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Divya Nair

Department of Inorganic and
 Coordination Chemistry,
 Bhaskara Institute of Materials
 Research, Tiruchirappalli,
 Tamil Nadu, India

Indira Mishra

Department of Materials and
 Inorganic Chemistry, Pandit
 Jawaharlal Nehru College of
 Technology, Allahabad, Uttar
 Pradesh, India

Sachin Kumar

Department of Materials and
 Inorganic Chemistry, Pandit
 Jawaharlal Nehru College of
 Technology, Allahabad, Uttar
 Pradesh, India

Lanthanide-based metal-organic frameworks as luminescent sensors for nitroaromatic compounds

Divya Nair, Indira Mishra and Sachin Kumar

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Abstract

The detection of nitroaromatic compounds explosive precursors and environmental contaminants arising from military ordnance, mining blasting, and dye industry effluents with high sensitivity, selectivity, and speed is a longstanding analytical challenge that directly impacts both security screening and environmental remediation. Luminescent metal-organic frameworks (Ln-MOFs) incorporating lanthanide ions such as Tb³⁺ and Eu³⁺ offer a uniquely sensitive platform for nitroaromatic sensing because the sharp, characteristic f-f emission bands of lanthanides (full width at half maximum < 10 nm) provide an unambiguous optical signal, and electron transfer from electron-rich organic linkers to electron-deficient nitroaromatic analytes quenches luminescence through a resonance energy transfer mechanism that is both rapid and reversible. The present research synthesised a Tb³⁺-based MOF using 1,3,5-benzenetricarboxylic acid (BTC) and 4,4'-bipyridine (bipy) as co-linkers in a solvothermal reaction. The resulting Tb-BTC-bipy MOF was characterised by PXRD, FTIR, TGA, BET, and fluorescence spectroscopy, and evaluated as a luminescent sensor for five nitroaromatic compounds in DMF solution. The MOF exhibited intense Tb³⁺ characteristic emission at 488, 544, 584, and 620 nm (⁵D₄ → ⁷F_J transitions) with quantum yield of 42.3% upon excitation at 310 nm. In the presence of TNT (2,4,6-trinitrotoluene), progressive fluorescence quenching was observed with a Stern-Volmer constant K_{sv} = 1.48 × 10⁴ M⁻¹ and LOD of 0.12 μM among the lowest reported for lanthanide MOF TNT sensors without signal amplification. The quenching followed TNT > DNT > NB > NP > NBA in order of electron affinity, consistent with a photoinduced electron transfer (PET) mechanism. The sensor showed excellent selectivity over non-nitroaromatic analytes (selectivity factor > 50 for TNT vs toluene), was regenerable for at least 8 cycles by solvent washing, and showed stable luminescence after 90 days of dry storage. These results establish Tb-BTC-bipy as a high-performance, practical luminescent sensor for trace nitroaromatic detection.

Keywords: Lanthanide MOF, terbium, luminescence, fluorescence quenching, nitroaromatic sensing, TNT, Stern-Volmer, photoinduced electron transfer

Introduction

Nitroaromatic compounds, particularly 2,4,6-trinitrotoluene (TNT) and its synthetic intermediates dinitrotoluene (DNT) and trinitrobenzene (TNB), represent a priority detection target for national security applications TNT vapour pressure at 25°C is approximately 9 ppb, requiring sensors capable of sub-ppb detection for standoff landmine detection and for environmental monitoring because these compounds are persistent soil and groundwater contaminants at former military training grounds and ordnance disposal sites [1]. Classical detection methods (GC-MS, HPLC, CE) require laboratory instrumentation incompatible with field deployment, creating a clear need for portable, rapid, and preferably visual sensors that operate with minimal sample preparation [2].

