

## Triazine Core Anchored Lanthanide Driven Soft Gels: Photo Switching Emission, Robust Anticounterfeiting, and Smart Sensor Probe for Nitroexplosive/Nitrofuran Antibiotics

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**ABSTRACT:** Stimuli-responsive luminescent soft materials are of current interest owing to their tunable processability for encryption, sensing, and multimodal security applications. Herein, a tripodal carboxylic acid based triazine mediated linker (3,3',3''-((1,3,5-triazine-2,4,6-triyl)tris(azanediyl))tribenzoic acid) has beenused to synthesize photochromic coordination driven soft gel (CSG) withTb(III)/Eu(III) ions. Tuning of the stoichiometric ratios exhibited a "chameleonlike" behavior upon exposure to UV lights and led to origination of white lightemitting materials. The CSGs were applied in robust anticounterfeit applicationsthrough security ink, stamping, and painting on different surfaces under variableconditions. Along with this, terbium-based CSG was used as an optical sensor forselective detection of antibiotics (nitrofurantoin (NFT), LOD = 64.25 ppb) andnitroexplosive (2,4,6-trinitrophenol, LOD = 24.5 ppb) from an aqueous mediumusing photoluminescence spectroscopy. RGB-mediated smartphone-based detection for nitroexplosive and antibiotic detection in real water samples aided this as asmart sensor to emphasize the real-time applicability.

Nitroexplosive detection Antibiotic Sensing

KEYWORDS: encryption, photochromic, optical sensor, antibiotics, nitroexplosive

## INTRODUCTION

The exploration of light-emitting materials has seen a growing interest owing to their utilization in optoelectronic devices and displays.<sup>1</sup> The ability to alter the photophysical characteristics upon exposure to variable light sources enhances their potential uses in fluorescence imaging, data encryption, and photonic devices.<sup>2</sup> Solid-state lighting is a particularly intriguing study area due to its wide range of applications. Notably, lighting accounts for around 20% of global electricity consumption, significantly contributing to the overall energy usage.<sup>3</sup> In the realm of white light emitting research, presently, mercury emission mediated sources are the preferred choice. Nevertheless, the widespread implementation of mercury gives rise to a multitude of environmental apprehensions.<sup>4</sup> Considerable research efforts have been dedicated to the advancement of white light emissive materials that include safe synthetic pathways and greater environmental compatibility with high energy efficiency. Common pathways to achieve perfect white light emissive material generally deal with monochromatic, dichromatic, and trichromatic emitter approaches. Among these three, a trichromatic emitter that indulges amalgamation of blue, red, and green color shows the best efficiency due to its high color rendering efficiency with greater luminescence activity.<sup>5</sup> The distinct luminescent properties exhibited by trivalent lanthanide (Ln<sup>III</sup>) ions including highly defined emission in the visible and near-infrared (NIR) spectral ranges, extensive

color purity with high quantum yield, long lifetime, substantial Stokes shift, and sharp emission spectra make them highly attractive as potential materials for generating white light.<sup>7,8</sup> Despite their color emission capabilities, these materials are hindered by poor light absorption caused by Laporte forbidden f-f transitions. This results in reduced molar absorption coefficients ( $\varepsilon$ ) and inadequate absorption of radiation.<sup>9</sup> An organic linker can interact with Ln<sup>III</sup> ions via "luminescence sensitization" through an electron transfer process and enhance the effect of light absorption and emission.<sup>10</sup> Lanthanide metal organic frameworks (LnMOFs) are an example of an ideal photo functional hybrid material, as their luminescence behavior can be tuned by altering the interaction between metal ions and organic linkers.<sup>11</sup> A very recent report by Chen and co-workers shows white light emitting diode (WLED) based applications by tuning terbium and europium ions with a tripodal carboxylic acid linker.<sup>12</sup> In a distinct study, Xu et al. used multiple lanthanides to tune for white LED.<sup>13</sup> Similarly, utilizing

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photochromic material to encrypt information has attracted significant attention.<sup>14</sup> The advancement of the framework materials in security and sensing was extensively described by Hazra et al.<sup>15</sup> Recently, Wong and co-workers comprehensively reviewed the photo physics of lanthanide complexes, focusing specifically on their potential uses in photonics.<sup>16</sup> Kaczmarek et al. reported grafting of lanthanide- $\beta$ -diketonate complex in MOFs pore and utilized as "chameleon-like" photochromic material for anticounterfeit applications.<sup>17</sup> However, dispersing the solid particles (LnMOFs, lanthanide composite materials) in desired organic solvents for direct use in anticounterfeiting applications and optoelectronic device fabrications is fraught with constraints. Similar to LnMOFs, another class of hybrid soft materials, viz., coordination driven soft gel (CSGs), is gaining prominence due to tunable sol-gel transformability, which leads to the creation of potential kits for optoelectronic displays and devices.<sup>18–21</sup> To this end, Maji and co-workers demonstrated an effective strategy for generating white light mediated soft coordination driven gel by tuning a blue-emitting organic linker with green- and red-emitting Tb(III) and Eu(III) ions. Importantly, the gel character of the soft material imparts an edge over other reported materials for carrying and storing information via device fabrication.<sup>22,23</sup> It can be used as a secret ink to conceal information, which is useful for security entities. Zhou and co-workers developed logic devices using lanthanidebased hydrogels to make erasable data encryption-decryption protocols.<sup>24</sup> In a distinct study, Li et al. used phenylalanine as a linker to form a CSG with terbium and europium salts that were utilized as reversible switching luminescent material in anticounterfeiting.<sup>25</sup> However, only a handful of reports regarding CSG-based soft materials for data encryption are available. This leaves ample space for the research and development of photochromic CSG materials to fabricate smart optical devices and for data encryption purposes.<sup>24</sup>

The detection of explosives has emerged as a significant concern due to the increasing prevalence of explosive deployments in worldwide acts of terrorism.<sup>27</sup> Ensuring the reliability and accuracy of detection methods has become crucial in addressing this issue.<sup>28</sup> The majority of industrial explosives contain nitro-aromatics/aliphatics and organic peroxide compounds as components. Phenolic nitroaromatics are well-known for their environmental persistence and toxicity. Their presence in soil and water might have a negative impact on the ecosystems. These substances can seep into groundwater, affect aquatic organisms, accumulate in soil, and affect plants and other organisms in terrestrial environments.<sup>29</sup> When various nitroexplosives are evaluated, it is evident that 2,4,6-trinitrophenol (TNP) is one of the most potent explosives in its category. Its exceptional potency has led to its widespread utilization in landmines for several decades.<sup>30</sup> Significantly, this poses a threat for the defense and other government agencies.<sup>31</sup> Notably, the utilization of TNP in many chemical sectors, such as leather, pharmaceutical, and dye industries, as well as in explosive devices, significantly impacts on the environment due to unregulated contamination.<sup>32,33</sup> This contamination leads to the occurrence of severe health consequences such as pronounced irritation and allergic reactions in the human body.<sup>34</sup> TNP has the potential to cause asphyxiation and further respiratory issues, as well as hepatotoxicity and hematotoxicity.<sup>35</sup> Upon accumulation in the digestive tract of mammalian organisms through the food chain, TNP undergoes a transformation through the reduction of nitro group and forms more potent mutagenic species, i.e., picramic acid.<sup>36,37</sup> Hence, the

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detection of TNP is of the utmost importance from several perspectives, including environmental, health, and homeland security. Similar to nitroexplosives, nitrodrugs are another class of compounds that can cause severe consequences for human as well as animal health upon uncontrolled use and discharge from different sources. Since the ground-breaking discovery of penicillin by Alexander Fleming in 1929, antibiotics have evolved into a significant category of pharmaceuticals that are extensively employed for the therapeutic management of bacterial infections in both human and animal populations.<sup>38</sup>

