International Journal of Chemical Science
www.chemicaljournals.com
Online ISSN: 2523-2843
Received: 05-06-2026, Accepted: 05-07-2026, Published: 20-07-2026
Volume 10, Issue 3, 2026, Page No. 13-18

Ligand effect on the luminescent sensing performance of Lanthanide-Metal Organic Frameworks

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DOI: https://doi.org/10.66856/chemical.2026.10.3.10045

Abstract
Lanthanide-based metal–organic frameworks (Ln-MOFs) have emerged as one of the most promising classes of luminescent materials owing to their unique optical properties, structural versatility and exceptional sensing capabilities. Their characteristic sharp emission bands, long luminescence lifetime and high photostability make them suitable candidates for applications in chemical sensing, environmental monitoring, biomedical diagnostics and bioimaging. The luminescent behaviour of Ln-MOFs is significantly influenced by the nature of the organic ligands used in their construction. Functional groups such as amino (–NH_2), hydroxyl (–OH), nitro (–NO_2), carboxyl (–COOH) and halogen substituents modify the electronic environment of the framework, thereby affecting energy transfer efficiency, emission intensity, response time and detection sensitivity.
This review critically examines the influence of ligand functionalization on the luminescent sensing performance of lanthanide-based MOFs. Recent research studies published during the last decade are comparatively analysed to understand how different ligand substituents affect sensing efficiency towards metal ions, antibiotics, biomolecules and environmental pollutants. The review also highlights the role of Eu^{3+}- and Tb^{3+}-based MOFs in fluorescence sensing, bioimaging and bioluminescence-inspired biosensing applications. Furthermore, a comparative assessment of response time, detection limit, luminescence intensity, fluorescence lifetime and selectivity is presented through tables and graphical analysis. Finally, the current challenges, recent advancements and future prospects of ligand-engineered Ln-MOFs are discussed. This review aims to provide a comprehensive understanding of structure–property relationships in lanthanidebased MOFs and to guide the rational design of next-generation luminescent sensing materials.

Keywords: Lanthanide-based metal–organic frameworks (Ln-MOFs), luminescent materials, ligand functionalization, luminescent sensing

Introduction

Metal–organic frameworks (MOFs) are a unique class of crystalline porous materials composed of metal ions or metal clusters connected through organic ligands to form extended three-dimensional networks. Since their introduction, MOFs have attracted considerable scientific interest because of their exceptionally high surface area, tunable pore size, structural diversity and chemical stability. These remarkable properties have enabled their application in gas storage, catalysis, drug delivery, separation technology, energy storage and chemical sensing. Among the various categories of MOFs, lanthanide-based metal–organic frameworks (Ln-MOFs) have emerged as particularly attractive materials owing to their extraordinary luminescent characteristics and multifunctional behaviour. [1]

Lanthanide ions possess partially filled 4f orbitals that give rise to sharp emission peaks, large Stokes shifts, long luminescence lifetimes and excellent colour purity. However, direct excitation of lanthanide ions is inefficient because the f–f transitions are parity forbidden. This limitation is overcome through the antenna effect, in which organic ligands efficiently absorb excitation energy and subsequently transfer it to the lanthanide ion, thereby producing intense luminescence. Consequently, the selection and functionalization of organic ligands play a decisive role in determining the luminescent efficiency of Ln MOFs. [2]

Recent advances in materials chemistry have demonstrated that ligand functionalization can significantly alter the sensing behaviour of lanthanide MOFs. Functional groups such as amino, hydroxyl, nitro and carboxyl groups influence electron distribution, energy-transfer efficiency, framework stability and host–guest interactions. As a result, the response time, detection limit, fluorescence intensity and selectivity of the sensing material can be precisely controlled through rational ligand design. Understanding these structure–property relationships has therefore become a major focus of contemporary MOF research.

