects were observed for other ions, ranging from 5% to 13% (Fig. 3(b)). Quantitative determination of quenching behaviour was also analyzed using the Stern–Volmer (S–V) equation, expressed as follows:

$$\frac{I_0}{I} = K_{\rm SV}[\rm C] + 1 \tag{2}$$

where K_{SV} denotes the S–V constant (M⁻¹), and *C* denotes the molar concentration of the analytes (quencher).^{53,54} The upward linearity deviation with increasing ferric ion concentration in the S–V plot may be due to the involvement of energy transfer or a self-absorption mechanism.⁵⁵ The K_{SV} value of 7.16 × 10³ M⁻¹ was calculated with a satisfactory linear correlation factor ($R^2 = 0.9819$) (Fig. 3(c)). A 2D S–V plot shows selectivity for Fe³⁺, and a similar deviation in linearity with higher concentration of analyte was noted (Fig. 3(d)).



Fig. 3 (a) Fluorescence titration for Fe^{3+} detection by Zr–CPG suspension. (b) Quenching efficiency of different metal ions in aqueous medium. (c) K_{SV} curve for Fe^{3+} (inset: lower concentration fitting) quenching. (d) 2D S–V diagram for all analytes (quenching phenomena with increasing analyte concentration). (e) Visual detection of Fe^{3+} under a UV light (λ_{ex} = 365 nm). (f) Smart sensing of Fe^{3+} through a paper-strip-based detection approach.

In addition, the LOD (68 ppb) value was also calculated using the standard equation, $3\sigma/K$ (σ = standard deviation of 20 consecutive blank measurements, and K = slope of the linear curve) (Fig. S16, see the ESI†).⁵⁶ The high value of K_{SV} and detection at the ppb level indicate that this xerogel material is quite efficient, and comparable with reported benchmark materials (Table S2, see the ESI†). Most interestingly, the detection limit of iron ions in aqueous medium is very much commensurable and much lower than the value recommended by the World Health Organization (WHO), 0.3 ppm.⁵⁷

Efficiency as a sensor probe. To be an effective real-time luminescent sensor, a material should be able to exhibit its selective sensing of a particular metal ion in the presence of other interfering ions. The photoluminescence titration experiment revealed that it can detect Fe³⁺ in the presence of interfering metal ions. The quenching due to other metal ions was not appreciable, while the presence of Fe³⁺ nearly quenched the characteristic PL peak (Fig. S17a–l and S18, see the ESI†). This result also corroborates with visual detection of Fe³⁺ (under a UV source). Quenching of blue luminescence ($\lambda_{ex} = 365$ nm) was only observed in the case of Fe³⁺, and the remainder of the cation showed little to no effect after being added to the suspension (Fig. 3(e)).

With a portable paper strip-based detection technique, there would be increased viability and convenience with our sensor probe. Whatman filter paper coated with xerogel dispersion was prepared for this facile detection technique, following the same procedure as that described in our previous report.⁵⁸ The xerogel-coated paper strips exhibited blue luminescence in the presence of a UV light ($\lambda_{ex} = 365$ nm). After drop-casting individual metal ions of 10 mM concentration (10 µL) onto the respective paper strips, the optical response was only quenched for Fe³⁺. In comparison, the other ions displayed no quenching, which affirmed the material's selective ability to sense ferric ions (Fig. 3(f)).

The material was repeatedly rinsed with water and then acetone after each cycle of the sensing experiment to eliminate the ferric ion from the dispersed solution. After filtration, the material was dried in a vacuum oven (at 60 °C) overnight before going through consecutive cycles. There were no apparent differences in sensing activity after the fifth cycle, and the characteristic fluorescence intensity was nearly coincidental with subsequent cycles (Fig. S19, see the ESI†). Before and after the completion of five sensing cycles, the FT-IR study revealed almost superimposable spectra, suggesting no such changes were observed in the local chemical environment (Fig. S20, see the ESI†).