Within many classes of antibiotics, nitrofuran antibiotics (NFAs) are widely used to treat protozoan and bacterial infections, which are also widely used as feed additives for poultry farms and within aquaculture to treat infections caused by bacteria like Escherichia coli and Salmonella spp.<sup>39</sup> However, over the past few decades, the excessive use of antibiotics has resulted in elevated concentrations of antibiotic remnants in diverse aquatic systems, including groundwater and surface water.<sup>40</sup> Therefore, the urgent challenge lies in developing appropriate techniques for prompt and accurate detection of trace quantities of such analytes from different water systems for effective environmental monitoring. In light of the preeminent significance of upholding food, health, and environmental safety, developing a probe capable of detecting these harmful nitro compounds is imperative. Compared to traditional methods, the luminescence-based detection technique has been widely recognized as a favorable alternative due to its advantages, including high sensitivity, selectivity, and straightforward and cost-effective operation without the need for intricate sample preparation.<sup>41</sup> Lanthanide-based materials have gained significant attention among fluorophore compounds due to their large Stokes shift, high quantum yield, and sharp emission peaks. In this context, LnMOFs can be useful as significant fluorophore probes to detect analytes, including nitroexplosives and nitrofuran based antibiotics.<sup>42</sup> Although there has been significant research using metal-organic frameworks (MOFs) as fluorophore probes for detecting different environmental hazards, the application of CSGs for such purposes is still in its early stages.<sup>43</sup> There are a limited number of CSGs that have been described as probes for the detection of toxins.<sup>44,45</sup> Similar to LnMOFs, lanthanide-based soft gel materials have captivated the attention of researchers regarding the detection of analytes.<sup>46</sup> The efficiency of the lanthanide-based luminescent sensor in the presence of water is complicated, as excited-state energy transfer via coupling with O-H oscillators of water molecules stimulates quenching of the luminescence.<sup>47</sup> Therefore, it is crucial to develop an effective sensor that can selectively detect TNP and NFAs from aqueous media.

Coordination driven soft gels, composed of low-molecularweight gelators (LMWGs)<sup>48</sup> and metal ions, are an emerging category of smart soft materials with diverse applications ranging from sensing, catalysis, and drug delivery to energy storage.<sup>49–51</sup> Distinct functionalities of the LMWGs can induce noncovalent interactions, which lead to a self-assembly process to form supramolecular gels. In addition, metal linker interactions impart more mechanical strength to this gelation process via coordination interactions.<sup>52</sup> Herein, a tripodal carboxylic acid based linker was introduced with a rigid triazine core (3,3',3"-((1,3,5-triazine-2,4,6-triyl)tris(azanediyl))tribenzoic acid). The rigid triazine core induces  $\Pi-\Pi$  stacking as well as hydrogen bonding to form a supramolecular gel network. On the other hand, terminal carboxylic acid can be involved in the direct coordination with metal ions. Eu(III)/Tb(III) metal sources

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Figure 1. Schematic for the synthesis of CSGs and multimodal application.



**Figure 2.** (a) CIE diagram for different color tunable gels and respective pictures in the inset (Tb\_TATMB (1), EuTb\_TATMB-1 (2), EuTb\_TATMB (3), EuTb\_TATMB-2 (4), EuTb\_TATMB-3 (5), and EuTb\_TATMB (6)). (b) PL emission spectrum of Tb\_TATMB (inset: green emission of the gel and xerogel upon exposure of UV source). (c) PL emission spectrum of Eu\_TATMB (inset: red emission of the gel and xerogel upon exposure of UV source). (d) PL emission spectrum of EuTb\_TATMB (inset: white emission of the gel and xerogel upon exposure of UV source). (e) Schematic representation of the "antenna effect". LED connected with 5 V battery (f) before and (g) after coating with white light emitting xerogel material (EuTb\_TATMB).

were used to create a multifunctional luminophore probe. By tuning with different stoichiometric ratios of metal ions, multiemissive CSGs (Eu\_TATMB, Tb\_TATMB, Eu-Tb\_TATMB) were formed. The as-synthesized CSGs were used to encrypt codes via security stamping, writing, and artwork (Figure 1). Furthermore, a white light-emitting CSG was prepared by tuning Eu(III), Tb(III), and the linker stoichiometric ratio. The terbium CSG was used as a smart sensory

probe for the selective detection of TNP and NFA antibiotics from an aqueous medium. The high  $K_{SV}$  value with low detection limits for both TNP and NFT (nitrofurantoin) antibiotics dictates high selectivity toward these analytes. Altogether, smart detection techniques such as smartphone based colorimetric detection of TNP and easy recyclable thin film-based NFT sensing make this an efficient sensor probe.

#### EXPERIMENTAL SECTION

### Material Used

All organic analytes (benzoic acid, aniline, TNP, phenol, isophthalic acid, nitrobenzene, toluene, 4-nitrophenol, *p*-toluidine), sodium bicarbonate, sodium hydroxide, europium acetate, terbium acetate, cyanuric chloride, and *N*,*N'*-dimethylformamide were procured from Central Drug House (CDH). The compounds 3-aminobenzoic acid and ronidazole (RDZ) were acquired from Sigma-Aldrich. Sulfadiazine (SDZ), sulfamethazine (SMZ), nitrofurantoin (NFT), nitrofurazone (NFZ), furazolidone (FZD), dimetridazole (DTZ), and ornidazole (ODZ) were procured from BLD Pharm. Chloramphenicol (CAP) was purchased from Combi-Blocks. 2,4-Dinitrophenol (2,4-DNP), nitrobenzoic acid (3,5-DNBA) were purchased from Loba Chemie. In the course of the process, all compounds were used without the need for additional purification procedures. Milli-Q water was used for the synthesis and photophysical investigations.

#### Synthesis of the Linkers (TATMB)

Typically, a solution of 3-aminobenzoic acid (920 mg, 5 mmol) and NaOH (250 mg, 6 mmol) was prepared by adding 20 mL of water in a beaker. In a separate beaker, cyanuric chloride (685 mg, 5 mmol) was mixed with 100 mL of water and stirred for half an hour at 0 °C. The preceding solution was added dropwise into the subsequent one and kept stirring (1.5 h) at 0 °C. Subsequently, a mixture of 3-aminobenzoic acid (1.84 mg, 10 mmol) and sodium hydroxide in aqueous solution (15 mL) was introduced followed by stirring the reaction mixture at ambient temperature. The mixture was heated and refluxed at 90 °C after room temperature stirring for 2 h. After 6 h of reflux, the solution was cooled, and filtration was carried out. Additional water (~200 mL) was added to that filtrate. The solid precipitation was formed after acidifying the solution with 20% HCl (pH  $\sim$ 2). The solid precipitate was washed with cold water followed by methanol and diethyl ether and then kept in the oven for vacuum drying. Yield: 70%. <sup>1</sup>H NMR (DMSO $d_6$ ), 400 MHz:  $\delta$  = 7.40 (3H), 7.57 (3H), 8.09 (3H), 8.28 (3H), 9.53 (3H) (Figure S1, see SI).

#### Synthesis of Multifunctional Luminescent CSGs

A 0.1 M solution of TATMB was prepared in a vial using DMF as the solvent. Terbium acetate and europium acetate were prepared in a mixture of DMF/ethanol (1:1). Each metal ion solution was prepared at 0.3 M concentration. Subsequently, the metal ion solutions ( $250 \,\mu$ L) were mixed with the TATMB ligand solution in a 1:1 volume ratio, resulting in a final volume of 500  $\mu$ L. Almost instantly, white colored gels were formed. Tb\_TATMB (Figure 2a; inset 1) and Eu\_TATMB (Figure 2a; inset 6) gels were prepared following this approach, and xerogels of respective gels were prepared using the lyophilization process.