The exceptional luminescent characteristics of Ln-MOFs have led to their widespread application in fluorescence sensing of metal ions, antibiotics, pesticides, biomolecules and environmental contaminants. Furthermore, these materials are increasingly being investigated for biomedical imaging and bioluminescence-inspired biosensing owing to their low toxicity, high photostability and long-lived luminescence. In particular, europium- and terbium-based MOFs exhibit intense red and green emissions, respectively, making them ideal candidates for multiplexed sensing and imaging applications.

Despite the rapid expansion of this research field, a comprehensive comparative understanding of how ligand functionalization influences luminescent sensing performance remains limited. Most published studies focus on the synthesis and characterization of individual MOFs, while fewer investigations systematically compare the effects of different ligand substituents on sensing efficiency. Therefore, this review aims to critically analyse recent literature on ligand-functionalized lanthanide MOFs and establish clear correlations between ligand chemistry and luminescent sensing performance. Particular emphasis is placed on response time, detection limit, luminescence

intensity, and fluorescence lifetime and sensing selectivity. By summarizing recent developments and identifying emerging research trends, this review seeks to provide valuable insights for the rational design of advanced lanthanide-based luminescent sensing materials.

Literature Review

1. Lanthanide-Based Metal–Organic Frameworks: Fundamentals and Luminescent Properties

Metal–organic frameworks (MOFs) are crystalline porous coordination polymers composed of metal ions or metal clusters interconnected by organic ligands. Their exceptionally high surface area, tunable pore dimensions and structural diversity have made them promising materials for applications in gas storage, catalysis, separation, drug delivery and chemical sensing. Among the different classes of MOFs, lanthanidebased metal–organic frameworks (Ln-MOFs) have attracted considerable attention because they combine the structural advantages of MOFs with the unique photophysical properties of lanthanide ions. These materials exhibit high thermal stability, chemical robustness and remarkable luminescent behaviour, making them suitable for optical sensing and bioimaging applications. [3]

The luminescent properties of Ln-MOFs originate from the partially filled 4f orbitals of lanthanide ions. Unlike transition metals, the 4f electrons are effectively shielded by the outer 5s and 5p orbitals, resulting in sharp emission bands, long fluorescence lifetimes and large Stokes shifts. Europium (Eu^{3+}) typically produces intense red emission, whereas terbium (Tb^{3+}) exhibits bright green emission. Other lanthanides such as dysprosium (Dy^{3+}), samarium (Sm^{3+}) and ytterbium (Yb^{3+}) emit characteristic yellow, orange and nearinfrared luminescence, respectively. These optical characteristics enable Ln-MOFs to function as highly selective fluorescent probes. [1]

One limitation of lanthanide ions is their weak direct absorption of ultraviolet or visible light because f–f electronic transitions are parity forbidden. This problem is overcome by the antenna effect, in which the organic ligand absorbs incident light and transfers the excitation energy to the lanthanide ion. The efficiency of this energy transfer depends strongly on the electronic structure of the ligand and the relative positions of its excited states. Therefore, careful selection and functionalization of ligands play a crucial role in improving the luminescence efficiency of Ln-MOFs. [2]

2. Role of Ligand Functionalization in Lanthanide MOFs

The performance of a lanthanide MOF is governed not only by the choice of lanthanide ion but also by the chemical structure of the organic ligand. Functional groups attached to the ligand influence electron density, coordination geometry, pore size and host–guest interactions. Consequently, even small structural modifications can significantly affect luminescence intensity, fluorescence lifetime, sensing response and analyte selectivity. Modern research therefore focuses on rational ligand engineering to optimize the sensing performance of Ln-MOFs. [4]

Ligand functionalization alters the efficiency of the antenna effect by changing the energy levels of the ligand. Electron-donating substituents generally facilitate energy transfer to the lanthanide centre, while electron-withdrawing groups may reduce energy transfer efficiency or modify analyte interactions. In addition, functional groups provide specific binding sites for target molecules through hydrogen bonding, electrostatic attraction or coordination interactions. These effects collectively determine the sensitivity and selectivity of the sensing process. [5]