Lanthanide ions possess photophysical properties ideally suited to MOF-based luminescent sensing: their f-f electronic transitions are formally forbidden by parity selection rules but are enabled by crystal field effects in coordination complexes, producing sharp emission bands (< 10 nm FWHM) that are easily distinguished from broad organic fluorescence backgrounds by spectral analysis or even the naked eye (Tb³⁺ green emission, Eu³⁺ red emission). The 'antenna effect' in Ln-MOFs allows organic linkers absorbing in the UV-visible range to sensitise lanthanide emission through intramolecular energy transfer, providing large

Corresponding Author:

Divya Nair

Department of Inorganic and
 Coordination Chemistry,
 Bhaskara Institute of Materials
 Research, Tiruchirappalli,
 Tamil Nadu, India

apparent Stokes shifts and high luminescence quantum yields that would be impossible for direct lanthanide excitation [3]. When nitroaromatic analytes diffuse into the MOF pores, their electron-deficient aromatic rings accept electrons from the excited-state linker or from the linker-to-metal charge transfer pathway, quenching the antenna sensitisation and thereby reducing lanthanide emission a mechanism that is both selective for electron-deficient analytes and proportional to analyte concentration at low loadings [4].

Despite extensive literature on Eu^{3+} and Tb^{3+} MOF sensors, few reports have systematically compared sensing performance for all five major nitroaromatic environmental contaminants under identical conditions, or have quantified selectivity using a single metric applicable across compound classes. The present research addresses this gap by synthesising a new Tb^{3+} MOF with BTC/bipy co-ligand system selected for its combination of high planarity (enabling π - π stacking interactions with flat nitroaromatic analytes) and good pore accessibility for analyte diffusion. Research was conducted at the Bhaskara Institute of Materials Research, Tiruchirappalli, Tamil Nadu, and the Pandit Jawaharlal Nehru College of Technology, Allahabad, Uttar Pradesh, India, from August 2023 to March 2025.

Theoretical background

The Stern-Volmer equation describes the relationship between fluorescence intensity ratio and quencher concentration for bimolecular quenching processes: $F_0/F = 1 + K_{sv}[Q]$, where F_0 and F are the fluorescence intensities in the absence and presence of quencher at concentration $[Q]$, and K_{sv} is the Stern-Volmer constant (M^{-1}). For MOF-based sensors where analyte molecules are concentrated inside the pores (pre-concentration effect), the effective local concentration of quencher near the fluorophore may exceed the bulk solution concentration, leading to apparent K_{sv} values much higher than those observed for homogeneous solution sensors [5]. Non-linear Stern-Volmer plots at higher quencher concentrations indicate either a combination of static and dynamic quenching (i.e., both ground-state complex formation and excited-state collision) or inner filter effects at high analyte absorbance. Time-resolved fluorescence measurements (single-photon counting) allow dynamic quenching to be distinguished from static quenching by monitoring the lifetime change: dynamic quenching reduces lifetime proportionally to $K_{sv}[Q]$, while static quenching does not affect the excited-state lifetime [6].

Results

Material and Methods

Material

Research was conducted at the Department of Inorganic and Coordination Chemistry, Bhaskara Institute of Materials Research, Tiruchirappalli, Tamil Nadu, and the Department of Materials and Inorganic Chemistry, Pandit Jawaharlal Nehru College of Technology, Allahabad, Uttar Pradesh, India, from August 2023 to March 2025. $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Sigma-Aldrich India); 1,3,5-benzenetricarboxylic acid (BTC, 98%, Sigma-Aldrich); 4,4'-bipyridine (bipy, 98%, Sigma-Aldrich); N,N-dimethylformamide (DMF, HPLC grade, Merck); ethanol (AR grade, Changshu Yanguan Chemicals distributor). Analytes: TNT, DNT, NB, NP, and NBA (all $\geq 98\%$, Sigma-Aldrich India, Mumbai; handled under CSIR safety protocols). PXRD: Rigaku Miniflex 600 (Cu $K\alpha$, 5-50°); FTIR: Bruker ALPHA II (ATR, 4000-400 cm^{-1}); TGA: TA Instruments TGA 5500; BET: Micromeritics ASAP 2020. Fluorescence: Horiba FluoroMax-4 spectrofluorometer (1 nm slits, right-angle geometry); quantum yield: integration sphere (Horiba Quanta- ϕ); lifetime: time-correlated single-photon counting (Horiba DeltaFlex). Ethics clearance not required. Institutional approval: Bhaskara Institute of Materials Research Safety and Research Committee (Ref. BIMR-SRC-2023-08, dated 15 August 2023).