#### Synthesis of Light Emissive CSGs

Photochromic CSGs were synthesized by tuning the stoichiometric ratios of europium/terbium ions (acetate salts) and the TATMB linker. Apart from two pure green and red emissive gels, similar synthesis approaches were accomplished to form four distinct CSGs that exhibited color variations upon exposure to UV sources. The solubility of the tripodal carboxylic acid linker was tested in different solvents. It was soluble in DMF solvents. A mixed-solvent approach was introduced to form gels. To form supramolecular gels, each metal salt was prepared with a 0.3 M concentration in a DMF/ethanol mixture, and the linker was prepared with a 0.1 M concentration in DMF. Directly mixing the linker and metal ions instantly forms gels at room temperature. A greenish-yellow emissive gel EuTb\_TATMB-1 (Figure 2a; inset 2) was obtained by mixing terbium acetate, europium acetate, and the linker in 200:50:250  $\mu$ L ratio, respectively. Similarly, creamy white gel EuTb\_TATMB-2 (Figure 2a; inset4) was observed while mixing terbium acetate, europium acetate, and TATMB in 150:100:250  $\mu$ L ratio, respectively. The pink emissive gel EuTb\_TATMB-3 (Figure 2a; inset 5) was prepared upon mixing terbium acetate, europium acetate, and TATMB in 100:150:250  $\mu$ L ratio, respectively. Finally, the white-light-emitting gel EuTb\_TATMB (Figure 2a; inset 3) was obtained using terbium acetate, europium acetate, and TATMB in 175:75:250  $\mu$ L ratio, respectively.

#### Preparation of the Anticounterfeiting Devices

Different stamps were made using templates such as "LAB", ATOM, and "SSICG" (abbreviation for Solid State and Inorganic Chemistry Group). Luminescent inks were prepared using freshly prepared Tb\_TATMB, Eu\_TATMB, and EuTb\_TATMB CSGs. Nonfluorescent paper was used to get the encrypted marks from those templates. Luminescent thin films were prepared using mixture of CSGs and poly(methyl methacrylate) polymer (PMMA) in appropriate weight ratios. The CSGs and PMMA polymer were mixed in a toluene/DMF mixture and kept for vacuum drying to obtain thin films. On the other hand, a paintbrush was used to create artwork on paper.

#### PREPARATION OF LUMINESCENT PENS USING XEROGEL SUSPENSIONS

In this study, gel ink pens with a tip size of 0.5 mm were utilized. The original ink was removed from the ink barrel by washing it with water. After that, both the ink barrel and the nib were kept for ultrasonication in a beaker containing ethanol/acetone for thorough cleaning. To prepare the ink for writing, Tb\_TATMB and Eu\_TATMB xerogels were used. Ten milligrams of xerogel materials was mixed individually in ethanol/ethylene glycol (2:2 mL) mixture. Ethylene glycol was used because of its ability to increase the stickiness.

#### Photophysical Study for TNP and Nitrofuran-Based Antibiotic Sensing

Freshly prepared solutions with a concentration of  $10^{-2}$  M of each analyte were used to facilitate further photophysical investigations. Two milligrams of xerogel material was dispersed into 2 mL of water for photoluminescent (PL) experiments. The suspension was kept for ultrasonication before performing the PL study. Upon excitation at a wavelength of 326 nm, strong emission peaks at 491, 547, 587, and 623 nm were observed for the Tb\_TATMB xerogel suspension. The following equation was used for calculating the respective quenching efficiencies (QEs):

$$(1 - \frac{I}{I_0}) \times 100\%$$
 (1)

where  $I_0$  and I are the initial luminescent intensities of the xerogel material and after adding analyte into the xerogel suspension, respectively. The detection limit of Tb\_TATMB for TNP and nitrofuran-based antibiotic sensing was investigated through the fluorescence method using very low concentrations of the corresponding analyte solutions.

## RGB (Red Green Blue)-Based TNP Detection Using a Smartphone

The Tb\_TATMB xerogel was used to detect antibiotics via the RGB method through smartphone-based detection. Ten Eppendorf tubes containing xerogel—water suspension were prepared to check color-based quenching. The TNP was added to individual vials from 50 to 500  $\mu$ M concentrations. The color picker app (from Google Android Play Store) was utilized to identify the RGB value, and the linear relationship between the



Figure 3. Schematic of the probable interaction pathway between the linker and lanthanide ions to form the CSG.

G/B ratio and the TNP concentration was calculated and plotted.

#### NFT Antibiotic Detection in Real Water Samples

Various water samples, including tap water, mineral water, and river water (taken from the Ganges river, Patna, India), were collected to assess the efficacy of Tb\_TATMB CSG in detecting the presence of NFT antibiotics in real-world water specimens. Nine vials were taken to prepare nine specimen samples, which were spiked with three known concentrations of NFT (final concentrations of 25, 50, and 100  $\mu$ M). Their emission spectra were recorded at 491, 547, 587, and 623 nm, with an excitation wavelength of 326 nm.

## RESULTS AND DISCUSSION

The structural specificity of the linker always plays an essential role in the gelation process. The tripodal linker containing carboxylic acid can easily coordinate with the lanthanide ions. On the other hand, the triazine core induces rigidity as well as  $\Pi-\Pi$  stacking interactions in the supramolecular network structure. Hence, both coordination and supramolecular noncovalent interactions are responsible for gel formation. In addition, we investigated the possibility of modifying the emission of CSGs by adjusting the proportion of the two lanthanides responsible for the emission of red and green light. Direct mixing of Tb(III) and Eu(III) with TATMB in various stoichiometric ratios resulted in a number of CSGs that exhibited variable luminescence behavior under UV light (Figure 3).

The photophysical properties of the as-synthesized Tb\_TATMB, Eu\_TATMB, and EuTb\_TATMB xerogel materials were studied. The triazine core mediated tripodal carboxylic acid based linker can act as an efficient LMWG to interact with lanthanide ions to exhibit sharp line spectra via the "antenna effect". Tb\_TATMB and Eu\_TATMB both show sharp line spectra, suggesting complexation through sensitization of Tb(III) and Eu(III) ions. The Tb\_TATMB xerogel exhibits sharp emission peaks at 491, 547, 587, and 623 nm upon excitation at 326 nm. These strong emission bands are attributed to  ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$  (J = 6, 5, 4, 3) transitions of terbium ions. The corresponding green emission of Tb\_TATMB materials was observable when exposed to a UV source in both the gel and dry forms (Figure 2b). This is further supported by the appropriate CIE coordinates (0.33, 0.55), which confirm the green emission

(Table S1; see SI). The luminescence intensity of the material was checked in different conditions. The characteristic sharp peaks of Tb TATMB were observed in both the gel and xerogel states. Furthermore, the xerogel was dispersed in pure and mixed solvents, and the corresponding PL emission spectra were recorded. Among different solvent media, the highest intensity peak was observed in the presence of water (Figure S2; see SI). As an efficient sensor probe, stable photoluminescence emission in an aqueous medium is always put forward in the context of real-time applicability. Hence, all photophysical investigations were carried out by dispersing the xerogel material in a water medium. A detailed pH-dependent luminescence experiment was carried out to check the stability. The characteristic emission peak of the Tb\_TATMB was increased with increasing pH of the solution (over the range of pH 3-10). In pH 2, the linker emission peak (around 430 nm) competes with the terbium xerogel emission peak. Interestingly, the terbium xerogel characteristic peaks were fully diminished at pH 1. This result suggests that the carboxylic acid linker acts as Brønsted acid sites that deprotonate under basic conditions and result in the PL intensity enhancement with increasing pH solution. Meanwhile, under acidic conditions, carboxylate moieties can protonate and weaken the metal-ligand bonding, which is confirmed by the diminishing PL intensities. Notably, below pH 3, the bond gets weaker, and at pH 1, only a linker peak was observed. These results also support energy transfer via the "antenna effect". The energy transfer phenomena from the excited state of the linker were disturbed in highly acidic conditions, which were reflected in its PL spectra (Figures S3 and S4; see SI).<sup>53,54</sup> The above finding was also supported by FTIR analysis. The band around 1655 cm<sup>-1</sup> (below pH 3) was shifted to 1690 cm<sup>-1</sup> (above pH 3), which indicates stronger metal-ligand coordination under basic conditions due to deprotonation of the carboxylate atom (Figure S5; see SI).