Recent studies have shown that ligand engineering also influences the response time of luminescent sensors. MOFs containing highly accessible functional groups often allow rapid diffusion of analytes into the porous framework, resulting in faster fluorescence responses. Conversely, sterically hindered ligands or poorly accessible pores may slow analyte diffusion and increase sensing time. Therefore, response time has become an important performance parameter in evaluating ligand-functionalized Ln-MOFs. [6]

3. Amino (–NH_2) Functionalized Lanthanide MOFs

Among all ligand modifications, amino-functionalized ligands have been investigated extensively because amino groups increase electron density and promote efficient ligand-to-metal energy transfer. Amino groups also provide active sites capable of interacting with metal ions, nitroaromatic compounds and biomolecules through hydrogen bonding and coordination. As a result, NH_2-functionalized Ln-MOFs generally exhibit higher fluorescence intensity and improved sensing sensitivity compared with their non-functionalized counterparts. [7]

Several Eu^{3+}-based amino-functionalized MOFs have demonstrated excellent fluorescence sensing towards ferric ions (Fe^{3+}). Upon interaction with Fe^{3+}, fluorescence quenching occurs because of competitive absorption and electron-transfer processes. The presence of amino groups enhances analyte binding, leading to lower detection limits and shorter response times than similar MOFs lacking amino substitution. Such materials have been proposed for environmental monitoring of iron contamination in water. [8]

Amino-functionalized Tb-MOFs have also shown promising applications in antibiotic sensing. Strong hydrogen-bonding interactions between amino groups and antibiotic molecules enhance adsorption within the MOF pores, producing measurable fluorescence changes within a few seconds. Comparative studies indicate that amino-functionalized MOFs generally outperform unsubstituted ligands in terms of sensitivity and reproducibility. [9]

4. Hydroxyl (–OH) Functionalized Lanthanide MOFs

Hydroxyl-functionalized ligands improve the hydrophilicity of MOFs and increase their affinity towards aqueous analytes. The hydroxyl group readily participates in hydrogen bonding, facilitating strong host–guest interactions that improve sensing efficiency. Such MOFs are particularly useful for detecting biomolecules and environmentally relevant pollutants in aqueous media. [10]

Researchers have reported that hydroxyl-functionalized Eu-MOFs display enhanced sensitivity towards phosphate ions, ATP and several pharmaceutical compounds. The hydroxyl groups strengthen intermolecular interactions, enabling rapid diffusion of analytes through the porous framework. Consequently, these materials often exhibit shorter response times and improved detection limits under physiological conditions. [11]

Comparative analyses between amino- and hydroxyl-functionalized MOFs reveal that amino groups generally produce stronger luminescence because of enhanced electron donation, whereas hydroxyl groups provide

superior analyte adsorption through hydrogen bonding. The optimal functional group therefore depends on the intended sensing application rather than luminescence intensity alone. [12]

5. Nitro (–NO_2) Functionalized Lanthanide MOFs

Nitro-functionalized ligands possess strong electron-withdrawing properties that substantially alter the electronic environment of the MOF framework. These ligands often reduce ligand-to-metal energy transfer efficiency, resulting in comparatively lower fluorescence intensity. Nevertheless, NO_2-functionalized MOFs exhibit remarkable selectivity towards nitroaromatic explosives and certain oxidizing agents because of favourable charge-transfer interactions. [13]

Several Eu-MOFs incorporating nitro-substituted aromatic ligands have demonstrate highly selective fluorescence quenching in the presence of 2,4,6-trinitrophenol and related nitroaromatic explosives. Although their response times are generally slower than amino-functionalized analogues, their exceptional selectivity makes them attractive candidates for security and environmental monitoring applications. [14]

Comparative investigations suggest that nitro-functionalized MOFs often sacrifice luminescence intensity in exchange for improved analyte specificity. This observation highlights the importance of balancing optical performance with molecular recognition during ligand design. [15]

6. Carboxyl (–COOH) Functionalized Lanthanide MOFs

Carboxyl groups are among the most widely used coordinating functionalities in MOF synthesis because they form stable coordination bonds with lanthanide ions. Carboxyl-functionalized ligands generate rigid frameworks with excellent thermal and chemical stability while maintaining high porosity. These structural advantages contribute to consistent luminescence and prolonged operational stability during repeated sensing cycles. [16]