Sensing under a replicated physiological condition. According to literature reports, fluorescence titration was performed using 20 mM HEPES (pH 7) solution to simulate the physiological condition.⁵⁹ Because we observed an almost 50% turn-off response to the characteristic luminescence peak of xerogel material after gradually adding Fe³⁺ (up to 100 μ L) into the suspension, it therefore is a viable sensor material under such conditions (Fig. S21, see the ESI†).

The detection of antibiotics in aqueous medium

Sensing experiments were carried out with four common classes of antibiotics that are widely used, i.e., nitrofuran-based (nitrofurantoin (NFT), furazolidone (FZD), nitrofurazone (NFZ)), sulphonamide-based (sulfamethazine (SMZ), sulfadiazine (SDZ)), nitroimidazole-based (dimetridazole (DTZ), ronidazole (RDZ), ornidazole (ODZ)), and chloramphenicol (chloramphenicol (CAP)). The photoluminescence behaviour of a xerogel suspension (in water) upon addition of these antibiotics was investigated. All antibiotics at 10 mM concentration were gradually added to that suspension, and quenching behaviour was monitored using the fluorescence titration method (Fig. S22a-h, see the ESI[†]). Among all of these antibiotics, NFT showed the highest quenching efficiency (approximately 85%). The order of quenching efficiencies is as follows: (NFT > FZD > NFZ > ODZ > RDZ > DTZ > CAP > SMZ > SDZ (Fig. 4(a)). Most interestingly, upon addition of NFA-based antibiotics into the xerogel suspension, the peak was quenched and redshifted (Fig. 4(b)).

Quantitative detection of NFT through xerogel material was analysed using the S–V equation (eqn (2)). Using the S–V plot, a K_{SV} value of $1.53 \times 10^4 \text{ M}^{-1}$ was calculated that exhibited a satisfactory linear correlation ($R^2 = 0.9734$) in the lower concentration region. The upward bent nature of the curve with increasing analyte concentration indicates self-absorption or energy transfer phenomena (Fig. 4(c)). The 3D K_{SV} bar diagram also reflects the factor of the upward bent nature of the curve for all analytes with increasing concentrations (Fig. 4(d)). The LOD value (50 ppb) was calculated using the above-mentioned method (Fig. S23, see the ESI†). Because of the high K_{SV} and very low detection limit, this material has the potential to be an efficient sensor for NFA antibiotics, and these results are also comparable with reported benchmark materials (Table S3, see the ESI†).

Selectivity and recyclability. The selective sensing towards nitrofuran antibiotics was studied in the presence of other interfering antibiotics. The highest quenching efficiency was observed in case of NFT antibiotic, and therefore, further selectivity tests were performed with respect to NFT only. In all cases, little to moderate quenching was observed. However, the addition of NFT ($200 \ \mu L$, $10^{-2} M$) into the suspension resulted in an appreciable change in the quenching efficiency, suggesting high selectivity for NFT (Fig. S24a–f and S25, see the ESI†). In terms of recyclability, the sensing activity was unchanged for five consecutive cycles. After completion of the first cycle, the suspension was washed thoroughly with water, followed by acetone, and dried in a vacuum oven (at 60 °C for 2 hours) to use for the next cycle (Fig. S26, see the ESI†).

As a smart sensor. A thin film-based detection technique was introduced for the rapid detection of NFT. A homogenous mixture of xerogel suspension (in DMF) and poly(methyl methacrylate) (PMMA) was prepared with an equal amount of each material in toluene. The mixture was transferred into a glass Petri dish, and then dried in a vacuum oven (at 50 °C for 3 hours). The as-prepared thin film was cut into rectangular shapes (approximately 2 cm \times 3 cm) for further use as a sensor probe.



