



The Chemistry and Applications of Europium-Based Metal-Organic Frameworks (Eu-MOFs)

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Abstract

Metal-Organic Frameworks (MOFs) received great interest in different application due to its super adsorption characters and high surface area, the most interesting MOFs is Europium based MOFs (Eu-MOFs), it is a class of versatile porous materials, Eu-MOFs have shown enormous potential for different applications such as Hg²⁺ ions, Fe³⁺, pesticides, phenols, dyes and other ions, drugs, hypochlorite, selenite & arsenate, miscellanies material, and anticounterfeiting detection. Eu-MOFs were applied in high technology like supercapacitor (SCs), pH & temperature sensing applications. Moreover, Eu-MOFs were applied in biological system dopamine and histadine, 1-hydroxypyrene (1-HP), various types of antibiotic, enzyme detections, and adenosine triphosphate (ATP) detections. Additionally, Eu-MOFs were applied in catalysis for the cyanosilylation and reduction reactions. Eu-MOFs is not only worked in previous application but also worked in gas state for gases and different vapor detections. The present review highlights the recent advances in the field of application, followed by the directions for future research.

Keywords: Europium-Metal-organic frameworks (Eu-MOFs), catalysis, sensor, gas storage, water treatment

Abbreviations

MOFs= Metal-organic frameworks; PL= Photoluminescence; XRD= X-ray powder diffraction; TGA= Thermal gravimetric analysis; FTIR; Fourier-transform infrared spectra; DMF= Dimethylformamide; BTC, Benzene tricarboxylic acid; BDC= Benzene-1,3-dicboxylate; PSM= Post synthetic modification; PEC= Photoelectrochemical; QDs= Quantum dots; TNP= 2,4,6-trinitrophenol; UIO= University of Oslo; EDTA= Ethylene diamine tetraacetic acid; 4-NP= 4-nitrophenol; PPS= Polyphenylene sulfide; DPA= Dipicolinic acid; AD= Alzheimer's disease; NB= Nitrobenzene; MG= Malachite green; DMA = N,N-Dimethylacetamide; 2-AA= 2-Aminoacetophenone; TC= Tetracycline; ECL= Electrochemiluminescence; DA= Dopamine; 1-HP= 1-hydroxypyrene; PAHs= Polycyclic aromatic hydrocarbons; SiQDs= Silicon quantum dots; SMZ= Sulfamethazine; GMP= Guanosine monophosphate;

GSH= Glutathione; DMA= N, N-dimethylacetamide; MB= Methylene blue CR= Congo Red; ATP= Adenosine triphosphate; RhB= Rhodamine B; MO= Methyl orange.

Table of contents

1. Introduction
2. Synthesis of Eu-MOF
 - 2.1. Hydro/solothermal synthesis
 - 2.2. Microwave synthesis
 - 2.3. Postsynthetic modification synthesis
3. Application in wastewater research
 - 3.1. Eu-MOF and Hg²⁺ ions detection
 - 3.2. Eu-MOF and Fe³⁺, pesticides, phenols, dyes and other ions detections
 - 3.3. Eu-MOF and drugs detections
 - 3.4. Eu-MOF and hypochlorite, selenite & arsenate detections

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- 3.5. Eu-MOF and miscellaneous material detections
- 4. Application in high technology
 - 4.1. Eu-MOF and supercapacitor (SCs) applications
 - 4.2. Eu-MOF and pH & temperature sensing
 - 4.3. Eu-MOF and anticounterfeiting detections
- 5. Application in biological system
 - 5.1. Eu-MOF and dopamine & histidine detections
 - 5.2. Eu-MOF and 1-hydroxypyrene (1-HP) detections
 - 5.3. Eu-MOF and various types of antibiotic detections
 - 5.4. Eu-MOF and enzyme detections
 - 5.5. Eu-MOF and Adenosine triphosphate (ATP) detections
- 6. Application in catalysis
 - 6.1. Eu-MOF as catalyst for the cyanosilylation
 - 6.2. Eu-MOF as catalyst for the reduction
- 7. Application in gas state
 - 7.1. Eu-MOF and gases detections
 - 7.2. Eu-MOF and different vapor detections
 - 7.3. Eu-MOF and various types of acid detections
- 8. Conclusion
- 9. References
- 1. Introduction

Metal-organic frameworks (MOFs) are a charming family of materials with permanent porosity, high surface area, and adjustable chemical functionalities [1, 2]. The specific qualities of MOF materials have positioned them at the forefront of studies involving gas storage [3, 4], catalysis [5-7], separation [8], water treatment [9-11] and drug delivery [12, 13]. Among the diverse metal-organic frameworks, lanthanide based metal-organic frameworks (LMOFs) have attracted great attention, not only because of their fascinating characteristic coordination and unique optical properties arising from 4f electrons, but also due to their potential applications in anticounterfeiting barcodes [14], luminescent sensors [15, 16], and lightemitting devices (LEDs) [17]. The aforementioned qualities have also aroused the interest of many scientists in the use of LMOFs as smart membranes, lighting apparatus, sensor devices, and many other nanotechnological devices [17]. The advances and emergencies to use Eu-MOFs rather than the most

common easily, cheaper M-MOFs (M= Zn, Cu, Ni, Co ...) was also mentioned [18-20].

2. Synthesis of Eu-MOF

2.1. Hydro/ solvothermal synthesis

Eu-MOFs composed of oxalic acid and Eu building units were hydrothermally synthesized. Eu-MOFs exhibited highly efficient luminescent property. Solid-state photoluminescence (PL) measurements revealed phosphorescence emission bands of Eu-MOF centered at 618 nm (red emission) upon excitation at 396 nm. Eu-MOF displayed a phosphorescence quantum yield of 53%. Time-resolved PL analyses showed very long lifetime values, at $600 \pm 1 \mu\text{s}$ for Eu-MOF [21].

2.2. Microwave synthesis

Nanoscale europium (III) metal-organic frameworks, $\text{Eu}(\text{BTC})(\text{H}_2\text{O})\cdot\text{DMF}$, were synthesized by rapid microwave-assisted method. The components of the as-prepared products were confirmed by the elemental analysis, X-ray powder diffraction (XRD), thermal gravimetric analysis (TGA) and Fourier-transform infrared spectra (FTIR) analyses. $\text{Eu}(\text{BTC})(\text{H}_2\text{O})\cdot\text{DMF}$ with various morphologies, including particle-like, rod-like, straw-sheaf-like nanostructures, could be simply prepared by controlling the concentrations of the starting reactants. The optical measurements on the obtained $\text{Eu}(\text{BTC})(\text{H}_2\text{O})\cdot\text{DMF}$ indicated that all the nanomaterials show the characteristic emissions of the Eu^{3+} ions at 578, 590, 612, 650, and 699 nm, which were attributed to $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J=0-4$) transitions of the Eu^{3+} ion, respectively. It was also noticed that the luminescent properties of the as-prepared products were heavily dependent on the morphologies and sizes of the nanomaterials. The assembled straw-sheaf-like architectures displayed the strongest emissions and the longest luminescence lifetime, which was mainly due to the fewest surface defects [22].

2.3. Post-synthetic modification synthesis

Eu-BDC-PC, Eu-BDC-MA, Eu-BDC-SA, and Eu-BDC-DPC were synthesized with different organic linker's through post synthetic modification (PSM) strategy using Eu-BDC-NH₂. The obtained Eu-MOFs were investigated for photoluminescence studies. Pristine Eu-BDC-NH₂, functionalized Eu-BDC-PC and Eu-BDC-DPC depicted very intense red emission. While, Eu-BDC-MA and Eu-BDC-SA depicted fairly low red emission, this is attributed to differences in energy transfer from linkers to europium metal. The asymmetry ratio values of pristine Eu-BDC-NH₂ and functionalized Eu-BDC-PC suggested that very low symmetry around

europium ion. On the other hand, asymmetry value is relatively lower in Eu-BDC-DPC indicates the high symmetry around europium metal compared to Eu-BDC-NH₂ and Eu-BDC-PC. The fluorescence lifetime values of all the functionalized Eu-MOFs (<0.57 ms) are less than the pristine Eu-BDC-NH₂ (0.87 ms). The color correlated temperature (CCT) value of Eu-BDC-MA (10,000 K) and Eu-BDC-SA (4800 K) suggested near white emission with bluish hue known as cool white [23].

3. Application in wastewater research

3.1. Eu-MOF and Hg²⁺ ions detection

Trace analysis of mercury ions (Hg²⁺) is of great significance to human health and environmental protection. The preparation of a dual emission Ln-MOF material (Eu-Ca-MOF) using Ca-MOF as the parent framework and introducing Eu³⁺ ions into its channels through post-synthesis modification. Eu-Ca-MOF has good photoluminescence properties and can be used as a ratiometric fluorescence sensor to detect Hg²⁺ ions in water sensitively. The peak-to-height ratio of the two emissions can be used to achieve highly sensitive detection of Hg²⁺ ions even in the presence of other potentially competing analytes. At the same time, Eu-Ca-MOF has a wider detection range (0.02–200 μM), and a lower limit detection (2.6 nM) for Hg²⁺ ions [24]. Photoelectrochemical (PEC) biosensor was developed for the ultrasensitive detection of Hg²⁺ based on the MOFs-like composite/CdS quantum dots (QDs) as photoactive substrate materials. The MOFs-like composite in situ formed by hydrophobically modified alginate (HMA) with europium ion (Eu³⁺) not only offered a friendly platform for bioconjugation but also resulted in enhancing sensor photocurrent response. Furthermore, the immobilized thymidine-rich probe DNA on the MOFs-like composite surface was bent to produce a T-Hg²⁺-T structure in the presence of Hg²⁺, resulting in enlarged steric hindrance on the electrode surface and decreased the proposed biosensor PEC response. This proposed photoelectrochemical sensing system displayed selective detection of Hg²⁺ with a linear range from 0.1 pM to 1.0 μM with a detection limit of 0.067 pM. The utilization of semiconductor quantum dots as light-harvesting components and the MOFs-like composite as sensitizers broadens the possible design ideas for photoelectrochemical sensing systems[25]. In-situ growth of CsPbBr₃ nanocrystal into Eu-BTC was realized for synthesis of dual-emission CsPbBr₃@Eu-BTC by a facile solvothermal method.

A novel ratiometric fluorescence sensor based on the CsPbBr₃@Eu-BTC was prepared for rapid, sensitive and visual detection of Hg²⁺ in aqueous solution (figure 1). The ratiometric fluorescence sensor shows high analytical performance for Hg²⁺ detection with a wide linear range of 0–1 μM and a low detection limit of 0.116 nM. In addition, it also shows high selectivity for the detection of Hg²⁺ and can be successfully applied to detect Hg²⁺ in environmental water samples[26].

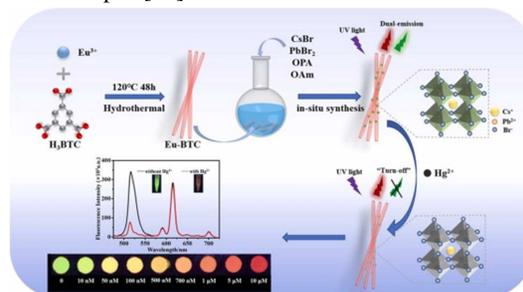


Figure 1. The synthetic procedure of CsPbBr₃@Eu-BTC and its ratiometric and visual sensing of Hg²⁺ [26].

A series of new, phenanthroline-decorated 3D lanthanide metal organic frameworks (Ln-MOFs) valorising an original combination of four different lanthanides and two organic ligands, i.e. thiois(4-methylene-benzoic acid) (H₂tmba) and 1,10-phenanthroline (phen), have been successfully synthesized, namely ([Ln₄(tmba)₆(phen)₄]_n·m(H₂O)(phen)_n) [Ln = Ce, m = 3 (1); Pr, m = 1 (2); Eu, m = 3 (3); and Tb, m = 3 (4)]. It is proved that compound (3) sensitively and selectively acts as an excellent luminescent probe for the detection of Hg²⁺ ions in waters, with a detection limit of 1.00 μM. As additional assets, (3) display superb stability over a wide pH range (3-12) of the aqueous media, as well as convenient recycling after completion of the detection experiments [27].