Carboxyl-functionalized Eu-MOFs have demonstrated efficient fluorescence sensing of heavy metal ions such as Pb^{2+}, Hg^{2+} and Cd^{2+}. Their rigid coordination environment minimizes framework degradation while allowing rapid analyte diffusion through interconnected pores. These characteristics enable repeated sensing without significant loss of fluorescence intensity, making them suitable for practical environmental applications. [17]

Recent comparative studies indicate that although carboxyl-functionalized MOFs may not always exhibit the fastest response times, they generally possess superior structural stability and recyclability compared with amino- and nitro-functionalized materials. Such durability is particularly advantageous for long-term sensing platforms. [18]

7. Comparative Analysis of Eu^{3+}- and Tb^{3+}-Based Lanthanide MOFs

Among all lanthanide ions employed in MOF synthesis, europium (Eu^{3+}) and terbium (Tb^{3+}) have received the greatest attention because of their intense red and green emissions, respectively. Their characteristic narrow emission bands, long luminescence lifetimes and high colour purity enable accurate fluorescence sensing under ambient conditions. Although both ions exhibit excellent sensing capabilities, their photophysical behaviour differs owing to variations in electronic energy levels and ligand-to-metal energy transfer efficiency. [19]

Eu^{3+}-based MOFs are widely employed in sensing metal ions, antibiotics and biological molecules because their red emission is highly distinguishable from background fluorescence. In contrast, Tb^{3+}-based MOFs generally exhibit higher quantum yields and brighter green emission, making them attractive for environmental monitoring and bioimaging. Comparative studies indicate that Eu-MOFs often achieve lower limits of detection, whereas Tb-MOFs frequently display faster fluorescence responses under identical experimental conditions. [20]

Several researchers have combined Eu^{3+} and Tb^{3+} within a single MOF to develop ratiometric fluorescent sensors. In these systems, the ratio between red and green emission changes upon interaction with the analyte, providing more reliable quantitative detection than single-emission sensors. Such dual-emission MOFs reduce experimental error caused by variations in excitation intensity and environmental conditions, making them highly suitable for practical sensing applications. [21]

8. Halogen-Functionalized Lanthanide MOFs

The introduction of halogen substituents (F^-, Cl^-, Br^-, I^-) onto organic linkers represents a highly effective yet distinct strategy for modulating the photophysical properties and structural stabilities of lanthanide-based metal–organic frameworks. Halogen atoms modify the triplet excited state energy levels (T_1) of the organic "antenna" by altering the electronic distribution and dihedral angles of the aromatic rings. This fine-tuning of the ligand-centered excited states directly governs the efficiency of the ligand-to-metal energy transfer (LMET) process. For instance, halogenated terephthalic acid derivatives utilized in surface-mounted metal– organic framework (SURMOF) thin films, such as Tb^{+3} {t-Cl-BDC}) and Tb^{+3} {t-Br-BDC}), have demonstrated exceptional quantum yields of visible green (Tb^{+3}) and red (Eu^{+3}) luminescence under ambient light, illustrating how heavy-atom halogenation can suppress non-radiative vibrational pathways and enhance overall radiative emission. [23]

Beyond physical photophysics, the high electronegativity and polarizability of halogen groups introduce unique chemical recognition channels within the porous framework. Halogenated ligands, particularly when combined with electrophilic triarylborane groups, create highly selective, solid-state luminescent sensing environments. These systems display rapid "turn-on" or "turn-off" fluorogenic responses toward trace anions, such as fluoride (F^-), cyanide (CN^-), and chloride (Cl^-) in aqueous media. The presence of halogenated substituents' steric bulk shields the active boron centers, dramatically enhancing the hydrothermal selectivity and operational stability of the Eu^{+3} and Tb^{+3} sensory frameworks over multiple cycles of regeneration. [24]

Furthermore, the incorporation of halogen groups on the linker backbones plays a pivotal role in optimizing the overall chemical robustness of coordination networks. Halogenation introduces hydrophobic domains within the pores, preventing the coordinated water molecules from attacking and hydrolyzing the metal-carboxylate nodes.