Fig. 4 (a) Quenching efficiency (3D bar diagram) of different antibiotics in aqueous medium. (b) Fluorescence titration for detection of NFT antibiotic using Zr-CPG xerogel suspension. (c) K_{SV} curve for NFT (inset: lower concentration fitting) quenching. (d) 3D S-V diagram for all antibiotics (quenching phenomena with increasing antibiotic concentration). (e) Zr-CPG-PMMA composite thin-film-based smart detection for NFT antibiotic.

Because the xerogel-PMMA thin film was capable of rapid detection of NFT and was reusable for several cycles, this composite material exhibits characteristics of an efficient sensor probe. Fig. 4(e) clearly displays the blue luminescence of the thin film quenched while adding NFT onto it (under a UV source of 365 nm). After washing with water followed by drying (in an oven at 50 $^{\circ}$ C for 30 min), the film was ready to use in consecutive cycles without losing its efficiency as a sensor. In addition, a kinetic study was performed to validate the ultrafast detection of NFT antibiotics using photoluminescence

spectroscopy. Rapid equilibrium upon quenching of the emission intensity was observed during each volume addition into the xerogel suspension (10 μ L, 100 μ L, and 200 μ L of 10 mM NFT solution) (Fig. S27, see the ESI†). All of these studies show that Zr–CPG has the potential to be used as a potent sensor for NFT antibiotics.

Plausible sensing mechanism for Fe³⁺ and NFT detection

There are a number of possible processes for quenching phenomena, including static quenching, dynamic quenching, and, most commonly, competitive absorption. The ground-state complex formation may lead to static quenching. However, an excitedstate collision process might be involved in dynamic quenching. Time-resolved photoluminescence (TRPL) decay experiments were carried out to obtain additional information regarding static and dynamic mechanisms.

After adding the ferric solution to the suspension, a noticeable change in the average lifetime of the pristine xerogel material (from 2.40 ns to 1.94 ns) was observed. Hence, the possibility of static quenching and competitive absorption was ruled out (Fig. 5(a)). As a result, two primary mechanisms can contribute to photoluminescence quenching of the material's characteristic emission – long range fluorescence resonance energy transfer (FRET) and/or short range photoinduced electron transfer (PET).^{24,60,61}

To understand the FRET mechanism involvement, the absorbance bands of all respective cations were confirmed through UV-Vis spectroscopic analysis. A distinct overlap appeared between the ferric ion (acceptor excitation) absorbance band and the xerogel emission spectrum (donor emission) (Fig. 5(b)). Apart from ferric ions, no other ions showed such an explicit overlapping zone with the emission spectrum of the fluorescence probe, suggesting that FRET may be involved in Fe³⁺ sensing. However, an electron-rich triazine backbone may interact with the Lewis acid metal (Fe³⁺) centre, which eases the pathway of the electron transfer process for quenching the emission peak. Apart from these possibilities, quenching may arise due to the destruction of the framework. However, nearly identical FT-IR spectra before and after sensing indicated that the local chemical environment remained unchanged, and no encapsulation of Fe³⁺ was perceived in the framework structure (Fig. S28, see the ESI[†]). EDX analysis of the xerogel material was performed to determine the possibility of quenching due to ion exchange. In the EDS analysis, no prominent peak for iron was observed, which ruled out the possibility of zirconium ion replacement from the supramolecular framework (Fig. S29, see the ESI⁺). To further investigate the fluorescence 'turn-off' of the characteristic luminescence peak of the xerogel material in the presence of NFT, a few experimental and theoretical approaches are presented. The nearly superimposable FT-IR spectra before and after NFT sensing revealed retention of the chemical environment, and thus, sensing through the framework



Fig. 5 (a) Lifetime decay profile for pristine xerogel and after adding NFT and Fe^{3+} analytes into the individual system. (b) Absorbance of all metal ions and emission of Zr–CPG suspension. (c) The HOMO–LUMO for the linker (H₃TATAB) and NFT molecule. (d) Absorbance of all antibiotics and emission of the Zr–CPG suspension.