3.2. Eu-MOF and Fe³⁺, pesticides, phenols, dyes and other ions detections

Effective detection of contaminants in water, such as pesticides, excess Fe³⁺ and MnO₄⁻, is critical to human health and environmental protection. They can be quantitatively detected by a new luminescent sensor based on a water stable (Eu-MOF). It exhibits high selectivity for Fe³⁺, MnO₄⁻, and nicosulfuron (NSF) in water through luminescence quenching with low detection limit, and fast response (figure 2), indicating that Eu-MOF is a reliable analysis platform for multi-responsive sensing [28]. A

luminescent metal-organic framework (Eu-MOF [Eu₆L₆(μ₃-OH)₈(H₂O)₃]₈·H₂O)_n) was constructed by a solvothermal method with a linear organic ligand L (10-[(2-amino-4-carboxyl-phenyl)ethynyl]anthracene-9-carboxylic acid) based on anthracene and alkyne groups and using Eu³⁺ as the metal center. Interestingly, Eu-MOF exhibited high selectivity and sensitive fluorescence burst properties towards Fe³⁺ ions and 2,4,6-trinitrophenol (TNP) in DMF solution. For Fe³⁺, the KSV value is $5.06 \times 10^5 \text{ M}^{-1}$ and the LOD value is $5.1 \times 10^{-7} \text{ M}$. For TNP, the KSV value is $1.92 \times 10^4 \text{ M}^{-1}$ and the LOD value is $1.93 \times 10^{-6} \text{ M}$. This work provides an excellent fluorescent sensor for the detection of Fe³⁺ and 2,4,6-trinitrophenol (TNP) residues in contaminants [29].

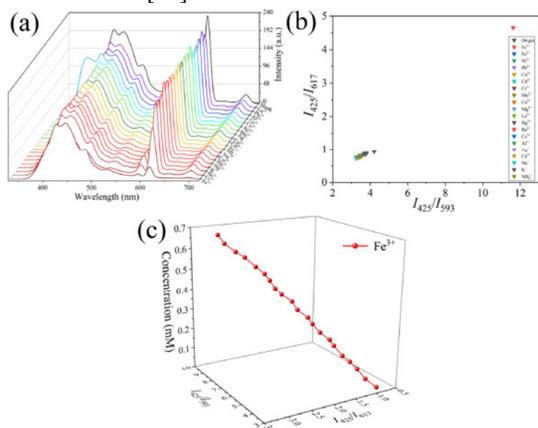


Figure 2. (a) Emission spectra of Eu-MOFs excited at 310 nm for different cations. (b) 2D decoded images of different cations (0.1 mM) based on the I_{425}/I_{593} and I_{425}/I_{617} emission intensity ratios. (c) The derived 3D ratiometric sensing of Fe³⁺ when concentration is added as the third dimension [28].

A dual-emissive Eu³⁺-loaded MOF is designed and successfully fabricated by introducing 2-hydroxyterephthalic acid (H₂BDC-OH) and Eu³⁺ ions into an UiO-66-type MOF material (EuUCH). The EuUCH is characterized by a high selectivity and sensitivity toward Fe³⁺ and Al³⁺, which yield different responsive modes [30]. To develop smart luminescence sensors towards heavy metal ions and acid anions, two new lanthanide(III)-based MOFs: ([Ln₂(btpdc)₃·DMF·2H₂O]₂·2DMF·4H₂O)_n (Ln = Eu (1), Tb (2), H₂btpdc = benzo[b]thiophene-2,6-dicarboxylic acid) were designed and synthesized under solvothermal condition based on a dicarboxylate ligand H₂btpdc. The luminescence sensing experiments performed on (1) reveal that it

can be employed as a smart “turn-off” luminescence sensor for the detection of Fe³⁺ or S²⁻ in aqueous solution with high selectivity, low detection limit, good anti-interference ability and recyclability. The obtained quenching constant K_{sv} and detection limits are $2.316 \times 10^4 \text{ M}^{-1}$ and 0.26 μM, respectively, for Fe³⁺, and $1.38 \times 10^4 \text{ M}^{-1}$ and 1.05 μM, respectively, for S²⁻ [31]. The varied particle sizes of Eu-MOFs are synthesized by adjusting the synthesis process parameters, and their variation rules combining the single factor analysis method with machine learning technology are studied. More importantly, this kind of Eu-MOFs can also be used to identify varied ions (Fe³⁺, F⁻, I⁻, SO₄²⁻, CO₃²⁻, and PO₄³⁻) and citric acid [32]. [M₂O (BDCPO)_{1.5}(H₂O)₇]₂·2H₂O (Eu for CUST-621, Tb for CUST-622) are successfully constructed using π-electron riched ligand N,N'-bis(2,4-dicarboxyphenyl)-oxalamide (H₆BDCPO) and Eu and Tb metal ions under solvothermal conditions. Moreover, CUST-621 and CUST-622 can be used as multi-responsive luminescence sensors to Fe³⁺ and Cr₂O₇²⁻, with high sensitivity, long-time stability and remarkable selectivity with resistance to interference from other ions [33]. The complex based on 3,5-bis(triazol-1-yl)-benzoic acid (HL) was synthesized by solvothermal reaction, namely [Eu(HL) (NO₃)₃·H₂O] (1). UV-visible spectroscopy studies have shown that complex (1) (Eu-MOF) can effectively adsorb Congo red (CR) dye, and after repeating 3 times, it can still quickly adsorb CR dye in the aqueous solution, and the adsorption efficiency can reach 86.29%; Fluorescence emission experiments show that complex 1 can selectively recognize Fe³⁺ (detection limit: 0.016 μM, KSV = $1.1 \times 10^7 \text{ M}^{-1}$) and Cr₂O₇²⁻ (detection limit: 1.46 μM, KSV = $1.57 \times 10^5 \text{ M}^{-1}$) in aqueous solution through fluorescence quenching effect, in addition, the complex 1 can detect Al³⁺ (detection limit: 2.95 μM, KSV = $6.78 \times 10^5 \text{ M}^{-1}$) and Cr³⁺ (detection limit: 0.17 μM, KSV = $2.24 \times 10^5 \text{ M}^{-1}$) through the fluorescence “on” effect. In addition, complex 1 can also selectively detect ethylenediamine, m-chloroaniline, nitrobenzene, aniline, 2-chloro-4-nitroaniline, m-methylaniline and o-methylbenzene by fluorescence quenching effect and the quenching degree is 0.010%, 0.016%, 0.075%, 0.153%, 0.402%, 0.718%, 0.933%, respectively [34]. ([Eu(qptca)_{1/2}(H₂qptca)_{1/2}(H₂O)₂]₂·DMF)_n (referred to as SLX-1), was synthesized and used as a water-stable and highly selective luminescent sensor for

Fe^{3+} in aqueous solution with a comparable detection limit using Ln-MOF probes ($6.45 \mu\text{M}$) through the antenna effect of SLX-1 [35]. $([\text{Eu}_3(\text{BTDC})_4(\text{HCOO})(\text{H}_2\text{O})_2] \cdot \text{solvents})_n$ was successfully obtained by the solvothermal reaction of 2,1,3-benzothiadiazole-4,7-dicarboxylic acid (H2BTDC) and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. The fluorescence experiments indicate that JXUST-9 could be considered as a good multi-responsive sensing material for detecting Fe^{3+} , MnO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ in aqueous solutions via the turn-off effect, and the detection limits are $0.94 \mu\text{M}$, $1.23 \mu\text{M}$ and $1.23 \mu\text{M}$, respectively [36]. $\text{Eu}(\text{BPDA})1.5\text{phen}@ \text{PAN}$ fluorescent fibers were successfully prepared by electrospinning using polyacrylonitrile (PAN) as substrate from self-assembled MOFs. $\text{Eu-MOF}@ \text{PAN}$ exhibited unique pertinence and excellent sensitivity in the detection of Fe^{3+} , the fluorescence dynamic quenching was deduced by fluorescence lifetime fitting. Compared with the functionalized MOFs previously reported, $\text{Eu-MOF}@ \text{PAN}$ had a lower limit of detection ($0.063 \mu\text{M}$) [37]. $([\text{Eu}(\text{TCPB})(\text{DMF}) \cdot \text{dioxane} \cdot 0.5\text{H}_2\text{O}]_n)$ has been assembled via 1,3,5-tris(4-carboxylphenoxy)benzene (H3TCPB), a tripodal ligand through utilizing the approaches of solvothermal. It has been investigated as a sensor for the detection of Fe^{3+} ions. [38]. Eu -based MIL-78 nanosheets exhibited unique selective photoelectrochemical sensing property toward trace amounts of Fe^{3+} ions in aqueous solution with a detection limit of $0.0899 \mu\text{M}$ at a signal-to-noise ratio of 3 [39]. $([\text{Na}@ \text{Ln}_8(\text{EDTA})_6(\text{H}_2\text{O})_{22}] \cdot \text{ClO}_4 \cdot x\text{H}_2\text{O})_n$ ($x \approx 28$, $\text{Ln} = \text{Gd}$ for 1, $\text{Ln} = \text{Eu}$ for 2) and $([\text{Na}@ \text{Ln}_9(\text{EDTA})_6(\text{H}_2\text{O})_{27}] \cdot (\text{ClO}_4)_4 \cdot x\text{H}_2\text{O})_n$ ($x \approx 26$, $\text{Ln} = \text{Gd}$ for 3, $\text{Ln} = \text{Eu}$ for 4) were prepared by ethylene diamine tetraacetic acid (H_4EDTA) to control the hydrolysis of lanthanide ions to form cluster-based secondary building blocks and hydrated metal ions as linkers. Luminescence studies showed that compounds 2 and 4 had a good recognition effect on the cyclohexane molecule, and 4 displayed excellent sensitive sensing and a detection effect on Fe^{3+} ions in methanol based on the high-sensitivity fluorescence quenching phenomenon [40]. $[\text{Eu}(\text{BCB})(\text{DMF}) \cdot (\text{DMF})1.5(\text{H}_2\text{O})_2(1)]_n$ was synthesized via solvothermal method using 4,4',4''-benzenetricarbonyltribenzoic acid (H3BCB) as a bridging ligand. Photoluminescence studies show that compound 1 emits bright red luminescence and behave as a multi-responsive luminescent sensor toward 4-