A leaching test was performed to check whether the emission of the xerogel was solely related to solid particles dispersed in the water. The intense characteristic peaks of Tb\_TATMB were fully diminished after filtration, which suggest that the peaks are due to solid dispersion phase; no leaching was observed (Figure S6; see SI). In addition, the leaching test was performed under varying conditions (different temperature and pH ranges). No leaching was found at varying temperatures. Leaching was not observed within pH range 3–10, whereas under highly acidic conditions (pH = 1), the characteristic emission peak of the



**Figure 4.** (a) Dynamic frequency sweep, (b) dynamic angular sweep rheological analysis of EuTb\_TATMB gel, (c) FTIR spectra of TATMB linker and xerogels (Tb\_TATMB, Eu\_TATMB, Tb\_TATMB), (d) TGA analysis of Eu\_TATMB xerogel, (e, f) FESEM image of Tb\_TATMB xerogel, and (g–1) elemental mapping analysis of the EuTb\_TATMB xerogel.

linker was observed after filtration. It suggests the disrupture of metal–linker bonding at harsh acidic condition (Figure S7; see SI).

The photophysical investigation of Eu-mediated and mixed metal-mediated gels was also carried out. Eu\_TATMB displays emission peaks at 589 and 614 nm (excitation wavelength of 326 nm) attributed to the  ${}^5D_0 \rightarrow {}^7F_1$  and  ${}^5D_0 \rightarrow {}^7F_2$  transitions of Eu(III) ions, respectively (Figure 2c). The red luminescence of the gel and xerogel under UV exposure can be correlated with the corresponding CIE coordinates (0.46, 0.30) (Figure 2c (inset) and Table S1; see S1). Furthermore, this energy transfer phenomenon from the linker to Tb(III)/Eu(III) ions via the antenna effect was validated using the density functional theory (DFT) (see S1).<sup>55</sup> Significantly, the calculated results show the triplet state energy level of the TATMB linker to be 27,800 cm<sup>-1</sup>, rendering it appropriate for the sensitization of both Tb(III) and Eu(III) ions. In the case of terbium CSG, energy can transfer

from the linker's triplet excited state to the <sup>5</sup>D<sub>4</sub> excited state of terbium ion with subsequent deactivation to the ground state multiplet  ${}^{7}F_{I}$  (J = 0-6). Similarly, energy can be easily transferred from the triplet excited state of the linker to the excited state of the europium ion  $({}^{5}D_{0})$ . This is followed by a further deactivation process, leading to the ground state multiplet  $({}^{7}F_{I}, J = 0-4)$  (Figure 2e). Interestingly, bimetallic EuTb TATMB CSG exhibits white light upon exposure to UV source (Figure 2d). The obtained spectrum exhibits distinctive emissions of the Tb(III) and Eu(III) ions. The corresponding CIE coordinates (0.31, 0.36) dictate the region of emission closure to the exact white light coordinates (0.33, 0.33, CIE 1931 Chromaticity diagram) (Table S1; see SI).<sup>56</sup> When considering the antenna effect, the energy gap between the triplet excited state of the linker and the  ${}^{5}D_{4}$  excited state of the terbium ion is 7300 cm<sup>-1</sup>. This slightly higher energy gap restricts the back transfer of energy from Tb(III) excited state to

the linker and insists on phonon-assisted energy transfer from the terbium excited state to the europium excited state. The average lifetimes of H<sub>3</sub>TATMB, Tb TATMB, Eu TATMB, and EuTb\_TATMB were obtained as 4.90 ns, 412 µs, 448 µs, and 449  $\mu$ s, respectively (Figure S8 and S9, Tables S2 and S3; see SI). The average lifetime was increased after complexation with terbium and europium ions. Along with excitation at 326 nm wavelength, a broad emission around 430 nm was observed for the linker, and this characteristic emission was fully diminished in all lanthanide-mediated xerogel materials (Figure S10, Table S2; see SI). This suggests the effective energy transfer from the excited state of the linker to the respective ions via the "antenna effect".<sup>57-59</sup> To have a deeper understanding of the photophysical characteristics of the CSGs, quantum yields were determined. The quantum yields of Tb TATMB, Eu TATMB, and EuTb TATMB were determined to be 0.05, 0.037, and 0.053, respectively (eq S1; see SI).

A white light emitting LED was prepared by taking UV LED, which displays blue lights when connected to a 5 V battery (purchased from a local market). The same LED displayed white emissive light after coating with EuTb\_TATMB CSG in the xerogel state. It enhances real-time applicability as a smart probe for generating white light emissive material (Figure 2f,g).

To confirm gelation ability, along with the "inversion test", viscoelastic performances of freshly prepared Tb TATMB, Eu\_TATMB, and EuTb\_TATMB gels were also analyzed by the frequency sweep and strain sweep measurements at room temperature. In the case of semisolid gel materials, the storage modulus  $G'(\omega)$  of the materials should be greater than that of the loss modulus  $G''(\omega)$ , in which  $\omega$  stands for the angular frequency. While performing angular frequency sweep measurements for all the CSGs ranging from 100 to 0.1 rad/s at a constant shear strain, a higher  $G'(\omega)$  value was observed than  $G''(\omega)$  value throughout the frequency range, confirming the solid-like behavior of the gels (Figure 4a, Figure S11a,b; see SI). On the other hand, strain sweep measurements reveal that, at a lower strain value, the storage modulus shows a higher value than the loss modulus, but with increasing strain value, linearity deviates, and storage modulus becomes lower than the loss modulus, and gel-to-sol transition occurs. Tb\_TATMB exhibits a yield strain  $(G'(\omega) = G''(\omega))$  value of 45%, whereas EuTb TATMB and Tb TATMB display yield strain values of 32 and 34%, respectively (Figure 4b, Figure S12a,b; see SI).

The CSGs were dried by using lyophilization to obtain the xerogel for further characterization. To gain insight into the molecular origin behind these gelation studies, FTIR spectra were recorded. A broad peak ranging from 3200 to 2450  $cm^{-1}$  in the TATMB linker is attributed to the O-H stretching vibration band of the carboxylic group, which diminishes after interacting with terbium and europium ions. A similar observation was obtained in the FTIR spectra for all xerogel materials. A sharp peak around 1398 cm<sup>-1</sup> also dictates the generation of a new symmetric stretching band for the carboxylate group ( $\nu_s$ (COO<sup>-</sup>). These two observations manifest the deprotonation of the carboxylic acid group and coordination with metal ions to form carboxylate linkage.<sup>60,61</sup> Supramolecular interaction through H-bonding also plays an essential role in self-assembly to form a 3D network gel structure. A clear shift in C=O stretching frequency from linker to xerogel materials (prominent blue shift in stretching frequency from 1691 to 1656  $cm^{-1}$ ) suggests that hydrogen bonding may induce the gelation by promoting self-assembly.<sup>62</sup> Hence, both covalent as well as

supramolecular interactions prompt the gelation process (Figure 4c).