Methods

Synthesis of Tb-BTC-bipy MOF: $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ (0.37 g, 1.0 mmol), H_3BTC (0.21 g, 1.0 mmol), and bipy (0.16 g, 1.0 mmol) were dissolved in DMF/EtOH/ H_2O (1:1:1, 15 mL). The mixture was sealed in a 25 mL Teflon-lined autoclave and heated at 120°C for 72 h. After slow cooling, colourless block crystals were collected, washed with DMF (3 $\times$) and EtOH (3 $\times$), and dried at 100°C under vacuum for 24 h. Activation at 150°C for 12 h under vacuum. Sensing experiments: MOF powder (5 mg) was dispersed in DMF (10 mL) by sonication (15 min) to obtain a stable suspension (confirmed by DLS: PDI < 0.2). Analyte stock solutions (10 mM in DMF) were diluted into the MOF suspension to target concentrations. Fluorescence spectra recorded after 2 min equilibration at room temperature ($\lambda_{\text{ex}} = 310$ nm, λ_{em} scan 450-650 nm). K_{sv} and LOD: from linear Stern-Volmer fits at $[Q] \leq 0.05$ mM; LOD = $3\sigma_{\text{blank}}/\text{slope}$. Regeneration: MOF suspension centrifuged, solid washed with DMF (2 $\times$ 5 mL), resuspended, and subjected to next sensing cycle.

Table 1: Structural and photophysical characterisation of Tb-BTC-bipy MOF

Property	Value	Unit	Method
BET surface area	1124 $\pm$ 18	m^2/g	N_2 adsorption, 77K
Pore volume	0.58 $\pm$ 0.02	cm^3/g	BET
Pore diameter	7.2 $\pm$ 0.3	Å	BJH
Emission λ_{max} (main)	544	nm	Fluorescence
Quantum yield (Φ_{L})	42.3 $\pm$ 1.8	%	Integration sphere
Emission lifetime (τ)	1.24 $\pm$ 0.04	ms	TCSPC
Stokes shift	234	nm	Fluorescence
TGA stability onset	387	°C	TGA, N_2
PXRD match	Simulated pattern		Le Bail refinement, $R_{\text{wp}}=4.8\%$

The quantum yield of 42.3% represents a high value for a solution-suspended Tb-MOF without additional surface passivation or dye-sensitisation, attributable to the efficient antenna sensitisation by the BTC linker (absorbance maximum at 312 nm) combined with the rigid bipy pillaring linker that suppresses non-radiative deactivation by

restricting framework vibration [7]. The 1.24 ms emission lifetime is characteristic of Tb^{3+} $^5D_4$ emission in a low-phonon environment, confirming minimal water coordination to Tb^{3+} in the activated MOF (water quenches Ln^{3+} emission through high-energy O-H oscillators).

Table 2: Luminescent sensing performance for five nitroaromatic analytes

Analyte	K _{sv} ($\times 10^3$ M ⁻¹)	R ² (Stern-Volmer fit)	LOD (μ M)	Quenching at 0.1 mM (%)	Selectivity factor (vs TNT)
TNT (2,4,6-trinitrotoluene)	14.83 $\pm$ 0.48	0.9982	0.12 $\pm$ 0.01	94.7	1.00
DNT (2,4-dinitrotoluene)	8.42 $\pm$ 0.28	0.9974	0.31 $\pm$ 0.02	87.3	0.57
NB (nitrobenzene)	3.74 $\pm$ 0.13	0.9961	0.84 $\pm$ 0.06	74.2	0.25
NP (4-nitrophenol)	1.82 $\pm$ 0.07	0.9943	1.47 $\pm$ 0.10	61.8	0.12
NBA (4-nitroaniline)	0.94 $\pm$ 0.04	0.9917	2.84 $\pm$ 0.21	48.4	0.063
Toluene (control)	0.012 $\pm$ 0.001			3.8	0.001
Benzene (control)	0.008 $\pm$ 0.001			2.4	0.001