nitrophenol (4-NP) and Γ^- and Fe^{3+} ions in water with high sensitivity, selectivity and low detection limits [41]. $(\text{Eu}0.075 \text{ Tb}0.925\text{-MOF})$ were successfully synthesised through the solvothermal reaction of $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and the ligand pyromellitic acid. The synthesised $\text{Eu}0.075 \text{ Tb}0.925\text{-MOF}$ can be used as a highly selective and recyclable sensing material for Fe^{3+} or $\text{Cr}_2\text{O}_7^{2-}$. The detection linear range for Fe^{3+} or $\text{Cr}_2\text{O}_7^{2-}$ is $10\text{--}100 \mu\text{M/L}$, and the detection limits are 2.71×10^{-7} and $8.72 \times 10^{-7} \text{ M}$, respectively [42]. $([\text{Eu}(\text{DTA})1.5(\text{H}_2\text{O})] \cdot \text{H}_2\text{O})_n$ (Eu-DTA) and $[\text{Tb}(\text{DTA})(\text{C}_2\text{O}_4)0.5(\text{H}_2\text{O})]_n$ (Tb-DTA) ($\text{H}_2\text{DTA} = 2,5\text{-di}(1\text{H-imidazol-1-yl})\text{terephthalic acid}$), are successfully synthesized via hydrothermal reaction. Furthermore, luminescence and sensing studies reveal that Eu-DTA and Tb-DTA can sensitively and simultaneously detect Fe^{3+} ions and nitrobenzene, which suggests that the two Ln-MOFs are promising bifunctional luminescence sensors [43]. $(\text{Eu}_2\text{bdc}_3 \cdot 4\text{H}_2\text{O})$ MOFs were synthesized by the ultrasound-assisted wet-chemical method. Size reduction results in broad-ened emission bands, an increase in the non-radiative rate constants and a decrease in both the quantum efficiency of the 5D0 level and Eu^{3+} and the luminescence quantum yields. Cu^{2+} , Cr^{3+} , and Fe^{3+} ions efficiently and selectively quench the luminescence of Eu_2bdc_3 , which makes it a prospective material for luminescent probes to monitor these ions in waste and drinking water [44]. A polyphenylene sulfide (PPS) paper-based sensor ($\text{Eu-MOF}@ \text{ALD-PPS}$) was designed and successfully fabricated for efficient sensing of Fe^{3+} . In addition, the obtained $\text{Eu-MOF}@ \text{ALD-PPS}$ showed high selectivity and sensitivity in response to Fe^{3+} among many metal ions (Na^+ , K^+ , Zn^{2+} , Ni^+ , Mg^{2+} , Ag^+ , Ba^{2+} , Ga^{2+} , Cu^{2+} , Gd^{2+} , Co^{2+} and Fe^{3+}). The sensing mechanism investigation revealed that the weak interactions of Fe^{3+} with oxygen atoms of hydroxyl and carboxylic acids protruding into the pores of MOFs quenched the luminescence of PPS paper-based sensor effectively [45]. $([\text{Ln}_2\text{L}_2(\text{DMF})_4] \cdot x\text{DMF} \cdot y\text{H}_2\text{O})_n$ ($\text{Ln} = \text{Ce}(1)$, $\text{Pr}(2)$, $\text{Sm}(3)$, $\text{Eu}(4)$, $\text{Gd}(5)$; $x=0, 1$; $y=0, 1$) and $([\text{Ln}_2\text{L}_2(\text{H}_2\text{O})_{2.5}]_n)$ ($\text{Ln} = \text{Dy}(6)$, $\text{Ho}(7)$), have been solvothermally synthesized based on the semi-rigid tripodal ligand 5-(4-carboxybenzyloxy)isophthalic acid (H3L). $\text{Eu}(4)$ exhibited efficient luminescence responses toward Fe^{3+} , $\text{Cr}_2\text{O}_7^{2-}$, and NPT/NZF antibiotics in aqueous medium with high sensitivity and selectivity. The detection limits (LODs) are 3.69

μM for Fe^{3+} ion, $4.01 \mu\text{M}$ for $\text{Cr}_2 \text{O}_7^{2-}$ anion and $9.92 \mu\text{M}/11.4 \mu\text{M}$ for NFT/NZF antibiotics, suggesting that Eu(4) is a good and simple multifunctional luminescent sensor [46]. Eu-MOFs can be used to detect Fe^{3+} and benzaldehyde in an aqueous environment with low detection limits of $0.027 \mu\text{M}$ for Fe^{3+} and $0.011 \mu\text{M}$ for benzaldehyde [47]. Eu(btc) MOFs were prepared by co-precipitation method via 1,2,4-benzenetricarboxylic acids (H3btc) connecting with Eu^{3+} ions, and the morphology was controlled from compact spherical to irregular honeycomb by adjusting the pH of reaction solutions. The sensing ability of Eu(btc) MOFs to 11 kinds of metal ions was investigated and a prominent quenching effect occurs in Fe^{3+} , Cr^{3+} or Ni^{2+} solutions [48]. Eu-doped Gd-MOFs have been synthesized through a one-pot green approach using commercially available reagents. The 1,4-benzenedicarboxylic acid ($\text{H}_2\text{-BDC}$) and 2,6-naphthalenedicarboxylic acid ($\text{H}_2\text{-NDC}$) were chosen as ditopic organic linkers to build the 3D structure of the network. Eu-doped Gd-MOF have been tested for sensing of the inorganic ions such as Fe^{3+} and $\text{Cr}_2 \text{O}_7^{2-}$ [49].

($[\text{Eu}(\text{L})(\text{DMF})_2]\text{n}$) was prepared by the reaction of rigid ligand H_3L (3,5-bis-(3-carboxyphenoxy)benzoic acid) and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ under solvothermal conditions. Luminescent detection of the nitroaromatic compounds and metal ions showed that the complex had high sensitivity to Fe^{3+} , o-nitrophenol, p-nitrophenol, and m-nitrophenol [50]. Based on a ligand-directed synthetic strategy, the acidic solvothermal reaction of ZnO , Eu_2O_3 , and 4,4',4''-(pyridine-2,4,6-triyl)tri(1,3-benzenedicarboxylic acid) (H_6PTTBA) generated a targeted robust double-walled honeycomb material ($[\text{EuIII}(\text{ZnII}(\text{HPTTBA})(\text{H}_2\text{O})] \cdot 4\text{DMF} \cdot 3\text{H}_2\text{O}$) (simplified as NUC-9), which featured excellent characteristics such as dual tubular nanochannels, high porosity, specific surface area, abundant exposed active metal sites, etc. Furthermore, the water-resistant framework of NUC-9 could selectively and sensitively discriminate Fe^{3+} in aqueous solution according to the fluorescence quenching effect [51].

3.3. Eu-MOF and drugs detections

Chiral drugs are of great significance in drug development and life science because one pair of enantiomers has a different combination mode with target biological active sites, leading to a vast difference in physical activity. Metal-organic

framework (MOF)-based chiral hybrid materials with specific chiral sites have excellent applications in the highly effective sensing of drug enantiomers. Sitagliptin and clonidine are effective curing drugs for controlling diabetes and hypertension, while insulin and norepinephrine are the biomarkers of these two diseases. Excessive use of sitagliptin and clonidine can cause side effects such as stomach pain, nausea, and headaches. MOF-based chiral hybrid material Eu-BTB@d-carnitine (H_3BTB = 1,3,5-benzenetrisbenzoic acid) was synthesized. Eu-BTB@d-carnitine can be applied in luminescent recognition toward sitagliptin and clonidine with high sensitivity and low detection limit (for sitagliptin detection, K_{sv} is $7.43 \times 10^6 [\text{M}^{-1}]$; for clonidine detection, K_{sv} is $9.09 \times 10^6 [\text{M}^{-1}]$; limit of detection (LOD) for sitagliptin is 10.21 nM , and LOD of clonidine is 8.34 nM). In addition, Eu-BTB@d-carnitine can further realize highly sensitive detection of insulin in human fluids with a high K_{sv} ($2.08 \times 10^6 [\text{M}^{-1}]$) and a low LOD (15.48 nM) [52]. A novel electrochemiluminescence (ECL) biosensor for ulinastatin drug (UTI) detection based on self-luminescent metal-organic framework (L-MOF) nanomaterials was developed. The L-MOFs could be simply prepared by one-pot methods using Eu^{3+} and 4,4',4''-s-triazine-1,3,5-triyltri-m-aminobenzoic acid (H_3TATAB) as the metallic center and organic ligand, respectively. The established sandwich ECL biosensor showed a wide linear range of $0.1 \text{ ng mL}^{-1} - 10^5 \text{ ng mL}^{-1}$ and a low limit of detection of 9.7 pg mL^{-1} for UTI detection. In addition, the developed ECL biosensor could also be successfully applied to the real UTI sample determination in serum. [53].

(Ln-BPTA) with different metal nodes (Eu, Sm, Dy and Tb) and the same nitrogen-abundant ligand have been successfully prepared via simple hydrothermal self-assembly. In particular, Eu-BPTA delivers the best response performance among the designed isostructural homologues, showing a rapid response (within seconds), an ultralow limit of detection (5.02 nM), excellent durability and high selectivity, even in the actual matrix [54]. $[\text{Eu}_2(3,5\text{-bct})(\text{phen})_2(\text{ox})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$, was constructed from 3,5-bis(3'-carboxyphenyl)-1,2,4-triazole (3,5-H₂bct), oxalate (ox) and 1,10-phenanthroline (phen) as a luminescent sensor. Based on the luminescent Eu-MOF, the sensing behavior for colchicine drug in the aqueous environment was studied (figure 3). Highly selective and sensitive detection ($\text{LOD} = 2.43 \times 10^{-5}$

mol L⁻¹) of colchicine was observed by the Eu-MOF even in the presence of potential interfering components. Highly sensitive and rapid detection of colchicine in wastewater was achieved using this Film@Eu-MOF, which could be identified by the naked eye [55].

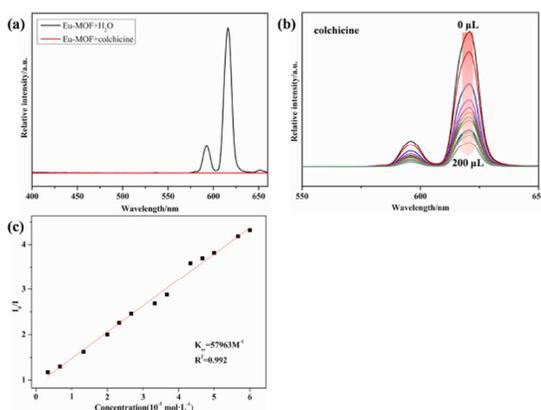


Figure 3. (a) Emission spectra of Eu-MOF dispersed in aqueous solution and colchicine solution. (b) The luminescent titration curve of Eu-MOF by colchicine. (c) The SV plot for the quenching of Eu-MOF in presence of colchicine [55].

(Eu-TDA) was synthesized to detect ENT by luminescence with excellent reusability and selectivity in the presence of main coexisting and interference species of plasma with a limit of detection of 5.01 µM [56]. Due to the anionic framework, Ln(iii) ions (Ln = Eu and Tb) can be encapsulated in the framework of H₂[Cd₉(DDB)₄(BPP)₄(H₂O)₁₄].4H₂O.2DMA (1), by a post-synthetic modification process to obtain Ln(iii)@1, where 1.09Eu(iii)@1 (1a) and 0.658Tb(iii)@1 (1b) can be obtained by soaking H₂[Cd₉(DDB)₄(BPP)₄(H₂O)₁₄].4H₂O.2DMA in a Eu(NO₃)₃·6H₂O or Tb(NO₃)₃·6H₂O aqueous solution for 48 h. The liquid-state emission spectra of Ln(iii)@1 can be tuned to be a white light emission by changing the Eu(iii)/Tb(iii) molar ratio in solution. Moreover, 1b can be used as a "turn-off" fluorescent probe for bilirubin with a low detection limit of 0.250 µM in phosphate buffer solution (pH = 7.4), which presents excellent sensitivity, high selectivity, and reusability. Furthermore, the devised fluorescent probe in serum also exhibits the fluorescence "turn-off" process with a low detection limit of 0.279 µM, and the recovery rate of bilirubin is 99.20-101.9% [57]. Eu-MOFs exhibited good biocompatibility, low cytotoxicity, and high imaging

efficiency. As they exhibited slow-release kinetics and targeted biodistribution profiles, these Eu-MOFs additionally hold great promise as potential anticancer agents in clinical settings. They designed a novel Eu-MOF active targeted drug delivery nanocarrier platform and found that it represents a promising therapeutic tool for cancer treatment [58].

3.4. Eu-MOF and hypochlorite, selenite & arsenate detections

Excessive hypochlorite will be transformed into highly toxic substances, while insufficient hypochlorite cannot completely kill bacteria and viruses in water. Therefore, it is desirable to develop a new analytical method to detect ClO⁻ in environmental water. An Acriflavine@lanthanide metal-organic framework (Acr@Eu(BTEC)) was designed by covalently integrating amino-rich dye (Acr) and carboxyl-rich Eu(BTEC) via post-synthesis method. Thus, Acr@Eu(BTEC) with two emissions was developed as a ratiometric fluorescence sensor for highly sensitive and selective detection of ClO⁻. The limit of detection (LOD) was as low as 10.75 nM [59]. 2-aminoterephthalic acid (BDC-NH₂) and dipicolinic acid (DPA) and Eu³⁺ ions as a metal node, denoted as Eu-BDC-NH₂/DPA (figure 4). The ratiometric sensing showed a self-calibration effect and reduced the background. Thus, the high sensitivity, visual detection, low detection limit (37 nM), and short response time (within 20 s) for the detection of HClO were realized with the MOF as a probe [60].