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destruction was ruled out (Fig. S30, see the ESI[†]). The photoluminescence characteristic peak was quenched, and a small redshift was observed with gradual addition of NFT to the xerogel suspension medium. A linker with a triazine core may induce the H-bonding phenomena with the NFT molecule that leads to weak interactions. H-bonding-type weak interactions generally decrease when there is an increase in temperature.⁶² Hence, a temperature-dependent photoluminescence quenching study was performed at three different temperatures (30 °C, 40 °C, and 60 °C). A decrease in the quenching efficiency was observed with increasing temperature, which suggested that H-bonding interactions were minimised at the higher temperatures that affected the quenching (Fig. S31, see the ESI[†]).

TRPL experiments were performed for pristine xerogel material. After adding NFT to that suspension, the average lifetime value decreased from 2.40 ns to 2.20 ns, which may have been due to the involvement of long-range energy transfer or shortrange electron transfer phenomena (Table S4, see the ESI†). Therefore, the two possible pathways of FRET and PET mechanisms may be involved in this quenching process. As discussed earlier, the material is basically ligand-cantered luminescent, and because NFT antibiotics contain a 5-nitrofuran ring, which is a highly electron-deficient moiety, the electron transfer process is thus favored from the electron-rich LMWG (higher energy LUMO) to the quencher (lower energy LUMO).

To validate this hypothesis, density functional theory (DFT) calculations at the B3LYP/6-31G** level were performed for determining the HOMO-LUMO gap of the linker and respective antibiotics.63 The electron transfer can easily be possible because the LMWG is more adept at processing high energy LUMO (-2.04 eV) as compared to respective NFA analyte LUMOs (for an example, -3.34 eV for NFT) (Fig. 5(c)). However, when we examined the order of quenching efficiency for all antibiotics, we cannot say that it is solely due to the PET mechanism because the CAP antibiotic also processes lower energy LUMO (-2.95 eV) comparable to the linker but demonstrated lower quenching efficiency than nitroimidazole- and nitrofuran-based antibiotics (Fig. S32 and Table S5, see the ESI[†]). Therefore, it is clear that long-range energy transfer phenomena are involved. The UV-Vis spectroscopic analysis confirms the large overlapping zone between the quencher absorbance band and the emission of the xerogel, which suggests that the FRET mechanism also contributes towards this 'turn-off' sensing (Fig. 5(d)).

Xerogel-PMMA composite thin film as a UV protector

A literature survey revealed that 1,3,5-triazine derivatives possess potent UV shielding ability.⁶⁴ This material also contains an LMWG with a triazine backbone, which encouraged us to fabricate a thin film-based composite material that may shield against UV rays. At first, only PMMA was used to create an optically transparent film, but it was found to be incapable of blocking UVA and UVB rays due to its inability to filter wavelengths longer than 250 nm. Hence, thin film-based composite material was prepared using PMMA and xerogel material to protect from UVA, UVB, and UVC radiation. Different thin films were produced with variations in the weight percentage of the xerogel material and PMMA. The xerogel material was dispersed in DMF and ultrasonicated for approximately 4 hours to produce a homogenous suspension. In another glass beaker, PMMA in DMF was ultrasonicated for approximately 30 min. Both mixtures were then transferred to a glass Petri dish (diameter of 9.5 cm) and placed in a vacuum oven (3 hours, 50 °C) for solvent evaporation to obtain a thin film.

The transmittance of each film was recorded using a UV-Vis spectrophotometer over the wavelength range of 200–800 nm to evaluate the effectiveness of these thin films as UV radiationblocking materials. We experimented with varying the wt% of the xerogel material, and found that a lower loading of xerogel material produced film with greater transparency. Interestingly, a decrease in the loading percentage of the material did not alter the transmittance efficiency of the thin film in the UV region (200–360 nm).