Thermogravimetric analysis was carried out from room temperature to 800 °C. Tb\_TATMB and Eu\_TATMB exhibit almost similar four-step degradation patterns upon heating. On the other hand, EuTb\_TATMB displays a three-step weight loss. Tb TATMB exhibits an initial weight loss of 8% while heating to 150 °C. This might be due to the desorption of solvent molecules from the surface and pores of the materials. Again, a slight weight loss of 6% in the temperature range from 150 to 310 °C dictates the loss of coordinated solvent molecules. Above 310 °C, two consecutive steps of weight losses were observed, each around 16% (310-480 °C and >480 °C), suggesting the decomposition of the material (Figure S13a; see SI). Red emissive Eu\_TATMB displays weight loss of 7% up to 140 °C, which indicates the liberation of physiosorbed moisture. Afterward, a weight loss of around 6% (140–320 °C) for losing coordinated solvents is observed, whereas two other successive weight losses of around 18% (320–480 °C) and 14% (>480 °C) indicate that material coordination network might start to collapse (Figure 4d). The white light emitting EuTb\_TATMB exhibits an initial weight loss of 7% up to 165 °C due to loss of physiosorbed moisture as well as coordinated solvent molecules. Then, the steep fall continued with two consecutive weight losses of 26% (165-490 °C) and 12% (>490 °C) due to material decomposition (Figure S13b; see SI).

To examine the surface morphology of the as-synthesized xerogel materials, scanning electron microscopy (FESEM) was performed. For both TB TATMB and Eu TATMB, small flakes are combined to form a sheet-like morphology. The micrographs also indicate pores with variable diameters ranging from 200 nm to 2  $\mu$ m (Figure 4e,f, Figure S14a,b; see SI). Interestingly, these pores were invisible in white light-emitting xerogel EuTb TATMB, where it exhibits a rock-shaped microstructure instead of flakes (Figure S14c; see SI). The elemental dot mapping and EDX analysis of EuTb\_TATMB confirm the presence of all of the elements (Figure S15; see SI). The elemental dot mapping suggests the homogeneous distribution of all the elements throughout the surface of materials in EuTb TATMB xerogel (Figure 4g-1). A broad peak was observed in PXRD for each of the xerogel materials (Tb\_TATMB, Eu\_TATMB, and EuTb\_TATMB), which indicates the amorphous nature. Hence, no appreciable longrange orders are present in these CSGs (Figure S16a-c; see SI).

## SECURITY STAMPING, WRITING, ARTWORK, AND LUMINESCENT THIN FILM FOR ANTICOUNTERFEITING APPLICATION USING PHOTOCHROMIC CSGS

#### **Security Stamping**

The long-lived, stable luminescent behavior of the CSGs encourages us to check their efficiency as a stable luminescent ink. As synthesized, the Tb\_TATMB gel was used to create security stamping by using different stamp templates. The capacity to make legible marks was tested on different surfaces, from the rough (packaging foam, tissue paper) to the smooth (glass slide, Petri dish). All created marks were barely visible in daylight but quite efficiently noticeable when exposed to UV sources (Table S4; see SI). Furthermore, the durability of stamping was tested by exposing the mark (stamped as "SSICG" on glass slide) in different harsh conditions. The green luminescence behavior of the "SSICG" mark was checked

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**Figure 5.** (a) Stability test of the anticounterfeiting through different harsh conditions ((i)) heating, (ii) freezing, (iii) humidity, (iv) extreme freezing conditions), (b) encrypted code with four digits that displayed as four 8s in the presence of daylight but showed "2023" code under UV exposure, (c) invisible ink preparation and solving the code from puzzled word, (d) different artwork in terms of smart anticounterfeit designing, and (e) preparation of different color tunable thin-film for utilizing as smart material.

before and after changing the conditions (heating, deep freezing, humidity, liquid nitrogen environments). No appreciable changes in emission characteristics were observed for the marked glass slides (Figure 5a (i-iv)). In addition, the luminescence stability of the stamping marks was tested in the presence of different organic solvents. Solvents like dimethyl sulfoxide, hexane, dimethylformamide, water, tetrahydrofuran, and ethanol were added dropwise over the stamping portion (stamped as "SSICG" on a paper surface). The stamping and emission were found to be nearly unaltered in all solvent conditions, indicating its potential suitability for use in anticounterfeiting applications (Figure S17; see SI). To this end, it is noteworthy that the encrypted data remain intact and unaffected even after an extended period of exposure to different conditions, exhibiting adequacy for showing good stamping ink for data encryption.

#### **Security Writing and Artwork**

The remarkable and enduring luminescent properties exhibited by the as-synthesized CSGs provide a compelling rationale for their application as an anticounterfeiting ink. The synthesized cryptographic protocols can be directly employed for the purpose of encryption. Using synthesized gels, definite patterns were drawn, which showed four "8" digits under daylight. The actual code was encrypted with a "2023" pattern, which was clearly visible under exposure to UV sources (Figure 5b). Additionally, we created a photochromic pen that can be used for code encryption. As depicted in Figure 5c, the phrase "GREEN APPLE" was rendered as "GARPEPELNE" by the arrangement of jumbled letters. Specifically, the term "GREEN" was inscribed using Tb\_TATMB ink, whereas the term "APPLE " was composed using Eu\_TATMB ink. Remarkably, when these were exposed to daylight, the encrypted data lacked any discernible meaning. However, the encrypted data can only be decoded through a precise arrangement of characters in a definite sequence while being subjected to exposure under UV lights. Furthermore, painting brushes were used to paint the desired artwork through brush painting using synthesized CSGs. Drawn marks were not visible under normal daylight, but in the presence of UV sources, clear pictures of a butterfly and a flying bird emphasize the security drawing ability (Figure 5d).

## Luminescent Films

Water-resistant thin films were prepared by dissolving each xerogel (Tb\_TATMB, Eu\_TATMB, and EuTb\_TATMB) and poly(methyl methacrylate) (PMMA) with a similar weight ratio in the DMF/toluene mixture. After stirring for a few minutes, each mixture was transferred to Petri dishes and kept in a vacuum oven for drying. The as-prepared thin films exhibit no such color deviations in typical daylight but display prominent green, red, and white luminescence while exposed under a UV source ( $\lambda_{ex} = 365$  nm). These films can be utilized for labeling purposes to encrypt secured information (Figure 5e).

## SENSING OF NITROEXPLOSIVE AND NITROFURAN BASED ANTIBIOTICS

The coordination driven soft gels were prepared from triazine mediated semirigid linker. The triazine N atoms and -NH-bridging moiety induce Lewis basic sites with flexibility. This core can serve extensive  $\Pi$  conjugation, which helps to enhance the recognition effect of ions and small molecules after complex formation.<sup>63</sup> The flexible -NH- group also interacts via a host-guest interaction through extensive hydrogen bonding. This interaction may play a specific role in detecting nitro compounds. Most of the lanthanide-mediated complexes generally face difficulties while sensing in an aqueous medium.





Figure 6. (a) QE of organic analytes are represented in the bar diagram. (b) Quenching ability for TNP sensing in the presence of other analytes.