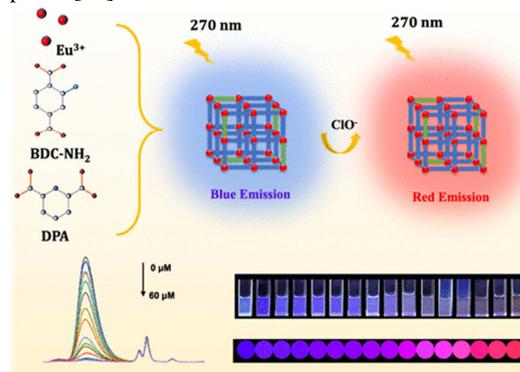


Figure 4. Eu-BDC-NH₂/DPA as ratiometric sensor for detection of HClO [60].

(Eu-MOF) characterized with ability of arsenate ion luminescence sensing and entrapping was constructed via solvothermal method based on the optimization of the organic ligand. The Eu-MOF aqueous dispersion sample displayed arsenate-triggered augment in

luminescence emission intensity with appreciable contrast and detection sensitivity with limit of detection down to 17.8 nM toward arsenate ion, which is less than one-fourth of the upper limit concentration of arsenic in drinking water that the World Health Organization (WHO) set for public health, 72 nM. The advantages that Eu-MOF nanostructure displays in terms of high sensitivity and recognition specificity in luminescence sensing of arsenate ion and the desired arsenate entrapping ability in aqueous milieu is expected to impart it potential for sensing and entrapping trace amount of arsenate in water in practical applications [61].

3.5. Eu-MOF and miscellaneous material detections

Zinc, which is the second most abundant trace element in the human central nervous system, is closely associated with Alzheimer's disease (AD). Terephthalic acid (H₂BDC) and 2,2':6',2''-terpyridine (TPY), with Eu³⁺ as a metal node was used. Eu-MOF/BDC-TPY not only displayed higher selectivity than other metal cations but also offered a highly accurate, sensitive, wide linear, color change-based technique for detecting Zn²⁺ at concentrations ranging from 1 nM to 2 μM, with a low limit of detection (0.08 nM) [62]. Vinyl-functionalized metal-organic framework (MOF), [(Me₂NH₂)₂][Eu₆(μ₃-OH)₈(BDC-CH=CH₂)₆(H₂O)₆] (Eu-BDC-CH=CH₂, BDC-CH=CH₂= 2-vinylterephthalic acid), was synthesized under solvothermal conditions. The vinyl groups in the ligands can not only modulate the "antenna effect" of the ligand on Eu³⁺ ions but also serve as an exposed reactive site to allow for the quantitative detection of H₂S by Eu-BDC-CH=CH₂. The ratiometric fluorescent probe has the advantages of water stability, acid-base stability (pH = 2-11), fast response (<2 min), high selectivity, and sensitivity (LOD = 38.4 μM) [63]. (Ln-MOFs) [Ln₂(L)₃(H₂O)₅]_n (Ln=Eu), based on 1-(4-carboxyphenyl)-1H-pyrazole-3-carboxylic acid (H₂L) showed excellent probe for nitrobenzene detecting [64]. The creation of defects into luminescent MOFs allows for manipulation of fluorescent properties and thus leads to the enhanced detection performance for technological applications. By elaborately tailoring defect numbers, the resultant Eu@UiO-MOFs-2 sensor with 0.53 missing linkers per Zr-O cluster showed a remarkably enhanced response slope and realized excellent trace detection under the range of 0–10 ppm with ultralow detection

limit to 5.67 × 10⁻⁷ M (114 ppb), acting as a powerful signal amplifier for trace detection of Cd²⁺ [65]. Benzothiadiazole-based

Eu-MOF ((CH₃)₂NH₂)[Eu(BTDB)₂·2H₂O]_n (JXUST-11) was obtained based on 4,4'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)dibenzoic acid (H₂BTDB), which exhibits a chain-based three-dimensional framework. Moreover, JXUST-11 is considered as a photoluminescent sensor to identify Al³⁺ and Ga³⁺ ions by fluorescence enhancement with the detection limits of 2.9 and 10.2 ppm, severally [66]. [Eu(Hpta)(C₂O₄)·3H₂O] prepared via reaction of the corresponding metal salts with a bifunctional organic ligand 2-(4-pyridyl)-terephthalic acid (H₂pta) under the solvothermal reaction conditions. The Eu(III)-based complex is highly selective and sensitive to Cu²⁺ in the water solution, and nearly 93% of its fluorescent intensity could be quenched when the Cu²⁺ ion concentration is 10⁻² mol/L [67]. The obtained Eu-MOFs@CD nanoprobe exhibits fluorescence at λ_{ex}/λ_{em} = 380/454 nm from CDs and λ_{ex}/λ_{em} = 275/615 nm from Eu-MOFs. On the other hand, Cu²⁺ quenches the fluorescence of Eu-MOFs due to the replacement of Eu³⁺ by Cu²⁺. Thus, Eu-MOFs@CDs enable extremely fast detection of Cu⁺ and Cu²⁺ within 1 min. [68]. A white light emitting composite material Eu/Tb@Bi-TDPAT was prepared by encapsulating Eu(III)/Tb(III) in Bi-TDPAT. In addition, the fluorescence sensing functions of Bi-TDPAT and Bi-TATAB showed that they could detect and recognize various nitrophenols, and the optimal limit of detection is as low as 0.21 μM, which can be reused even after five cycles [69]. Eu-MOFs based on 1,3,5-benzotricarboxylic acid (H₃BTC), 4,4'-azopyridine (4,4'-AZ) and N,N-dimethylformamide (DMF), was synthesized by the solvothermal method. The Eu-MOFs display a unique luminescence quenching effect to nitrobenzene (NB) and copper (Cu²⁺) ions. The sensing mechanisms are reasonably explained based on the electron and energy transfer [70]. (Eu³⁺@MIL-53 [Al]) was fabricated through a simple and effective approach. Malachite green (MG) effectively turned off the luminescence of Eu³⁺@MIL-53 (Al) via fluorescence resonance energy transfer (FRET), thus enabling MG sensing [71].

Ln-BTC-AC-FM: (CH₃)₂NH₂[Ln₂(BTC)(AC)₃(FM)]_n (Ln=Eu), H₃BTC=1,3,5-benzenetricarboxylic acid) were synthesized through the reaction of triangular polycarboxylic acid ligand (H₃BTC) and rare earth

nitrate $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with mixed formic acid (FM) and glacial acetic acid (AC) system. $(\text{CH}_3)_2\text{NH}_2[\text{Eu}_2(\text{BTC})(\text{AC})_3(\text{FM})]$ explore its detection performance for UO_2^{2+} in aqueous solution. At the same time, 4 has a good fluorescent response to UO_2^{2+} , with a higher KSV value of $8.56 \times 10^3 \text{ M}^{-1}$ and a lower detection limit of $4.12 \mu\text{M}$ [72]. $([\text{Ln}_2(\text{NH}_2\text{-BDC})_2.5(\text{CH}_3\text{COO})(\text{DMA})(\text{H}_2\text{O})] \cdot \text{DMA})_n$, Ln = Eu, $\text{NH}_2\text{-BDC}$ = 2-aminoterephthalic acid, DMA = N,N-Dimethylacetamide) with 3D network structures, are synthesized by hydrothermal synthesis. Due to the presence of uncoordinated amino groups in the ligands, a series of post-synthesis modified compounds are successfully synthesized through aldimine condensation reaction. Based on the good fluorescence properties and stable structure of coordination polymers and post-synthesis modified compounds in water or organic solvents, they are able to be used as potential fluorescence sensor for the detection of Th^{4+} , UO_2^{2+} , and $\text{Cr}_2\text{O}_7^{2-}$ [73]. 2-Aminoacetophenone (2-AA) is a metabolite produced in large quantities by the pathogenic bacteria *Pseudomonas aeruginosa* (PA), which is a biomarker for PA in water. Eu-MOF shows a high sensitivity toward 2-AA with a KSV value of $3.563 \times 10^4 \text{ M}^{-1}$, rapid luminescence response in 12 s and high-selectivity and anti-interference ability with the existence of common detection indexes in drinking water owing to the good match of the energy levels of Eu-MOF and 2-AA [74]. Ligand with tetracarboxylate group, 5,5'-(naphthalene-1,5-diyl)diisophthalic acid, have been synthesized solvothermally. (Eu-MOF) exhibit the characteristic emissions of Eu(III) benefiting from the excellent antenna effect of the ligand. It is noteworthy that the Eu-MOF, has been proven to be treated as a fluorescent switch for DMF with more than 2-fold enhancement and acetone, which triggers a superior luminescence quenching giving an almost 100% quenching efficiency, based on sensitively turned on and turned off effects, respectively [75]. The sensing of phosphate anion (PO_4^{3-}) is an important subject for human health and environmental monitoring. A unique ratiometric fluorescent nanoprobe based on postsynthetic modification of $\text{UiO-66}(\text{COOH})_2$ with Eu^{3+} and Ce^{3+} ions toward PO_4^{3-} was proposed (designated as $\text{Eu/Ce/UiO-66}(\text{COOH})_2$). Such a useful phenomenon is exploited for the construction of a ratiometric fluorescence platform for the detection of PO_4^{3-} . The assay exhibited a good linear response in the $0.3\text{--}20 \mu\text{M}$ concentration range with

the detection limit of $0.247 \mu\text{M}$ [76]. Selective and rapid detection of nitro explosives is one of the vital issues for human security as well as environmental safety. Eu-MOF extremely sensitive towards trace amount of nitrobenzene and show high selectivity among other non-nitroaromatic compounds as well [77]. Eu-bdo-COOH , H_4bdo = 2,5-bis(3,5-dicarboxylphenyl)-1,3,4-oxadiazole). The static water contact angles can controllably range from 43 to 142° , and the amylamine-modified MOF (AM) obtains the strongest hydrophobicity. In addition, a super hydrophobic aerogel is constructed with AM microspheres and reduced graphene oxide (rGO) for efficient oil-water separation. The AM-rGO aerogel (AM-rGA) exhibits fast and efficient absorption of various oily substances from water, and the adsorption capacity of dibromoethane reaches up to $14,728 \text{ wt } \%$ [78]. $([\text{Ln}(\text{BIPA-TC})_0.5(\text{DMA})_2(\text{NO}_3)] \cdot \text{DMA} \cdot \text{H}_2\text{O})_n$ (1-Ln, Ln = Eu) and $([\text{Ln}_2(\text{BIPA-TC})_{1.5}(\text{DMA})_3(\text{H}_2\text{O})_2] \cdot 2\text{DMA} \cdot 2\text{H}_2\text{O})_n$ (2-Ln, Ln = Eu), were successfully constructed via a solvent regulation strategy based on a π -electron rich tetracarboxylate ligand (H4BIPA-TC). Fe^{3+} exhibits the quenching effect for 1-Eu with the quenching efficiency of 93.1%. 2-Eu is the first MOF sensor for Mg^{2+} with the lowest detection limit of $1.53 \times 10^{-10} \text{ mol L}^{-1}$ and displays good recyclable capability [79].

4. Application in high technology

4.1. Eu-MOF and supercapacitor (SCs) applications

Enhanced performance of the fabricated novel electrode owing to its huge electroactive surface area and excellent electrochemical conductivity and good morphology. The rapid charge-discharge property of super capacitors based on metal-organic frameworks (MOFs) has seen excellent applications in energy storage equipment. Eu-MOF was used as a precursor for Eu transition metal to fabricate EuZrSe_3 via the wet chemical method. Specific capacitance (Cs) around 1543 F/g & detected a remarkable energy density of 97 Wh/kg at a current density around 3.0 A/g in 2.0 M alkaline KOH electrolyte. Despite its greater specific energy (97 Wh/kg) and high-power density (658.8 W/kg), it also has 93.58 % retention efficiency after 10,000 cycles [80, 81]. ZIF-series, UiO-66/67 , MIL-based, MOF-74, MOF-5, $\text{Ni}_3(\text{HITP})_2$, $\text{Cu}_3(\text{HITP})_2$ are widely used in MOF-based SCs. Furthermore, mixed-metal MOF and compositing materials such as PANI (conductive

polymers), graphene, CNTs, and nanomaterials or using as precursor material, provide higher surface area, simultaneous EDLC and pseudo capacitance effect which is desirable for electrochemical devices. The aqueous electrolyte such as KOH and H₂SO₄ are well-demanded to ease charge transfer in SCs [82].