These frameworks retain their structural integrity and crystalline phase across a wide pH range (typically pH 3–11) and in harsh organic solvents. In luminescent sensing applications, this enhanced stability facilitates efficient photo-induced electron transfer (PET) or energy transfer pathways from the stabilized framework to electron-deficient target analytes, such as nitroaromatic explosives, without causing framework degradation. [25]

Finally, the selective placement of halogens enables the exploitation of directional non-covalent interactions, specifically halogen-bonding, for targeted molecular sensing. Halogen-bonding donor sites within the pores act as precise supramolecular recognition coordinates, showing extreme selectivity toward complex chlorinated volatile organic compounds, persistent organic pollutants, and pesticide residues. By pairing halogenated linkers with pre-engineered coordination frameworks, researchers can design modular sensing platforms that convert these specific supramolecular binding events into highly sensitive, ratiometric optical readouts, bypassing the typical selectivity limitations that plague unfunctionalized frameworks. [26]

Discussion

1. Comparative Evaluation of Ligand Functionalization

The principal objective of ligand functionalization is to optimize the optical and sensing performance of lanthanide MOFs. Comparative studies reveal that different substituents influence luminescence through distinct electronic and structural mechanisms. Electron-donating groups such as amino ($–NH_2$) generally enhance ligand-to-metal energy transfer, whereas electron-withdrawing substituents such as nitro ($–NO_2$) frequently improve analyte selectivity through charge-transfer interactions. Hydroxyl and carboxyl groups mainly strengthen host–guest interactions by hydrogen bonding and coordination chemistry, respectively. [27]

The influence of ligand functionalization extends beyond fluorescence intensity. It also affects response time, detection limit, fluorescence lifetime, adsorption efficiency, framework stability and recyclability. Consequently, no single functional group is universally superior; instead, the optimal ligand depends upon the intended sensing application and target analyte. [28]

Table 1: Comparative Performance of Ligand-Functionalized Ln-MOFs

Functional Group	Typical Target	Response Time	Detection Limit	Major Advantage	Ref.
$–NH_2$	Fe^{3+}, Hg^{2+}	5–10 s	Very Low	Fast response, high sensitivity	[8]
–OH	ATP, phosphate	8–15 s	Low	Strong hydrogen bonding	[11]
–COOH	Pb^{2+}, Cd^{2+}	12–20 s	Moderate	Excellent stability	[17]
$–NO_2$	Nitroaromatic explosives	18–30 s	Low	Excellent selectivity	[14]
–X	F^-, CN^-, Volatile Organics	10-25s	Very Low	Highly robust frameworks, PH Stability	[15]

Discussion

The comparison clearly demonstrates that amino-functionalized MOFs generally provide the shortest sensing response times due to enhanced electron donation and efficient energy transfer. Hydroxyl-functionalized MOFs perform exceptionally well in aqueous sensing because hydrogen bonding facilitates rapid analyte adsorption. Carboxyl-functionalized MOFs offer superior structural stability and recyclability, whereas nitrofunctionalized MOFs exhibit outstanding molecular selectivity despite comparatively slower fluorescence responses. [28]

Table 2: Comparison of Eu^{3+} and Tb^{3+} MOFs

Property	Eu^{3+} MOFs	Tb^{3+} MOFs
Emission Colour	Red	Green
Main Emission	~615 nm	~545 nm
Sensitivity	Very High	High
Response Time	Moderate	Faster

Discussion

Europium-based MOFs generally provide higher analytical sensitivity because of their intense red emission and lower detection limits. Terbium-based MOFs, however, often exhibit brighter fluorescence and faster response times. Therefore, Eu^{3+} is commonly preferred for ultra-sensitive chemical detection, whereas Tb^{3+} is frequently selected for rapid environmental sensing and fluorescence imaging. [29]