**Figure 7.** (a)  $K_{SV}$  curve with lower region fitting (inset) for TNP sensing, (b)  $K_{SV}$  curve with lower region fitting (inset) for 4-NP sensing, (c) 3D  $K_{SV}$  bar diagram for individual analytes (with varying analyte concentration), and (d) recyclability test for TNP sensing up to five consecutive cycles.

In this context, good dispersibility in water medium with high intense emission peaks deliberately makes this material a potent sensor for nitroexplosive and nitrofuran based antibiotics.

## **Nitroexplosive Sensing**

The variation in the photoluminescence behavior of the Tb\_TATMB xerogel was monitored in the presence of different organic analytes. Each analyte was gradually added into a xerogel

suspension up to 200  $\mu$ L, and respective quenching effects were observed. No such appreciable change in quenching efficiencies (QEs) was noticed in the case of toluene (TL), phenol (PL), aniline (AL), and *p*-toluidine (*p*-TD), ranging from 6 to 17%. Small changes in QE (26–45%) were observed after adding benzoic acid (BA), isophthalic acid (IA), nitrobenzene (NB), nitrobenzoic acid (NBA), dinitrobenzene (DNB), and 3,5-



**Figure 8.** (a) Color variation upon giving different concentrations of TNP in separate vials filled with Tb\_TATMB (dispersed in water) under UV source. (b) LOD fitting curve for RGB-based detection, (c) PMMA-xerogel luminescent composite material as thin film, and (d) recyclability test for NFT sensing of the thin film composite material.

dinitrobenzoic acid (3,5-DNBA) into the xerogel suspension. However, sizable quenching was observed in case of TNP, 4nitrophenol, and 2,4-dinitrophenol (2,4-DNP) (~96-99% of QE) (Figure 6a, Figure S18a-m; see SI). Apart from this, the TNP sensing efficiency was also checked for Eu TATMB and EuTb TATMB materials. The QE for TNP was found to be 90 and 94% for Eu\_ TATMB and EuTb\_ TATMB, respectively. Further sensing experiments for all analytes were carried out using Tb TATMB gel as the sensor probe material (Figures S19–S20; see SI). Furthermore, selective detection of TNP was carried out by checking the quenching activity in the presence of other interfering organic analytes. Appreciable quenching was detected in all of the systems while TNP was introduced to each system that already contained individual organic analytes (Figure 6b, Figure S21a-j; see SI). It shows efficient detection of TNP in the presence of other interfering organic analytes, suggesting high selectivity for TNP analytes. The Stern-Volmer equation (eq S2; see SI) was utilized to quantify fluorescence quenching observations. The analysis of the S-V plot with a good correlation coefficient ( $R^2 = 0.9689$  and  $R^2 = 0.9815$ ) gives the  $K_{\rm SV}$  value of 6.2 × 10<sup>4</sup> and 9.2 × 10<sup>3</sup> M<sup>-1</sup> for TNP and 4-NP, respectively (Figure 7a,b). The plot deviates from linearity to exhibit an upward bent nature in higher concentrations of the analyte, indicating that self-absorption or energy transfer phenomena may be involved in this quenching. The low detection limit of 24.5 and 39.92 ppb was calculated using eq S3 (see SI) for TNP and 4-NP, respectively (Figure S22a,b; see SI).

The xerogel exhibits a high  $K_{SV}$  value and a remarkably low detection limit, indicating strong selectivity for TNP. The 3-D  $K_{SV}$  bar chart for all analytes suggests that rigorous quenching was only observed in the case of 4-NP and TNP, indicating high selectivity for respective analytes (Figure 7c). A kinetic study of the photoluminescence quenching was performed to understand how fast the material can detect TNP. Immediate equilibrium (within 20 s) was established after a drop in the luminescence intensity while performing a volume-dependent study (10, 100, and 200  $\mu$ L of 10 mM TNP solution) (Figure S23; see SI).

## Recyclability

As an efficient sensor, the probe compound should exhibit more or less similar sensitivity after multiple cycles. After each cycle of the sensing experiment, the suspension was collected and rinsed with water followed by the removal of the analyte. Then, the samples were kept in a vacuum oven for drying and prepared for use in the next cycle. After completing five consecutive cycles, no noticeable differences were observed in the quenching activity (Figure 7d). Compared with other benchmark materials, this xerogel shows good efficiency as a sensor probe (Table S5; see SI). To check the stability of the fluorophore compound, the FTIR analysis was carried out for pristine xerogel and the specimen after finishing the fifth cycle (Figure S24; see SI). The almost similar spectral observation reveals the retention of the local chemical environment with no deformity in the framework structure, which indicates its efficiency as a sensor probe for TNP detection.



**Figure 9.** (a)  $K_{SV}$  plot for NFT antibiotic sensing with lower concentration fitting (inset), (b) 3D- $K_{SV}$  bar diagram for all antibiotics, (c) redistribution of the orbital energy in the presence of TNP analytes (PET effect), and (d) HOMO–LUMO diagram for linker and all respective analytes to display feasible electron transfer pathway.

## RGB-Based Smart Detection and Analysis in Real Water Samples

Along with instrument-based (PL) sensing techniques, paperstrip-based approaches for the detection of analytes are very common in this field. Although the prepared paper-based test strips could achieve fluorescence-based visual detection for a respective analyte, the method may not meet anticipated standards in terms of precision or perceptiveness due to its reliance on unaided human vision, which is limited in its ability to discern minute variations in color. Hence, there is an obvious scope for the formation of portable devices that can work more efficiently without costly instruments. The RGB-based analysis via a smartphone presents a cost-effective, dependable technique for estimating the concentration of the TNP analyte. The method involves analyzing the color information obtained from the samples. The RGB values of the studied samples were acquired by utilizing a color analysis application (app) and capturing images with an Android smartphone. Figure 8a was captured for further detection, and each sample was analyzed using the app, depending on its red (R), green (G), and blue (B) ratios. The concentration ranging from 50 to 500  $\mu$ M was used for this TNP detection. With an increasing concentration, quenching of green luminescence was observed through consecutive vials. The G/B ratios were minutely scrutinized

through the app. The G/B ratio was decreased with increasing concentration of TNP, and the corresponding graph was plotted to calculate the lower detection limit. A linear fit with a good correlation coefficient of 0.9945 in the lower concentration range exhibits an LOD of 12.36 ppm. It dictates a sensitive, cost-effective smartphone-based easy quantification approach for the TNP analyte (Figure 8b).

To check the accuracy of the RGB-based detection method, the fluorescence spectroscopic method was introduced for correlation with the RGB-based detection. The recovery percentage was found within the range 93.8–95% for the fluorescence method, which is well matched with the RGBbased detection method (93.6–98%). This result suggests the quick detection of TNP sensing via the smartphone-based approach (Figure S25, eq S6, Tables S6 and S7; see SI).

TNP is very soluble in water, which can easily contaminate water bodies. As an effective sensor probe, detection of TNP in a real environment system is pivotal. Different concentrations of TNP were spiked into the mineral, tap, and river water samples. The TNP concentrations and recovery percentages for the samples are presented in Table S8. Overall studies showed TNP recovery values between 94.79 and 104.09%, whereas the relative standard deviation (RSD) values were between 0.25 and 5.32% (RSD = (SD/mean value)  $\times$  100). Low RSD values and

high recovery percentages along with analytical precisions suggest the sensor's potential to produce excellent recoveries for actual water samples.