4.2. Eu-MOF and pH & temperature sensing

The wide and even whole pH range electrochemiluminescence (ECL) is attractive for steroid estrogens detection under harsh conditions (such as strong acid and alkali). As ECL luminophore has been synthesized via the specific 2, 4-bis(3, 5-dicarboxyphenylamino)-6-oltriazine (H4BDPO) ligand with acid-base buffering effect. The constructed ECL biosensor based on the Eu-MOF realized sensitive detection of trenbolone under wide pH range (In order to maintain the biological activity of antigen and antibody, the studied pH value is 5–8.5), in which the limits of detection were 3.95 fg/mL (pH = 5.0), 2.36 fg/mL (pH = 7.4) and 5.48 fg/mL (pH = 8.5) respectively [83]. Eu(BTA)@CPP3 for wide range pH sensing (1.19–13.90) with blue (~430 nm) and red (~613 nm) luminescent centers. Interestingly, Eu(BTA)@CPP3 shows three types of luminescent response modes in the process of pH sensing, including red emission quenching (1.19 < pH < 7.56), red emission quenching while blue emission enhancing (8.36 < pH < 12.04), and blue emission quenching (12.20 < pH < 13.98). Furthermore, a luminescent pH test paper based on Eu(BTA)@CPP₃ is prepared and is used to determine the pH practically [84]. Eu connected benzophenone-4,4'-dicarboxylic acid (H₂BPND), 4,4'-dicarboxydiphenyl ether (H₂OBA), and terephthalic acid (H₂BDC) as the ligands produce Eu MOFs (figure 5). Eu_{0.0143}Tb_{0.9857}-L (L = BPND2-, OBA2-, and BDC2-) were carried out for temperature (T)-sensing [85].

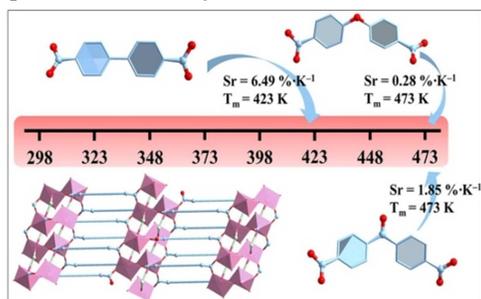


Figure 5. Eu_{0.0143}Tb_{0.9857}-L (L = BPND2-, OBA2-, and BDC2-) structure and temperature sensing [85].

4.3. Eu-MOF and anticounterfeiting detections

Lanthanide metal organic frameworks (Ln-MOFs) as excellent fluorescent materials have shown enormous potential applications, especially in fluorescence sensing and anticounterfeiting. However, very few examples of Ln-MOFs can realize both fluorescence sensing and anticounterfeiting simultaneously based on the same fluorescence response mechanism. A multifunctional platform constructed by a multicolour-switchable fluorescent Ln-MOFs (isostructural Eu-MOFs and Tb-MOFs) triggered by anti-cancer drugs (6-MP and 6-TG) were prepared by a simple hydrothermal method. The multifunctional platform is composed of a sensing platform for detecting anti-cancer drugs and an anticounterfeiting platform for information on encryption and decryption. The sensing platform based on Eu-MOFs exhibits great selectivity, high sensitivity, and low detection limit toward anti-cancer drugs (6-MP and 6-TG) with the assistance of sensing intermedium (Cu²⁺) [86]. The heterometallic MOFs based on combinations of Eu, Nd, and Yb with the tetratopic linker 1,3,6,8-tetrakis(4-carboxyphenyl)pyrene facilitate the intentional concealment of the visible emissions from Eu while retaining the infrared emissions of Nd and Yb, creating an optical tag with multiple covert elements [87]. A fluorescent composite containing Eu-MOFs, 0D Cs₄PbBr₆, and 3D CsPbBr₃ is synthesized. The permanent and unique photochromic effect enables anticounterfeiting and microsteganography with increased security through a micropatterning technique. Moreover, the RGB luminescence is highly stable after encapsulation by a transparent polymer [88]. A series of mCB-Eu/Tb1-y (y = 0-1) MOFs using a highly hydrophobic ligand mCBL1: 1,7-di(4-carboxyphenyl)-1,7-dicarba-closo-dodecaborane was synthesized. The materials are stable in water and at high temperature. The observed time-dependent emission (and color), in addition to the high QY, provides a simple method for designing high-security anticounterfeiting materials [89]. Eu-MOF and CH₃NH₃PbBr₃ (MAPbBr₃) perovskite were introduced onto pulp fibers (PFs) to prepare fluorescent anti-counterfeiting and encryption papers. Eu-MOF@PFs paper emitted red fluorescence at 254 nm UV excitation. The appropriate addition amount of lead nitrate was 0.6 mmol. Pb/Eu-MOF@PFs paper was immersed in MABr solution to prepare MAPbBr₃@Pb/Eu-MOF@PFs paper. The

above paper-based fluorescence materials were potential for advanced anti-counterfeiting and encryption applications [90]. $\text{Eu}_2(\text{L})_3 \cdot \text{DMF} \cdot \text{H}_2\text{O} \cdot \text{DMF} \cdot \text{H}_2\text{O}_n$ was constructed using the 4'-(1H-1,2,4-triazol-1-yl)-[1,1'-biphenyl]-3,5-dicarboxylic acid (H_2L) ligand and Eu^{3+} ions under solvothermal conditions. $1\text{-Eu}_{0.01}\text{Gd}_{0.6015}\text{Tb}_{0.3885}$ has a higher quantum yield (36.49%). Meanwhile, 1-Ln shows excellent performance in fluorescence sensing ($K_{\text{sv}} = 1.5143 \times 10^4 \text{ M}^{-1}$) and anticounterfeiting applications [91].

5. Application in biological system

5.1. Eu-MOF and dopamine & histidine detections

The amount of dopamine (DA) in the body is closely related to the occurrence and development of Parkinson's disease. However, DA detection in real body fluids is still challenging. A high-selectivity and high-sensitivity label-free lanthanide metal organic frameworks (MOFs) was developed to monitor DA in urine samples from Parkinson's patients (figure 6). A good response for DA in the range of 10^{-9} to 10^{-4} M and a limit of detection (LOD) of 0.65 nM were obtained, consistent with the detection range of DA in a variety of biological fluids. An efficient strategy for visual and on-site detection of DA in the clinic, which can assist in early diagnosis of Parkinson's disease [92]. Eu-BTC (1,3,5-benzenetricarboxylic acid) was synthesized and further modified to obtain Cu@Eu-BTC , which simultaneously plays multiple roles such as fluorescence internal standard, nanoreactor, cooperative catalysis effect and color shift enhancement. The Cu@Eu-BTC dispersion-based method exhibits ultra-sensitive (limit of detection, LOD is 0.01 μM) and wide-range linear response (0.04-30 μM) to Dopamine (DA) in real serum. More importantly, it has excellent selectivity for DA, even in the presence of epinephrine and norepinephrine analogs. Thus, this method realizes the accurate and precise quantification of DA in serum (recoveries: 98.1%-110.1%, relative standard deviation $\text{RSD} < 4.6\%$) [93]. After the introduction of Eu^{3+} ions in the lattice nodes of Bi-MOF, the Eu/Bi-MOF generates a strong red luminescence induced by antenna effect; Therefore, Eu/Bi-MOF could detect histidine as a ratiometric fluorescence sensor with "turn-on" response. More importantly, the proposed sensor exhibited fast response, high selectivity and low detection limit (0.18 μM) toward histidine [94].

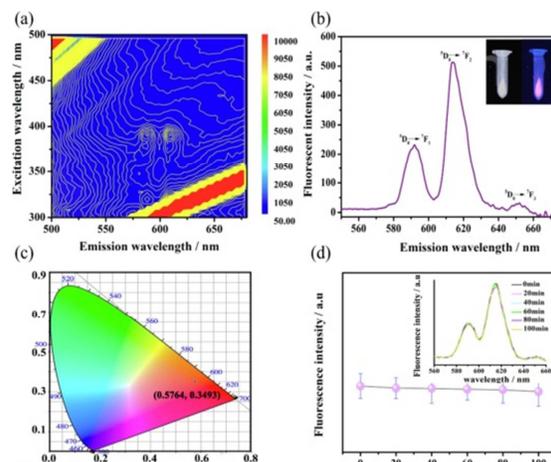


Figure 6. (a) The three-dimensional fluorescence spectrum of Eu- α CD nanoparticles. (b) Emission fluorescence spectrum of the Eu- α CD nanoparticles; the inset photograph shows Eu- α CD nanoparticle powder under bright-field light and 365 nm UV light. (c) The CIE color coordinate (0.5764, 0.3493). (d) The optical stability test of Eu- α CD nanoparticles with fluorescence intensity (the inset shows emission spectra of Eu- α CD nanoparticles at different times) [92].

5.2. Eu-MOF and 1-hydroxypyrene (1-HP) detections

$\text{Eu}(\text{TTA})_0.2@9\text{-1-UMOF}$ is developed as a ratiometric sensor for detecting 1-hydroxypyrene (1-HP, the biomarker of polycyclic aromatic hydrocarbons (PAHs)) and Cu^{2+} , which promotes the pre-diagnosis of human health. Notably, $\text{Eu}(\text{TTA})_0.2@9\text{-1-UMOF}$ exhibits excellent selective recognition ability for both 1-HP and Cu^{2+} with high sensitivity (LOD = 4.06×10^{-6} mg/mL, 3.85×10^{-7} mol/L, respectively) and fast response speed [95]. Europium connected 2,6-di(2',5'-dicarboxylphenyl)pyridine (H4ddpp) has an outstanding capacity for recognizing urinary 1-hydroxypyrene (1-HP) (figure 7) with a quite fast response and high sensitivity, giving the quenching efficiency of 98.2% after the immersion time for just 1 min and 73.2% with the amount of 1-HP only 0.05 mg/mL [96].

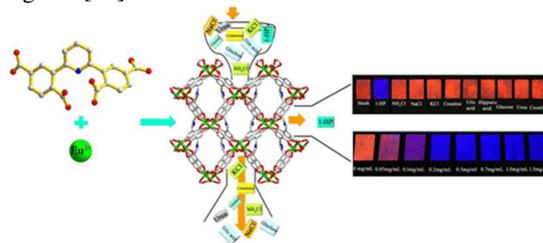


Figure 7. Eu-ddpp structure and application in detection of urinary 1-hydroxypyrene (1-HP) [96].

Sensors were developed by incorporating nonionic conjugated polythiophenes with a PLQY as high as 65% into lanthanide- MOFs (CP1-Eu-MOF and CP2-Eu-MOF) using an in-situ synthesis strategy. Significantly, the unique structure of CP2-Eu-MOF sensor displays superior performance with enhanced sensitivity (LOD \sim 1.02 pM) that is 1.63 times higher than that of CP1-Eu-MOF (LOD \sim 1.66 pM) for rapid 1-HP detection. Moreover, portable sensory films were fabricated by incorporating CP2-Eu-MOF into a poly(vinylidene difluoride) (PVDF) matrix to produce CP2-Eu-MOF/PVDF films for the visual detection of 1-HP levels as low as 25 pM. Finally, the feasibility of successfully analyzing the levels of 1-HP in urine was verified by testing real urine samples with satisfactory recoveries of 94.1-103.5% [97].

5.3. Eu-MOF and various types of antibiotic detections

The nitrofurans/nitroimidazole/sulfonamide antibiotics are significant chemotherapeutic agents for the prevention and treatment of infections by bacteria. However, the misuse of antibiotics can trigger antimicrobial resistance or even result in environmental pollution by antibiotic residues. Residual tetracycline (TC) in animal food caused by abuse of antibiotics leads to many chronic diseases in the human body. The misuse of tetracycline (TC) will cause adverse effects on environment and has become a serious problem threatening human health. Fluoroquinolone antibiotic (FQ) residues, such as ciprofloxacin (CIP) and ofloxacin (OFLX), have aroused public concerns owing to their serious impact in environmental water or food fields which influence human health. Rapid, facile, and accurate detection of antibiotic residues is vital for practical applications. A sensitive, visual, and rapid analytical method for sensitive detection of ciprofloxacin and chloramphenicol was used a nano-sized rod-shaped Eu-MOF (figure 8). A silicon quantum dots (SiQDs) hybride MOFs multicolor fluorescent nanosensor (SiQDs@MOF-Eu) was elaborately tailored for tetracycline detection. Upon the addition of TC, the emission intensity of the SiQDs decreased slowly while that of the Eu^{3+} ion increased significantly, accompanied by obvious blue-red color switching, resulting in ultrahigh sensitivity (detection limit 3.16 nM). [98].