Research Gaps and Future Perspectives

Despite significant progress in ligand-functionalized lanthanide MOFs, several challenges remain. Many reported sensors have been evaluated only under laboratory conditions using pure solutions, while their performance in complex environmental or biological samples is still insufficiently explored. Additionally, response times, fluorescence lifetimes and quantum yields are often reported using different experimental protocols, making direct comparison between studies difficult. Standardized testing methods would facilitate more meaningful evaluation of sensing performance across different MOF systems. [30]

Future research should focus on designing multifunctional ligands capable of simultaneously enhancing energy transfer, molecular recognition and structural stability. Artificial intelligence and machine learning are expected to accelerate ligand selection and MOF design by predicting structure–property relationships before experimental synthesis. Furthermore, hybrid systems integrating lanthanide MOFs with enzymes, DNA aptamers and nanomaterials are likely to expand applications in real-time biosensing, wearable diagnostics and precision medicine.

Conclusion

Lanthanide-based metal–organic frameworks have emerged as one of the most promising classes of luminescent materials because they combine the structural versatility of MOFs with the unique optical properties of lanthanide ions. Their sharp emission bands, long luminescence lifetimes, excellent photostability and high sensitivity make them attractive candidates for chemical sensing, environmental monitoring, biomedical diagnostics and bioimaging.

This review demonstrates that ligand functionalization plays a decisive role in determining the sensing performance of Ln-MOFs. Functional groups modify ligand-to-metal energy transfer, host–guest interactions, pore accessibility and

analyte recognition, thereby influencing fluorescence intensity, response time, and detection limit and sensing selectivity.

Comparative analysis indicates that amino-functionalized ligands generally provide rapid fluorescence response and enhanced sensitivity because of improved electron donation. Hydroxylfunctionalized ligands strengthen hydrogen-bonding interactions and perform well in aqueous sensing systems. Carboxyl-functionalized ligands contribute excellent structural stability and recyclability, whereas nitro-functionalized ligands exhibit superior selectivity towards electron-deficient analytes despite comparatively lower luminescence intensity.

Among the lanthanide ions, Eu^{3+}-based MOFs remain highly suitable for ultra-sensitive fluorescence sensing because of their intense red emission and low detection limits, while Tb^{3+}-based MOFs provide brighter green emission and rapid response characteristics. Mixed-lanthanide systems further improve sensing reliability through ratiometric fluorescence.

Although remarkable progress has been achieved, further research is required to develop multifunctional ligands, improve sensing performance in complex biological environments, reduce synthesis costs and establish standardized protocols for comparing luminescent properties across different MOF systems. Future integration of artificial intelligence, machine learning and computational materials design is expected to accelerate the development of next-generation lanthanide MOFs with superior sensing capabilities.

Summary

Metal–organic frameworks represent an important class of porous coordination materials with diverse scientific and technological applications. Among them, lanthanide-based MOFs have attracted widespread attention because of their exceptional luminescent properties and versatile sensing behaviour.

This review focused on understanding how ligand functionalization influences the luminescent sensing performance of lanthanide MOFs. Different functional groups such as amino, hydroxyl, nitro and carboxyl substituents were comparatively analysed to determine their effects on fluorescence intensity, response time, detection limit, selectivity and framework stability.

The review established that ligand engineering significantly improves sensing performance by modifying energy-transfer processes and host–guest interactions. Comparative analysis revealed that aminofunctionalized ligands generally produce the fastest sensing response, hydroxyl-functionalized ligands improve analyte adsorption, carboxyl-functionalized ligands enhance structural stability and nitrofunctionalized ligands increase analyte selectivity.

Applications of ligand-functionalized Ln-MOFs in environmental monitoring, heavy metal ion detection, antibiotic sensing, bioimaging and bioluminescent biosensing were discussed. The review further emphasized the importance of Eu^{3+} and Tb^{3+} as the most widely investigated lanthanide ions because of their characteristic red and green emissions.

Overall, ligand functionalization provides an effective strategy for optimizing the optical performance of lanthanide MOFs and offers promising opportunities for developing highly sensitive and selective luminescent sensing platforms for future biomedical and environmental applications.

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