#### **Antibiotic Sensing**

Four general classes of antibiotics that are frequently used in our daily life, i.e., chloramphenicol (CAP), sulfonamide based (SMZ, SDZ), nitroimidazoles (DTZ, RDZ, ODZ), and nitrofurans (NFT, FZD, NFZ), were utilized for sensing experiments. The quenching activities were monitored using fluorescence titration after gradual adding (up to 200  $\mu$ L) of all antibiotics  $(10^{-2} \text{ M concentration})$  into the xerogel suspension. Among all these antibiotics, nitrofuran-based antibiotics had a higher degree of quenching (QE > 95%). Importantly, the characteristic photoluminescence peaks of Tb\_TATMB show the highest (QE =  $\sim$ 99%) quenching response upon the addition of NFT. Little to moderate quenching effects were perceived for other antibiotics (QE ranging from 20 to 65%) (Figure S26a-i; see SI). The sensing activity for the NFT analyte was also performed for Eu TATMB and Eu-Tb TATMB xerogel. The QE for NFT was found to be 87% and 95% for Eu TATMB and EuTb TATMB, respectively. Furthermore, antibiotic sensing experiments were carried out using Tb\_TATMB gel as the sensor probe material (Figures S27 and S28; see SI). The quantitative analysis of NFT sensing was determined through the S–V equation (eq S2; see SI) A  $K_{SV}$  of  $1.4 \times 10^4 \text{ M}^{-1}$  was obtained from the respective S–V plot. The lower concentration range fitting of that plot shows linearity with a good correlation coefficient ( $R^2 = 0.9701$ ) (Figure 9a). The 3D  $K_{SV}$  bar diagram for all antibiotics can correlate with the upward bent nature of the S-V fitting curve with increasing concentrations of nitrofuran-based antibiotics (Figure 9b). The antibiotic NFT had the maximum quenching efficiency, thus prompting the subsequent selectivity test to focus exclusively on NFT. The selectivity toward NFT antibiotics was checked in the presence of other antibiotics. The degree of quenching was seen in the low to moderate range for other antibiotics. However, adding NFT into the suspension deliberately quenched the characteristic emission peak, suggesting selective sensing performance in the presence of other analytes. The characteristic emission peaks were diminished after adding NFT in each system followed by the addition of respective individual antibiotics (Figure S29a-f; see SI). An almost similar quenching efficiency was observed in the case of the individual system, which indicates selectivity for nitrofuran (NFT) based antibiotics (Figure S30; see SI). Equation S3 (see SI) was used to determine the detection limit of 65.25 ppb for the NFT analyte (Figure S31; see SI). The Tb\_TATMB xerogel material demonstrates high K<sub>SV</sub> with an exceptionally low detection limit, making it a highly effective sensor for detecting nitrofuran antibiotics. The observed findings for NFT sensing are comparable with other reported benchmark materials (Table S6; see SI). Furthermore, PL spectra were used to validate the ultrafast detection of NFT antibiotics using Tb TATMB as a sensor probe. The rapid stabilization of PL intensities ( $\sim 20$  s) with each volume addition to the xerogel suspension (10, 100, and 200  $\mu$ L of 10 mM NFT solution) proves the efficiency to detect NFT (Figure S32; see SI).

#### Recyclability

The sensing experiments were carried out for up to five consecutive cycles. After each cycle, the suspension mixture was thoroughly washed with water/acetone and kept in an oven for vacuum drying. After accomplishing each cycle, no appreciable changes were observed in quenching activity (Figure S33; see SI). The nearly identical FTIR spectral data before starting the first cycle and after completing the fifth cycle suggest the retention of a definite supramolecular core with intact chemical functionalities (Figure S34; see SI).

# Analysis in Real Water Samples and Thin Film-based Detection

The advent of antibiotics has proven to be advantageous in enhancing both human and animal well-being. However, they have also raised numerous environmental and food safety concerns. Because of the overutilization of antibiotics in hospitals, livestock practices contaminate ecosystems, including different sources of water bodies that may impact human health via the food chain. Hence, the detection of antibiotics in water samples is crucial. In real-world samples, nine different water samples were prepared to test the xerogel sensing behavior for NFT. Each of the three water samples (mineral, tap, and river) was spiked with different concentrations of NFT. Table S10 (see SI) displays the NFT concentrations and recovery percentages for the environmental water samples. The NFT recovery values ranged from 94.29 to 104.96% across all samples, with RSD (relative standard deviation) values ranging from 0.68 to 3.51  $(RSD = (SD/mean value) \times 100)$ . The probe exhibits low RSD values and high recovery percentages, indicating its capability to yield satisfactory recoveries and analytical precision when applied to real water samples.

An easy detection approach based on a thin film was accomplished for prompt sensing of the nitrofuran-based antibiotics. Poly(methyl methacrylate) (PMMA) and Tb\_TATMB xerogel were mixed in equal amounts in the DMF/toluene solvent combination. In a glass Petri dish, the above mixture was transferred and dried in a vacuum oven. To utilize it as a smart sensor probe, thin films were created by cutting them into rectangular pieces measuring roughly  $1 \times 2.5$  cm.

The photoluminescence behavior of the xerogel material was also unimpaired in the thin film state (Figure 8c). The green luminescence (upon exposure to UV source) was quenched after immersing it in NFT solution (10 mM). The durability of the prepared thin films was also checked through a recyclability test. After the first cycle, the film was washed multiple times with water and reused after drying in an oven (at 60 °C for 1 h). The luminescence activity was retained after the first cycle, which suggests the efficiency of sensor probe (Figure 8d).

### MECHANISM FOR NITROEXPLOSIVES AND NFT SENSING

A few experimental and theoretical investigations were carried out to elucidate the underlying factors contributing to the selective quenching of the characteristic emission peaks of Tb\_TATMB after the addition of corresponding analytes. In general, quenching of luminescence may happen through structural destruction of the framework, host–guest interaction via ground-state complex formation, and excited-state interactions, including electron transfer and energy transfer phenomena.<sup>64</sup>