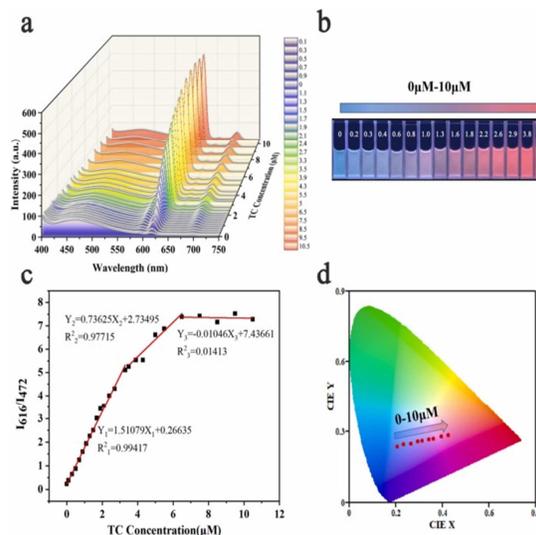


Figure 8. (a) FL spectra of the nanosensor in the presence of various concentrations of TC, (b) the FL discoloration images of SiQDs@MOF-Eu in the presence of various concentrations of TC under UV lamp ($\lambda = 365$ nm), (c) linear relationship between the ratio of emission intensity (I_{616}/I_{472}) and TC concentration, (d) CIE coordinates in the presence of various concentrations of TC [98].

Under the optimized experimental conditions, the detection limits of the developed method for ciprofloxacin and chloramphenicol detection were 0.0136 and 3.16 μM , respectively [99]. $([\text{Ln}(\text{ddpp})(\text{H}_2\text{O})] \cdot \text{CH}_3\text{CN})_n$ ($\text{Ln} = \text{Eu}$ and Gd , $\text{H}_4\text{ddpp} = 2,5\text{-di}(2',4'\text{-dicarboxylphenyl})\text{pyridine}$) were synthesized. Complex 1-Eu displays ultrahigh acid-base stability and thermal stability. Furthermore, luminescence measurements revealed that 1-Eu could detect quinolone antibiotics with an ultralow limit of detection in aqueous solution. The ratiometric probe properties for sensing antibiotics could be attributed to the incompletely sensitized Eu^{3+} ion of the ligand [100]. A ratiometric fluorescence biomimetic sensor featured with high sensitivity and selectivity was constructed based on magnesium and nitrogen co-doped carbon dots Eu-MOFs and incorporating molecularly imprinted polymer (Mg,N-CDs/Eu-MOFs@MIP). Benefiting from the efficient dual-channel strategy, Mg,N-CDs/Eu-MOFs@MIP exhibited a wide linear range ($0.02\text{--}50 \mu\text{g mL}^{-1}$) with a sensitive detection limit (6.6 ng mL^{-1}) and a marked color transformation (blue-to-red), which was highly desirable for monitoring of oxytetracycline. [101]. $\text{Eu}(2,6\text{-NDC})(\text{COO})$ (BUC-88) was developed by employing 2,6-NDC (2,6-naphthalenedicarboxylic acid) as bridging ligands. BUC-88 performed

different sensing process toward quinolone antibiotics and tetracyclines antibiotics in terms of fluorescence intensity and color. BUC-88 exhibited excellent selectivity and sensitivity detection property toward enrofloxacin (ENR), norfloxacin (NOR) and ciprofloxacin (CIP) over other Pharmaceutical and Personal Care Products (PPCPs), accomplishing the detection limit of 0.12 $\mu\text{mol/L}$, 0.52 $\mu\text{mol/L}$, 0.75 $\mu\text{mol/L}$, respectively. Notably, BUC-88 acted as an excellent fluorescence sensor for tetracyclines antibiotics with fast response time (less than 1 s), high selectivity and sensitivity (LODs = 0.08 $\mu\text{mol/L}$). The fluorescent detection method was successfully used for visual and ultrasensitive detection of ENR, NOR, CIP and tetracycline hydrochloride (TC) in lake water with satisfied recovery from 99.75% to 102.30% [102].

Eu(TATB) can be used for sensitively and rapidly specific recognition of Sulfamethazine (SMZ) with low detection limit (0.67 μM) and eminent recyclability. This provides a reliable and effective method for on-site detection of sulfonamide antibiotics in the field of environmental monitoring [103]. Plasmonic bimetal nanostructures can be employed to amplify electrochemiluminescence (ECL) signals. a high-performance ECL platform was constructed using a Eu-MOF as a luminophore and Au-Pt bimetallic nanorods (NRs) as a plasma source. Due to the SPR effect of Au-Pt NRs, the aptasensor exhibits 2.6-fold ECL intensity compared to that of pure polyaniline (PANI)-decorated perylene tetracarboxylic dianhydride (PTCA)/Eu MOF. Moreover, decoration with PTP greatly enhances the conductivity and stability of Eu MOF, resulting in sizeable plasmon-enhanced electrochemical luminescence. The as-designed plasmon-enhanced ECL aptasensor displayed highly sensitive detection for lincomycin (Lin). The as-proposed aptasensor could quantify Lin from 0.1 mg/mL to 0.1 ng/mL with a limit of detection (LOD) of 0.026 ng/mL [104]. (Eu-TCPE, H_4TCPE = tetrakis(4-carboxyphenyl)ethylene) was established through a solvothermal method. The Eu-TCPE sensor exhibited a fast and selective response towards TC detection with a low detection limit of 14 nM in a linear range of 0-50 μM [105]. The antibiotic pollutants can be quantitatively detected by a new luminescent sensor derived from $([\text{Eu}_2(\text{FDA})_3(\text{H}_2\text{O})_3(\text{DMF})\cdot\text{DMF}\cdot 2\text{H}_2\text{O}]_n)$ (Eu-MOF, H_2FDA = furan-2,5-dicarboxylic acid). The results indicate that Eu-MOF is qualified as a promisingly

favorable sensor for the sensitive detection of the antibiotics in water, being potentially beneficial for monitoring water quality [106]. Eu/Zr-MOF material that combines the high adsorption performance of water-stable Zr-MOF and the unique emission characteristics of Eu^{3+} , which enables both sensing and adsorption functions for TC. In such way, TC can be specifically detected in a wide dynamic range (0.001–0.5 $\mu\text{g/mL}$) with a low detection limit (0.00092 $\mu\text{g/mL}$). Moreover, by taking advantage of the unsaturated character of Zr–O centers, the Eu/Zr-MOF has a TC loading capacity as high as 289 mg g^{-1} [107]. (FSS@MOF-5/GMP-Eu) based on self-assembly of Eu^{3+} and guanosine monophosphate (GMP) on the surface of fluorescein loaded MOF-5 (FSS@MOF-5) is designed and fabricated for visual detection of tetracycline (TC). The proposed FSS@MOF-5/GMP-Eu displays an excellent linear relationship with TC (0–20 μM), providing a low detection limit of 18.5 nM [108]. Eu-MOF displays a red emission being excited at 260 nm. Upon exposure to TC, significant fluorescence quenching was observed due to the inner filter effect and photoinduced electron transfer. Moreover, the developed sensor was applied for the detection of TC in milk and beef samples with recoveries of 96.1% to 106.3%, respectively. More importantly, a portable test strip based on Eu-MOF was manufactured. It is a highly selective and sensitive portable device for TC detection. The results can be distinguished immediately by naked eyes, making it become an excellent choice to detect TC in real-time application [109]. Eu-MOF containing characteristic metal chains was successfully synthesized via a facile one-pot hydrothermal method and used in simultaneous detection and removal of TC. Subsequently, the prepared Eu-MOF showed significant fluorescence enhancement at 615 nm with a wide sensitive range (0.05-60 μM) and low detection limit (3 nM) for detection of TC under pH 9. The excellent adsorption behaviours (387.14 mg g^{-1}) of Eu-MOF toward TC were demonstrated by kinetic and equilibrium experiments [110]. Eu-MOF with unique 2D (4-c) (44.62)-connected topology, which holds the outstanding fluorescent property and excellent chemical stability in aqueous solution for 15 days. Thus, Eu-MOF can be considered as a highly sensitive chemo-sensor for sensing CIP and OFLX with different fluorescent color conversion (red changes to green for OFLX and to blue for CIP) and a low detection limit of 0.693 and 0.802 ppb,

respectively [111]. $[\text{Eu}_2(\text{dtztp})(\text{OH})_2(\text{DMF})(\text{H}_2\text{O})_{2.5}] \cdot 2\text{H}_2\text{O}$ was solvothermally synthesized. It can quickly detect metronidazole (MDZ) and dimetridazole (DMZ) antibiotics as well as 2,6-dichloro-4-nitroaniline (DCN) pesticide in water with good recyclability and low detection limit [112].

5.4. Eu-MOF and enzyme detections

Tyrosinase (TYR) monophenolase activity plays a key role in the development of diseases such as melanoma. The selective and sensitive detection of TYR monophenolase activity is a persistent challenge. The Ln-MOF was prepared with Eu^{3+} and monoaromatic ligand dipicolinic acid (DPA), and it plays multiple functions such as fluorescent internal standard, chromaticity shift enhancement and fluorescence sensing. Furthermore, chromaticity shift value-based quantification greatly improves the response linearity. The linear range is 0.05–2 U mL^{-1} ($r = 0.9966$), and the limit of detection is 0.004 U mL^{-1} . The precise and accurate quantification of TYR monophenolase activity in saliva samples is realized (recovery of 96.9–102.0%, relative standard deviation <9.56%) [113]. Pyrazole-functionalized Eu-MOF based sensing film exhibits 1.6-fold enhancement of ligand fluorescence and 50% quenching of Eu emission in the presence of glycerol after 20 s of exposure to saturated vapor of nerve agent simulant. Mechanism study indicates that phosphorylation of $-\text{OH}$ from glycerol occurs accompanied with the protonation of pyrazole group, much similar to the initial inhibition of acetylcholinesterase by nerve agents [114]. Eu(DTBA) fluorescent sensor showed remarkably, during sensing Glutathione (GSH), Eu(DTBA) has shown many appealing performances, such as broad a response window (0–20 mM), fast response (3 min), high sensitivity (LOD = 0.35 μM), and excellent anti-interference ability [115]. (Eu-MOF) at room temperature for the detection of H_2O_2 (figure 9). Under the optimized conditions, Eu-MOF showed high sensitivity and selectivity with linearity ($R^2 > 0.99$) from 1 to 150 μM and a limit of detection (LOD) of 0.65 μM and was employed for the determination of H_2O_2 in human serum [116].

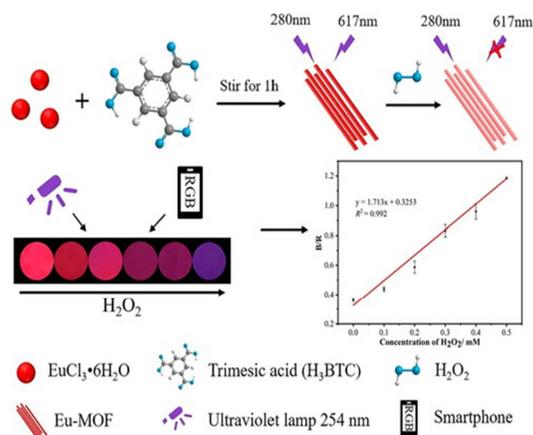


Figure 9. Preparation and detection of the europium-metal organic framework (Eu-MOF) [116].