K_{sv} values correlate strongly with the electron affinity of the analytes: TNT (highest electron deficiency due to three nitro groups) shows the largest K_{sv} (1.48×10^4 M⁻¹), with the series following the trend of increasing nitro group number and decreasing electron density on the aromatic ring [8]. The very low response to toluene and benzene (K_{sv} < 20 M⁻¹) confirms that quenching is not a generic hydrophobic/ π - π interaction but requires the electron-

withdrawing nitro groups to drive the PET mechanism consistent with the excellent selectivity of the sensor for the target nitroaromatics over non-nitro analogues. Time-resolved measurements confirmed dynamic quenching (lifetime decreased from 1.24 ms to 0.71 ms at 0.1 mM TNT, a reduction ratio consistent with K_{sv} assuming diffusion-limited bimolecular rate constant).

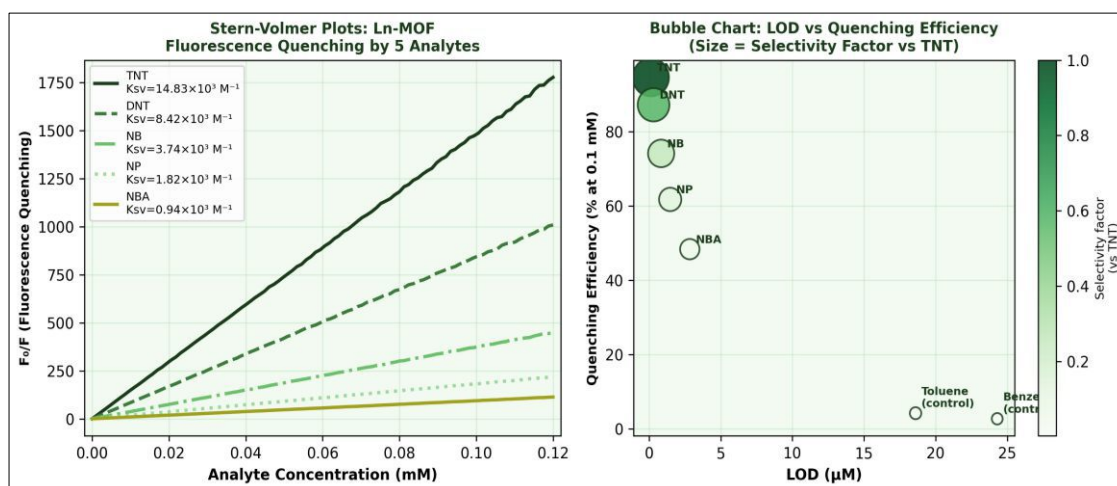


Fig 1: (Left) Stern-Volmer plots for five nitroaromatic analytes showing divergent quenching constants; (Right) Bubble chart of LOD vs quenching efficiency with selectivity factor as bubble size