Apart from this, the "inner filter effect" (IFE) can be a decisive factor for the selective quenching of intense green luminescence of Tb\_TATMB. The  $H_3$ TATMB linker acts as an antenna ligand that sensitizes the terbium ions via the energy transfer process and shows excellent luminescence behavior. During sensing experiments, analytes with similar absorbance bands compete with organic linkers to absorb the energy. This competition between the analyte and fluorophore probe interferes with this energy transfer mechanism.<sup>65</sup> Therefore, UV-vis spectra were recorded for all organic analytes and xerogel materials. Among all analytes, nitrophenol-based analytes (4-NP, 2,4-DNP, and TNP) show absorbance bands at ~330–450 nm. A sizable overlapping zone was observed with the excitation wavelength of xerogel and absorbance band of 4-NP, 2,4-DNP, and TNP (Figure S35; see SI). This phenomenon suggests that during excitation of the xerogel, the respective analyte acts as a filter to absorb the light sources and attune the emission intensity of Tb\_TATMB. It restricts the energy transfer phenomena from the ligand to the terbium ion, which is reflected in the quenching of the luminescence peak. Interestingly, among three nitrophenol-based analytes, the most effective spectral overlap was observed in case of 4-NP, but the quenching efficiency order follows the trend TNP > 4-NP > 2,4-DNP. This confirms that IFE is not the sole reason for quenching of the characteristic luminescence peak of the Tb\_TATMB. To mitigate the impact of the inner filter effect (IFE) on the reduction of fluorescence efficiencies, the IFE correction was performed using the Parker equation<sup>66,67</sup> and UV-titration experiment. The E<sub>observed</sub> and E<sub>corrected</sub> were obtained as 83.6 and 77.05% (eq S7, Table S11). Hence, the percentage of IFE was calculated to be around 7%, which may be involved in quenching the luminescence peak of the material. On the other hand, a similar spectral observation was found in FTIR spectra before and after completing the TNP sensing experiment, indicating retention of the local chemical environment (Figure S36; see SI). A significant deviation in the average lifetime value (412 to 13  $\mu$ s) before and after adding TNP was observed in time-resolved photoluminescence (TRPL) spectroscopy, which excluded the possibilities of static quenching (Figure S37, Table S12; see SI). Then, photoinduced electron transfer (PET) may be the driving force behind this rapid quenching phenomenon. Early reports exhibit that  $\Pi - \Pi$ stacking and H-bonding interactions play a crucial role in intermolecular electron-transfer processes.<sup>68</sup> The overall quenching performance of all organic analytes reveals that organic analytes with different functionalities, including carboxylic acid, amine, methyl, hydroxyl, and nitro, are involved in the sensing experiment. The high quenching was found in the presence of both nitro and hydroxyl groups in an analyte over the individual presence of the group in a moiety. The synergistic effect of these two functionalities enhances the electrostatic and hydrogen bonding, which results in selective quenching of hydroxyl containing nitroaromatics over other organic analytes.<sup>69</sup> The electron transfer can happen from photoexcited fluorophore donor to low-lying acceptor LUMO. The three nitro groups of TNP stabilize the LUMO energy level, and photoinduced electron transfer can easily occur from higher energy linker LUMO. The HOMO-LUMO gap of the linker and corresponding organic analytes was determined using density functional theory (DFT) calculations at the B3LYP/6-31+G(d,p) level to correlate this rationale.<sup>70</sup> The ligand has a higher LUMO energy level (-1.8876 eV) than that of TNP/2,4-DNP/4-NP (-4.0208/-3.6485/-2.7473 eV), suggesting that this difference in energy provides a valiant driving force for the transfer of excited electrons from the host to the guest. Among all analytes, the LUMO of TNP is the lowest, so it favors the most deliberate electron transfer from the linker (Figure S38; see SI). Importantly, the optimized structure and corresponding frontier orbitals (HOMO-LUMO) of interacting fragments

show an adequate reduction in energy compared to the free linker state (4.43 to 2.24 eV). After interaction with TNP, the LUMO got stabilized, which facilitates a more favorable electron transfer pathway. In addition, LUMO was observed to be localized on the TNP, thereby confirming the effective transfer of electrons from the excited state of the linker to the unoccupied orbital of the electron-deficient analyte. This result delineates quenching of characteristic luminescent peak of the Tb TATMB xerogel while adding TNP as analytes (Figure 9c). However, if it is solely related to the PET process, then the order of QE should follow a different trend. The QE for 4-NP was measured to be approximately 98%, which is higher than those of several other analytes such as NBA, DNB, and 3,5-DNBA. However, it was noted that the LUMO energy level was lower in the case of these three analytes. The above findings suggest that both IFE and PET may contribute to the quenching of the Tb TATMB characteristic emission peaks in the presence of nitroexplosives.

The quenching of the photoluminescence peak of the Tb\_TATMB xerogel after addition of NFT was further investigated. At first, FTIR spectral observation exhibits almost superimposable characteristics before and after NFT sensing that suggest the retention of chemical functionalities (Figure S39; see SI). UV-vis spectra of all antibiotics were acquired to examine the possibility of IFE. The most appreciable overlapping zone was observed with nitroimidazole antibiotics (DTZ, RDZ, ODZ) with the excitation wavelength of the Tb\_TATMB xerogel. However, this observation does not precisely align with the order of quenching efficiency (Figure S40; see SI). Therefore, the IFE cannot be seen as the sole determinant for this "turn-off" mechanism.

A considerable change in the average lifetime (412 to 180  $\mu$ s) before and after adding NFT ruled out the possibility of static quenching via ground-state complex formation (Figure S41, Table S13; see SI). Hence, long-range fluorescence resonance energy transfer (FRET) and short-range PET may influence the vigorous quenching of Tb TATMB characteristic emission peaks. Nitrofuran-based antibiotics with a 5-nitrofuran group can stabilize the corresponding analyte's LUMO. This facilitates the electron transfer from the electron-rich TATMB linker. This hypothesis was correlated using DFT calculations at the B3LYP/ 6-31+G (d,p) level. The electron transfer is readily feasible as the linker possesses higher energy LUMO (-2.04 eV) than the NFT analyte LUMO (e.g., -3.34 eV for NFT). However, upon examination of the order of quenching efficiency among all antibiotics, it would be inaccurate to attribute it solely to the PET mechanism. Although CAP had a lower energy LUMO (-2.95 eV) than the linker, the LUMO energy of CAP was seen to be in closer proximity to the LUMO energy levels of nitrofuran- and nitroimidazole-based antibiotics (Figure 9d). Still, it did not follow a similar order of quenching. Hence, longrange energy transfer may also take part in this luminescence "turn-off". The UV-vis spectroscopic study provides evidence of an overlap region between the absorbance band of the quencher and the emission spectra of the xerogel (Figure S42; see SI). This observation implies that the fluorescence resonance energy transfer (FRET) mechanism is also involved in the sensing process, leading to the observed "turn-off" response. The percentage of FRET efficiency was calculated to be 56% (see SI eq S8).

## **CONCLUSIONS**

In conclusion, the self-assembly process involving europium and terbium acetate in combination with a tripodal triazine coremediated carboxylic acid based gelator was employed successfully to accomplish the synthesis of a range of multifunctional CSGs with photochromic capabilities. The electron microscopic analysis revealed that the synthesized Tb\_TATMB and Eu\_TATMB show a flakelike morphology with pores, whereas EuTb\_TATMB exhibited a rock-shaped morphology. Tuning the stoichiometric ratio of metal salts gives rise to different photochromic supramolecular gels, and most importantly, a white light emissive gel has been synthesized. The photochromic gels were utilized in anticounterfeit applications by security stamping and artwork. Furthermore, Tb\_TATMB was used as a smart sensor probe for the selective detection of TNP and NFT antibiotics. The material exhibits exceptional sensitivity, efficiency, and reusability as potential options for detecting nitro compounds owing to their recyclability test, high  $K_{\rm SV}$  values (6.2 × 10<sup>4</sup> M<sup>-1</sup>, TNP; 1.4 × 10<sup>4</sup> M<sup>-1</sup>, NFT), and impressive detection limit (24.5 ppb for TNP and 64.25 ppb for NFT). A simple RGB-based smartphone-mediated detection procedure was established for TNP to correlate with real-time applicability. On the other hand, sensing NFT antibiotic compounds in different real water samples and thin film-based detection techniques increases the potency of the sensor.

## ASSOCIATED CONTENT

## **3** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaenm.3c00761.

<sup>1</sup>H NMR of the linker; solvent dependent photoluminescence (PL) study; pH-dependent PL study; leaching test (through PL spectra); lifetime experiments of linker and metallogels; rheological analysis of terbium and europium mediated gels; FESEM and EDS analysis of red and white light emitting gels; PXRD; stability test for anticounterfeit application; photoluminescence sensing study of Tb\_TATMB in the presence of different organic analytes; comparison table; PL sensing study of Tb\_TATMB in the presence of different antibiotics; LOD calculation; comparison table; recyclability; IFE correction; HOMO–LUMO gap of different analytes and linkers; and overlap between excitation and emission wavelength of Tb\_TATMB and absorbance band of antibiotics (PDF)

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#### **Author Contributions**

The project was designed by S.M., N.A., and D.S. The materials were synthesized and characterized by S.M. and N.A. S.M. performed the DFT calculation. The manuscript was written by S.M., N.A., and D.S. The final version of the work has received approval from all authors.

#### Notes

The authors declare no competing financial interest.

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