5.5. Eu-MOF and Adenosine triphosphate (ATP) detections

Adenosine triphosphate (ATP) is an important kind of metabolized biological molecule that is formed in organisms, especially in mitochondria, is used universally as energy, and is one of the most significant multifunctional biological molecules. $\text{Eu}_2(\text{sbdc})_3(\text{H}_2\text{O})_3(\text{Eu-sbdc})$, was successfully self-assembled with $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 5,5-dioxo-5H-dibenzo[b,d]thiophene-3,7-dicarboxylic acid (H_2sbdc) can quickly and effectively optically detect ATP via a luminescent quenching mechanism. The Ksv value of Eu-sbdc is $1.02 \times 10^4 \text{M}^{-1}$, and the lower detection limit of Eu-sbdc for ATP is 20 μM , which is more sensitive to ATP [117]. $[(\text{CH}_3)_2\text{NH}_2][\text{Eu}_3(\mu_3\text{-OH})(2,6\text{-NDC})_3(\text{HCOO})_3] \cdot (\text{sol})_x(\text{Eu}(2,6\text{-NDC}))$, where 2,6-H₂NDC = 2,6-naphthalenedicarboxylic acid) was synthesized. It exhibits ratiometric detection abilities for P1,P5-di(adenosine-5') pentaphosphate (Ap5A), for use as a biomarker of dry eye disease (figure 10), with a limit of detection (LOD) of 0.031 μM , as well as excellent anti-interference properties [118].

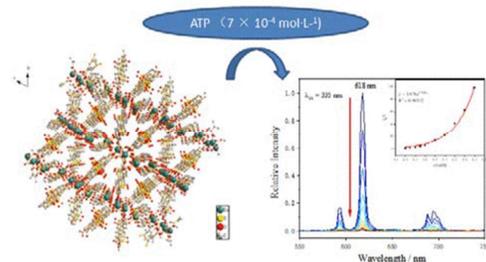


Figure 10. $[(\text{CH}_3)_2\text{NH}_2][\text{Eu}_3(\mu_3\text{-OH})(2,6\text{-NDC})_3(\text{HCOO})_3] \cdot (\text{sol})_x(\text{Eu}(2,6\text{-NDC}))$ structure and application in detection of biomarker [118].

6. Application in catalysis

6.1. Eu-MOF as catalyst for the cyanosilylation

Solvothermally promoted assembly of the multifunctional 3-amino-4-hydroxybenzoic acid ligand with the corresponding Eu salt gives rise to the formation of a porous metal-organic framework with the general formula $[\text{Eu}_5\text{L}_6(\text{OH})_3(\text{H}_2\text{O})_3] \cdot 5\text{DMF}_n$ that has been tested as heterogeneous catalyst for the cyanosilylation of a broad scope of ketones in solvent-free conditions (figure 11), using the lowest catalyst loading of 0.5 mol% ever reported, and exhibiting no leak and high recyclability [119].

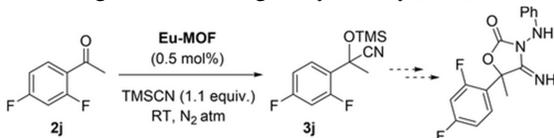


Figure 11. Potential application of the cyanohydrin product **2j** towards the synthesis of a fungicidal active compound [119].

Bifunctional ionic metal-organic frameworks (MOFs) containing Lewis acid sites (unsaturated metal sites) and halide ions (Cl^- , Br^- , and I^-) have attracted increasing attention due to their extra high activity for the cycloaddition of CO_2 with epoxides. A novel microporous MOF (1-Eu), namely, $[\text{Eu}_3(\text{L})_2(\text{HCOO})(\text{H}_2\text{O})_5] \cdot 14\text{H}_2\text{O}$ ($\text{H4L} = 2,6\text{-di}(2,4\text{-dicarboxyphenyl})\text{-4}-(\text{pyridine-4-yl})\text{pyridine}$), has been synthesized by using a new bipyridyl-based tetracarboxylate ligands (H4L). Therefore, three bifunctional N-methylation 1-Eu MOFs, 1-Eu-MeX ($\text{X} = \text{Cl}^-$, Br^- , and I^-), were successfully prepared from the 1-Eu MOF by a postsynthetic modification (PSM) method. Among them, the 1-Eu-MeI catalyst displays the highest catalytic performance [120]. Heterobimetallic Y/Eu porous metal-organic framework (MOF), based on 3-amino-4-hydroxybenzoic acid (H_2L) ligand, with the following formulae $([\text{Y}_{3.5}\text{Eu}_{1.5}\text{L}_6(\text{OH})_3(\text{H}_2\text{O})_3] \cdot 12\text{DMF})_n$ (in advance, namely Y/Eu-MOF), is described. Intriguingly, the porous nature allows for coordinated solvent molecules displacement, yielding unsaturated metal centers, which can act as a Lewis acid catalyst. This novel supramolecular entity has been tested in cyanosilylation and hydroboration reactions on carbonyl substrates of a diverse nature, exhibiting an extraordinary activity [121].

6.2. Eu-MOF as catalyst for the reduction

$[\text{Eu}_2(\text{BPTC})_2][(\text{CH}_3)_2\text{NH}_2]_2$ was prepared by 3,3',5,5'-biphenyltetracarboxylic acid (H4BPTC) and lanthanide ions by solvothermal reactions. The occupied $[(\text{CH}_3)_2\text{NH}_2]^+$ in the anionic channels exhibited excellent ion-exchange ability, which is favorable to Pd^{2+} and cationic dye adsorption. It used to load Pd nanoparticles to catalyze the reduction of nitrophenols and adsorb and desorb methyl blue (MB). The catalytic reaction efficiencies of Pd@Eu-MOF were higher than that of Pd/C (5 wt %) in the hydrogenation reaction of p-nitrophenol (p-NP) (figure 12). Moreover, Pd@Eu-MOF exhibited good cycle stability and achieved nearly 100% p-NP conversion after eight cycles. Meanwhile, compound 1 also exhibited a high adsorption ability of MB, possessing an adsorption capacity of $1.41 \text{ g} \cdot \text{g}^{-1}$ (second only to $1.49 \text{ g} \cdot \text{g}^{-1}$ reported in the literature) selectively over rhodamine B (RhB) and methyl orange (MO) in aqueous solutions [122].

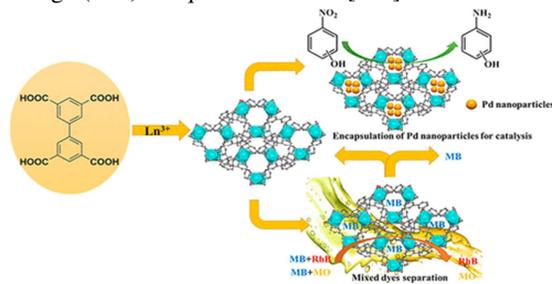


Figure 12. Pd@Eu-MOF structure and application in hydrogenation reaction of p-nitrophenol and separation of mixed dyes [122].

Eu-MOFs were applied to the catalytic reaction of C(sp³)-H bond, and it was found that the catalytic effect was gradually enhanced with the decrease of dimension and the increase of the size of channels. It showed the highest selectivity (~99%) and conversion (~99%). Moreover, catalytic cycling and stability tests showed Eu-MOFs can be a reliable catalyst [123]. $[\text{Ln}(\text{HTCPB})]$; H_4TCPB : 1,2,4,5-tetrakis(4-carboxyphenyl)benzene -as catalysts for the conversion of CO_2 to value-added products. Using these MOFs, describe the fixation of CO_2 into the epoxy ring of propylene oxide for the production of cyclic carbonates. Their study highlights the engineering of efficient catalysts capable of converting CO_2 into value-added products directly from its wet and mixed-composition streams (e.g., waste flue gas and biogas) [124]. The incorporation of both Lewis acidic lanthanide ions and the basic triphenylamine group into Eu(III)-based metal-organic frameworks using 4,4',4''-nitrilotribenzoic

acid (H_3NTB) in NMP-HCl solvent makes them efficient acid-base catalysts for both cycloaddition of epoxides with CO_2 and one-pot cascade deacetalization-Knoevenagel reactions [125]. Europium-cadmium MOF based on a zwitterionic carboxylate ligand, $[EuCd(pbbp)_2(SO_4)_2Cl_2(H_2O)_3]$, ($H_2pbbp \cdot 2Cl = 1,1'-(1,4\text{-phenylene-bis(methylene)-bis(3-carboxy pyridinium) dichloride)$, has been solvothermally synthesized. It shows interesting excitation-dependent luminescence at room temperature. The gas adsorption studies show that it exhibits highly selective adsorption of CO_2 over N_2 and H_2 under ambient conditions, which may be caused by the stronger interaction of CO_2 with the positively charged pyridinium functional groups. Photocatalytic shows good activity in rhodamine B dye degradation [126].

7. Application in gaseous state

7.1. Eu-MOF and gases detections

$([Ln_3L_6(OH)_3(DMF)_3 \cdot 5H_2O]_n)$ (where (H_2L) is 3-amino-4-hydroxybenzoic acid ligand) the heterometallic Eu-Tb mixed MOF that shows potential as ratiometric luminescent thermometers. the framework allowed showing the CO_2 sorption capacity [127]. LPC-MOF, $[Eu(Ccbp)(NO_3)(HCOO)] \cdot DMF_{0.3}(H_2O)_{2.5}$ with one-dimensional (1D) local positively charged rhomboid channels whose size matches well with the kinetic diameter of Xe (figure 13), leading to its superior Xe/Kr separation performance [128]. $[Ln(H_3pptd)] \cdot xSolvent$ [where $Ln^{3+} = Y^{3+}$ (1) and $(Y_{0.95}Eu_{0.05})^{3+}$ (1-Eu)] are converted into $[K_3Ln(pptd)] \cdot zSolvent$ [where $Ln^{3+} = Y^{3+}$ (1K) and $(Y_{0.95}Eu_{0.05})^{3+}$ (1K-Eu)] by immersing the powder of $[Ln(H_3pptd)] \cdot xSolvent$ [where $Ln^{3+} = Y^{3+}$ (1) and $(Y_{0.95}Eu_{0.05})^{3+}$ (1-Eu)] into an ethanolic solution of KOH for 48 h. The K^+ -exchanged Eu^{3+} -based material exhibits a considerable boost in CO_2 adsorption, capable of being reused for several consecutive cycles. This high adsorption selectivity is, additionally, observed for other gaseous mixtures, such as C_3H_6 and C_3H_8 [129]. Eu-DOBDC has demonstrated capabilities in the adsorption of acid gases, such as NO_2 , SO_2 , and H_2O . RE-DOBDC MOFs can exploit differences in binding of the gas molecule with the linker or the metal center [130].

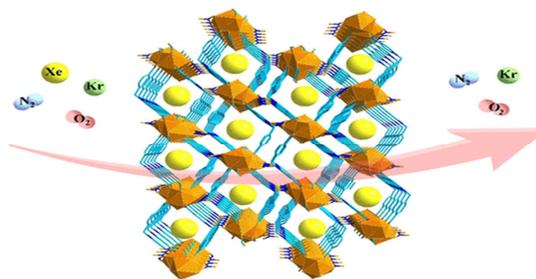


Figure 13. LPC-MOF structure and application in Xe/Kr separation [128].

7.2. Eu-MOF and different vapor detections

Eu-ETT obtained by self-assembly. Water vapor adsorption experiments showed that a large number of water molecules are adsorbed the hydrogen-bond network's being rebuilt by the adsorbed water molecules in the pore channel and thus optimizing the channels for proton transfer explained the MOF's high performance[131]. Eu^{3+} ions are introduced into ZnMOF-5- NH_2 frameworks to create a red emitting-center firstly. Next, methacrylic anhydride is incorporated to react with amino functional groups of Eu-ZnMOF-5- NH_2 to obtain Eu-MOF-L with unsaturated bonds by a covalent PSM strategy (figure 14). Furthermore, Eu-MOF-L@PBMA film is utilized for the detection of volatile organic vapors [132].