A deviation in transmittance spectra was observed with an increasing material-loading percentage. An increasing wt% loading of the material actually decreased the transparency of the film. A decrease in transmittance values was observed in the region from 800 nm to 360 nm (from 2 wt% loading to 50 wt% loading). However, similar spectral observations were observed in cases of all Zr–CPG–PMMA composite film from 360 nm to 200 nm. The transmittance of different films (50 wt%, 10 wt%, 7.5 wt%, and 2 wt% of the xerogel materials) exhibited nearly 99% absorption of UV light (200–360 nm), and thus, this composite film is an efficient UV-absorbent material (Fig. 6(a)).

Furthermore, a diffuse-reflectance spectra (DRS) analysis of xerogel (Zr–CPG) was carried out to confirm the transmittance of the material without any polymer added to it. Similar behaviour in transmittance spectra was observed for solid Zr–CPG material (Fig. S33, see the ESI†), which confirmed that this phenomenon is solely related to xerogel's efficiency in UV blocking. With a minimal loading of xerogel material (2 wt%) onto the polymer matrix, the film was able to emit the characteristic blue luminescence under a UV source ($\lambda_{ex} = 365$ nm) (Fig. 6(b)).

To confirm the transparency of these thin films, a quote written on white paper was legible, indicating the use of a feasible composite material with UV shielding characteristics and transparent behaviour (Fig. 6(c)). In addition, the visibility of the acronym 'SSICG' (on a white paper) was confirmed through different films, and the 2 wt% loading thin film showed the highest transparency in comparison to the other thin films (Fig. 6(d)).

Conclusions

We synthesized a coordination-driven Zr-based soft material with a triazine core containing a tripodal low molecular weight gelator (LMWG). The tripodal LMWG with a rigid triazine core induced characteristic photophysical properties that assisted in the creation of an efficient fluorophore probe with transparent UV-shielding properties. The xerogel material can efficiently





Fig. 6 (a) Transmittance of thin films (Zr–CPG–PMMA composite), varying in CPG wt% loading. (b) Characteristic blue luminescence of the thin film under UV source. (c) Transparency check for a film made of 2 wt% loading of CPG with PMMA. (d) Differences in visibility with variation in CPG loading percentage (different wt%).

detect Fe^{3+} and NFT in aqueous medium in the presence of other interfering analytes.

Because of the ppb level detection of such analytes (LOD = 68 ppb for Fe³⁺ and LOD = 50 ppb for NFT), this material is an efficient sensor for the trace discrimination of environmentally hazardous toxins. This xerogel material can be recycled up to five times without loss of its ability to detect quenchers, *viz.*, Fe^{3+} and NFT. In addition, colorimetric-, paper strip-, and thin film-based detection methods were developed so that the material would be suitable for use as a sensor probe. The xerogel–PMMA thin film can be used as a recyclable sensor probe that genuinely increases the applicability of the sensor material. A detailed mechanistic study indicated that FRET or PET are the possible mechanisms behind the sensing of Fe³⁺ and NFT.

The fabrication of xerogel–PMMA composite films through a straightforward and efficient solution casting method was established. Hence, they possess all the features desirable for use as suitable sensor materials and may impart direction for further study of new CPG materials for real-world sensing applications. The incorporation of xerogel material (as low as 2 wt%) into the polymer matrix enhances its UV-blocking ability in the wavelength range from 200 nm to 360 nm, which can shield against all UVC and UVB radiation and most of the UVA radiation with high optical transparency. This study not only proposes a potential technique for the bulk manufacturing of UV-blocking composites, but also aids in the comprehension and design of inorganic polymer composites with enticing features.

Author contributions

S. M. and D. S. designed the project. S. M. synthesised and characterised the material. S. M. performed DFT calculations. S. M. and D. S. co-wrote the manuscript.

Conflicts of interest

The authors declare no competing financial interests.

Acknowledgements

IIT Patna is acknowledged for the research infrastucture. D. S. acknowledges The Council of Scientific and Industrial Research, Government of India, for the research grant under sanction 01(3057)/21/EMR-II.

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