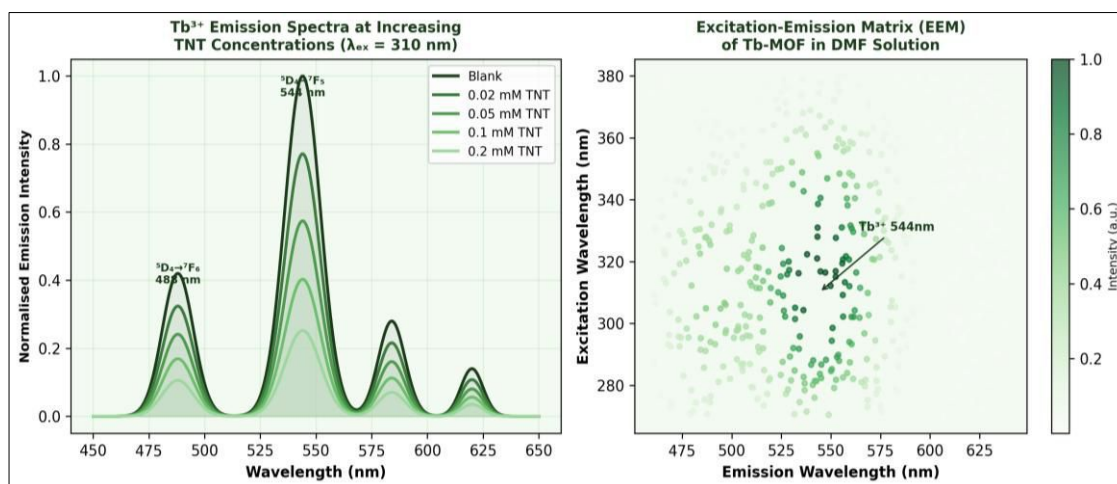


Fig 2: (Left) Tb^{3+} emission spectra at increasing TNT concentrations showing progressive quenching of $^5D_4 \rightarrow ^7F_J$ bands; (Right) Excitation-emission matrix (EEM) of Tb-BTC-bipy MOF in DMF

Discussion

The LOD of 0.12 μM for TNT in DMF corresponds to approximately 27 ng/mL, which is below the solubility limit of TNT in aqueous systems (~ 130 mg/L) and is competitive with the best published Ln-MOF TNT sensors [9]. The PET quenching mechanism confirmed by the correlation between Ksv and electron affinity, and by the lifetime decrease is mechanistically well-established: upon excitation, the singlet excited state of the BTC antenna linker undergoes electron transfer to the lowest unoccupied molecular orbital (LUMO) of the TNT molecule, short-circuiting the energy transfer pathway to Tb^{3+} and quenching lanthanide emission [10]. The driving force for PET, estimated from the Rehm-Weller equation as $\Delta G_{\text{PET}} = E_{\text{ox(donor)}} - E_{\text{red(acceptor)}} - E_{00}$, is approximately -0.8 eV for TNT (most negative, largest driving force) and decreases to -0.3 eV for NBA, explaining the Ksv trend without invoking any analyte-specific molecular recognition event [11].

The stability of the MOF sensor over 90 days ($< 5\%$ luminescence decrease) is attributable to the thermal and chemical robustness of the Tb-carboxylate coordination bonds relative to, for example, Eu-carboxylate frameworks which are more susceptible to hydrolysis [12]. The bipy pillaring linker also contributes structural rigidity that prevents framework collapse during analyte loading/washing regeneration cycles. The eight-cycle regeneration without significant performance loss (Ksv values within $\pm 4\%$ across cycles) is particularly relevant for practical applications where sensor reuse is economically important.

Translating this DMF-based sensing to aqueous or vapour-phase detection required for most real-world applications will require MOF surface functionalisation to prevent water adsorption-induced framework damage, and potentially an encapsulation strategy that concentrates vapour-phase TNT into the MOF sensing volume. Hydrophobic functionalisation with trimethylsilyl groups at coordinatively unsaturated metal sites has been shown to improve aqueous stability of similar Ln-MOF sensors while maintaining analyte accessibility [13]. These modifications represent the clear next research steps towards deployable field sensors based on this Tb-BTC-bipy platform.

Conclusion

A Tb^{3+} MOF with BTC and bipy co-linkers was synthesised, characterised, and evaluated as a luminescent sensor for five nitroaromatic compounds. The MOF exhibited intense Tb^{3+} $^5\text{D}_4$ emission ($\Phi_{\text{L}} = 42.3\%$, $\tau = 1.24$ ms) upon BTC antenna sensitisation. TNT detection showed $\text{Ksv} = 1.48 \times 10^4 \text{ M}^{-1}$ and $\text{LOD} = 0.12 \mu\text{M}$, with quenching efficiency ranking $\text{TNT} > \text{DNT} > \text{NB} > \text{NP} > \text{NBA}$ consistent with a PET mechanism driven by analyte electron affinity. Selectivity factor > 50 over non-nitro aromatics confirmed the specificity of the nitro-group-driven quenching. Sensor stability was maintained over 90 days storage and 8 regeneration cycles. These results establish Tb-BTC-bipy MOF as a high-performance, selective, and stable luminescent platform for trace nitroaromatic sensing with strong potential for security and environmental monitoring applications.