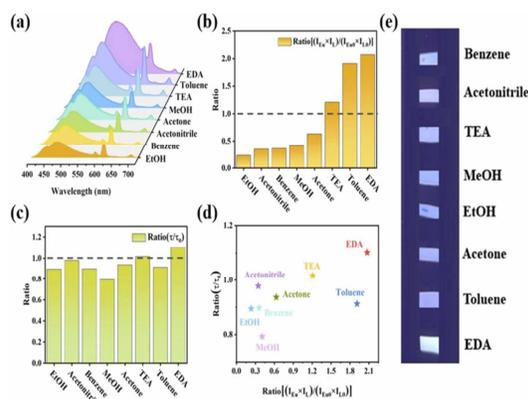


Figure 14. (a) The emission spectra of Eu-MOF-L@PBMA film in different VOC vapors; (b) the histogram of emission intensity value $[(I_{Eu0} \times I_L) / (I_{Eu0} \times I_{L0})]$; (c) the histogram of luminescence lifetime value τ/τ_0 ; (d) a 2D decoded map based on $[(I_{Eu0} \times I_L) / (I_{Eu0} \times I_{L0})]$ and τ/τ_0 ; (e) the photograph of Eu-MOF-L@PBMA film in different VOC vapors [132].

7.3. Eu-MOF and various types of acid detections

(Eu-MOF@Tb) has been developed by incorporating hexanuclear europium cluster and 2,2'-bipyridine-5,5'-dicarboxylic acid as well as coordination with Tb(III). Taking advantage of this phenomenon, a ratiometric luminescent method for detection of dipicolinic acid (DPA), a biomarker for *Bacillus subtilis* spores, was developed through differential sensitization toward lanthanide ions. This analysis method allowed for the detection of DPA in the 0.2–10 μM concentration range, with a detection limit of 60 nM. It was further validated by spiked recoveries (89.3–110%) of real-world samples with RSD values in the range 3.9–11%. The effectiveness of the proposed approach was explored in the detection of bacterial spores in real biological and environmental samples and indicated great potential for applications as a real-time monitoring system against the anthrax threat [133]. The solvothermal synthesis of a non-luminescent $\text{NH}_2\text{-BDC-Eu-MOF}$ using Eu^{3+} and 2-aminoterephthalic acid ($\text{NH}_2\text{-BDC}$) was reported. This MOF can act as a dual emission “turn-on” probe for DPA detection (figure 15). The detection limits (LOD) of this DPA probe are about 0.8 μM in ethanol and 0.36 μM in water, which are much lower than an infectious dosage of bacillus anthracis spores (60 μM) for human being [134]. A single-functionalized ligand single- Ln^{3+} based dual-emission Ln-MOF fluorescent sensor was established for portable and visual dipicolinic acid (DPA, *Bacillus anthracis* biomarker) detection. Tb^{3+} and Eu^{3+} were selected as metal luminescence centers, PTA-X (PTA: p-phthalic acid, X = NH_2 , CH_3 , H, OH) with different functional groups as one-step functionalization ligands, and the luminescent feature of four Tb-MOFs and four Eu-MOFs was predicted with the model. Then, Tb-PTA-OH was applied to DPA detection by ratiometric fluorescence, and an ultra-low limit of detection (13.4 nM) was obtained, which is much lower than the lowest anthrax infectious dose (60 μM). A portable visual assay method based on paper-microchip and smartphone integrated mini-device was further established (limit of qualification 0.48 μM) [135]. Sensitive, efficient and rapid detection of 2, 6-pyridinedicarboxylic acid (DPA), commonly labeled as the main biology marker for bacillus anthracis, is of far-reaching consequence to eliminate potential threats. A 3D Eu-MOF ($[\text{Eu}(\text{DHBDC})_{1.5}(\text{DMF})_2]\cdot\text{DMF}$) that has outstanding thermal and water stability was synthesized. Therefore, based on the high detection sensitivity of Eu-MOF (the detection limit is 1.3 μM)

and outstanding anti-interference ability, it is expected to become a prospective ratiometric fluorescence sensor for the detection of DPA [136].

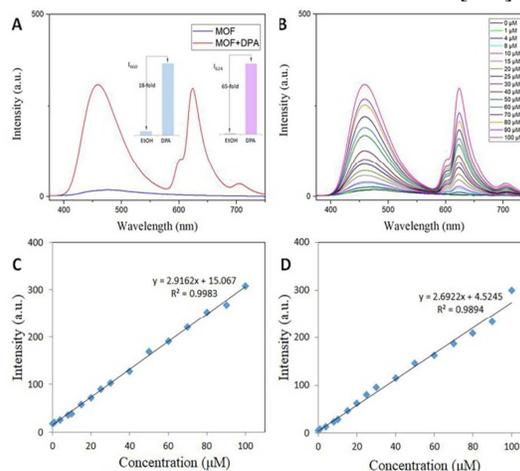


Figure 15. The fluorescence spectra of $\text{NH}_2\text{-BDC-Eu-MOF}$ in EtOH before and after the addition of DPA (A). The fluorescence spectra of $\text{NH}_2\text{-BDC-Eu-MOF}$ in EtOH under different concentrations of DPA (B). The relationship between the fluorescence intensity of $\text{NH}_2\text{-BDC-Eu-MOF}$ at 460/624 nm and DPA concentrations (0–100 μM) in EtOH (C, D) [134].

Novel composite fluorescent probes were prepared by growing Ln-MOFs (Tb-MOF, Eu-MOF, and Tb/Eu-MOF) on carboxylated porous graphene oxide (PGO-COOH). Furthermore, the unexpected antenna effect of the PGO-COOH substrate on Ln^{3+} was supposed to be another reason for the improved PL properties. The composites present ultralow detection limits as low as 5.6 nM for 2,4-dinitrotoluene and 2.3 nM for dipicolinic acid as turn-off and ratiometric fluorescent probes, respectively, which was attributed to the incorporation of PGO-COOH that dramatically enhanced inner filter effects and effectively protected the energy transfer process in the MOF components from the interference of the surrounding water [137]. Bimetallic MOFs have been reported to be advantageous over their single-metal counterparts for diverse applications. The $\text{Tb}_{1.7}\text{Eu}_{0.3}(\text{BDC})_3(\text{H}_2\text{O})_4$ acted as the probe for ratiometric fluorescent sensing of dipicolinic acid (DPA), with the performance similar to other Tb-Eu MOFs synthesized by the conventional methods. [138]. Carbon dots (CDs) chelated Eu^{3+} @metal-organic framework (Eu-MOFs) as dual-emissive ratiometric fluorescent (RF) probe was successfully fabricated by a simple one-pot in situ selective self-assembly synthetic strategy. CDs@Eu-MOFs RF probe can detect CaDPA effectively in the range of 8–170 $\mu\text{g/L}$ with good

linear relationship, and exhibited a remarkable selectivity for CaDPA [139]. (Eu-MOFs) fluorophore which constructed by the coordination polymerization of europium ions (Eu^{3+}) with 3,5-Dicarboxybenzeneboronic acid (BBDC) used for the visual detection of Gallic acid (GA). The highly colorimetric fluorescence provides a significant color change from red to blue and furtherly improves the detection precision, resulting in a visual and rapid detection of GA with a limit of detection (LOD) of 22.0 nM [140]. The Eu-MOF showed strong and stable red emission fluorescence (excited at 270 nm), and the emission was significantly quenched upon exposure to folic acid due to the inner filter effect. Folic acid was visually detected. In solution, the calculated LOD was 0.3 μM with a dynamic linearity range from 1.0 to 12.50 μM . Meanwhile, in the visual detection based on a smartphone integrated with a paper test strip, the linearity was from 1.0 to 9.0 mM with 0.12 mM as the LOD. The luminescent probe was applicable to detect folic acid in various drug tablets with recovery data ranging from 95 to 103% [141]. $\text{Eu}(\text{HDPB})(\text{phen})$ (HDPB = (1,1':3',1''-terphenyl)-3,3'',5,5''-tetracarboxylic acid, phen = 1,10-phenanthroline), was showed strong red fluorescence emission at room temperature and could be used as a selective and sensitive chemical sensor for pH and folic acid (FA) detection [142]. $[\text{Eu}(\text{L}-\text{N}_2)_2 \cdot (\text{L}-\text{Cl}_4)1.5 \cdot \text{H}_2\text{O}]$ (CUST-506). ($\text{L}-\text{Cl}_4$ = 2,3,5,6-tetrachloroterephthalic acid, $\text{L}-\text{N}_2$ = 1,10-phenanthroline) exhibit not only the integrity and the metronidazole, picric acid (PA) sensing nature of Eu-MOF powder, but also excellent processability [143]. $[\text{Eu}(\text{L})2\text{NO}_3]_n(\text{HL} = 3,5\text{-bis}(\text{triazol-1-yl})\text{-benzoic acid})$, has been designed and synthesized from the combination of the ligand containing triazole moiety and lanthanide Eu(III) ion. The application of the ratio of dual-signal improves the accuracy for detecting amino acids. The limit of detection for L-tryptophan in the range of 0–633 μM is 0.00424 μM , reaching a μM level [144]. An enzyme-free fluorescent sensing platform based on lanthanide metal-organic framework (Eu-BDC, BDC:1,4-benzenedicarboxylic acid) doped electrospinning fiber membrane. (Eu-BDC@FM) was established for the detection of uric acid (UA) in human urine. The Eu-BDC@FM has Eu^{3+} characteristic emission, excellent fluorescence stability in pH 4.5–8.0, appropriate hydrophilicity and good reusability (at least 5 cycles). The quenching constant is 10.6×10^3

M^{-1} and the limit of detection is 0.6 μM . The Eu-BDC@FM-based fluorescent sensing platform was applied to detect UA in real urine samples [145]. Two Eu-based MOF fluorescent sensors, $\text{Eu}_2(\text{CHDA})_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4(1)$ (CHDA = 1,4-cyclohexanedicarboxylic acid, C_2O_4 = oxalate group) and $\text{Eu}_2(\text{PDA})_3(\text{H}_2\text{O})_3(2)$ (p-phenylenediacetic acid = PDA), were prepared for the rapid detection of uric acid (UA) and adenosine triphosphate (ATP). The results reveal that compound $\text{Eu}_2(\text{CHDA})_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4$ suspension can selectively recognize ATP by fluorescence quenching, and compound $\text{Eu}_2(\text{PDA})_3(\text{H}_2\text{O})_3$ suspension exhibits a special selectivity for UA, all of which are due to the spectral overlap and energy competition and transfer. The two MOF-based sensors feature high quenching efficiencies K_{sv} ($5.49 \times 10^4 \text{M}^{-1}$ for ATP; $1.14 \times 10^4 \text{M}^{-1}$ for UA), low detection limits (ATP: 0.490 μM ; UA: 0.601 μM) and fast response times (in seconds). In addition, the two fluorescent MOFs can also enable the fabrication of test strips, which provided a low cost, simple and flexible way to detect trace amounts of UA and ATP in aqueous solutions or organisms [146]. $[\text{Eu}_4(\text{L})_4(\text{H}_2\text{O})_8] \cdot 10\text{H}_2\text{O}$ (H_3L = biphenyl-3'-nitro-3,4',5-tricarboxylic acid), has been constructed via solvothermal technology. Complex (H_3L = biphenyl-3'-nitro-3,4',5-tricarboxylic acid) with typical emission of Eu^{3+} ion represents dramatic luminescence quenching affect for picric acid (PA) and the linear Stern-Volmer plot was surveyed in the consistence, ranging from 0.05 to 0.15 mM ($K_{\text{sv}} = 98,074 \text{M}^{-1}$) [147]. $[\text{Eu}_2(\text{HBDPP})_2(\text{H}_2\text{O})_2(\text{DMF})_2(\text{H}_2\text{O})_2]$ (H_4BDPP = 3,5-bis(3,5-dicarboxylphenyl) pyridine; DMF = N,N-dimethylformamide) (Eu-MOF), can be considered an excellent luminescence-based sensor with a high sensitivity and low detection limit (0.1 μM) for the detection of trace amounts of ascorbic acid [148].

8. Conclusion

The present review highlights the progress made in the last few years to develop very persistent europium based organic frameworks. Certainly more and more fundamental studies will appear in this direction, which should enhance the practical application of this type of new porous material for use in different fields. Eu-MOFs contain multiple functional groups, conjugate bonds, and metal ions that can help for different uses. Our future outlook was based on the

stability of Eu-MOFs, much work must be done for enhanced the stability of Eu-MOFs. Eu-MOFs are highly expensive, so the researchers must synthesized Eu-MOFs with low expensive precursors. The powder form of Eu-MOFs is difficult to used in large scale, so it must be formulated as pellets or granule, also it is better to doped with some elements have magnetic properties for easy separation and successful for future field applications.

9. References

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