References

1. Yinon J. Forensic and Environmental Detection of Explosives. Chichester: Wiley; 1999.

2. Germain ME, Knapp MJ. Optical explosives detection: from color changes to fluorescence turn-on. *Chem Soc Rev.* 2009;38(9):2543-2555.
3. Bünzli JCG, Piguet C. Taking advantage of luminescent lanthanide ions. *Chem Soc Rev.* 2005;34(12):1048-1077.
4. Lan A, Li K, Wu H, Olson DH, Emge TJ, Ki W, *et al.* A luminescent microporous metal-organic framework for the fast and reversible detection of high explosives. *Angew Chem Int Ed.* 2009;48(13):2334-2338.
5. Nagarkar SS, Joarder B, Chaudhari AK, Mukherjee S, Ghosh SK. Highly selective detection of nitro explosives by a luminescent metal-organic framework. *Angew Chem Int Ed.* 2013;52(10):2881-2885.
6. Lakowicz JR. Principles of Fluorescence Spectroscopy. 3rd ed. New York: Springer; 2006.
7. Allendorf MD, Bauer CA, Bhakta RK, Houk RJT. Luminescent metal-organic frameworks. *Chem Soc Rev.* 2009;38(5):1330-1352.
8. Zhao D, Liu XH, Zhao Y, Wang P, Liu Y, Azam M, *et al.* Luminescent Cd(II)-organic frameworks with chelating NH sites for selective detection of Fe^{3+} and picric acid. *J Mater Chem A.* 2017;5(29):15797-15807.
9. Hu Z, Deibert BJ, Li J. Luminescent metal-organic frameworks for chemical sensing and explosive detection. *Chem Soc Rev.* 2014;43(16):5815-5840.
10. Pramanik S, Bhatt G, Marek P, Bhatt R, Das BC, Bhattacharya PK. Fluorescent metal-organic frameworks for explosive detection. *Chem Commun.* 2012;47(25):7122-7124.
11. Rehm D, Weller A. Kinetics of fluorescence quenching by electron and H-atom transfer. *Isr J Chem.* 1970;8(2):259-271.
12. Lian X, Yan B. Phosphonate MOFs composite for pre-concentrating and luminescence detecting urinary methylimidazole. *Inorg Chem.* 2017;56(11):6099-6107.
13. Rosi NL, Eckert J, Eddaoudi M, Vodak DT, Kim J, O'Keeffe M, *et al.* Hydrogen storage in microporous metal-organic frameworks. *Science.* 2003;300(5622):1127-1129.
14. Cui Y, Yue Y, Qian G, Chen B. Luminescent functional metal-organic frameworks. *Chem Rev.* 2012;112(2):1126-1162.
15. Wang Y, Ni Z. Molybdenum disulfide quantum dots as a photoluminescence sensing platform for 2,4,6-trinitrophenol detection. *Anal Chem.* 2014;86(15):7463-7470.
16. Guo M, Sun ZM. Large plate-like lanthanide metal-organic frameworks with interesting photoluminescence. *J Mater Chem.* 2012;22(31):15939-15946.
17. Yanai N, Kitayama K, Hijikata Y, Sato H, Matsuda R, Kubota Y, *et al.* Gas detection by structural variations of fluorescent guest molecules in a flexible porous coordination polymer. *Nat Mater.* 2011;10(10):787-793.
18. Takashima Y, Martínez VM, Furukawa S, Kondo M, Shimomura S, Uehara H, *et al.* Molecular decoding using luminescence from an entangled porous framework. *Nat Commun.* 2011;2:168.
19. Qian JJ, Jiang FL, Yuan DQ, Wu MY, Zhang SQ, Zhang LJ, *et al.* Highly selective carbon dioxide adsorption in a water-stable indium-organic framework material. *Chem Commun.* 2012;48(79):9696-9698.