I&EC research
Industrial & Engineering Chemistry Research

pubs.acs.org/IECR

Review

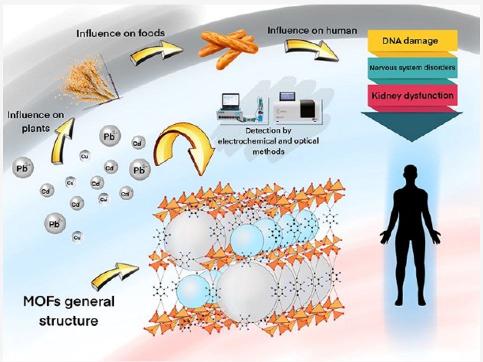
Metal–Organic Framework-Based Biosensing Platforms for the Sensitive Determination of Trace Elements and Heavy Metals: A Comprehensive Review

Hessamaddin Sohrabi, Shahin Ghasemzadeh, Sama Shakib, Mir Reza Majidi, Amir Razmjou, Yeojoon Yoon,* and Alireza Khataee*

Cite This: *Ind. Eng. Chem. Res.* 2023, 62, 4611–4627

Read Online

ABSTRACT: Heavy metals in food and water sources are potentially harmful to humans. Determination of these pollutants is critical for improving safety. Effective recognition systems are a contemporary challenge; several novel technologies for the quick, easy, selective, and sensitive determination of these compounds are in demand. Metal–organic framework (MOF)-based sensors and biosensors have crucial applications in identifying these potentially harmful substances. Here, we review electrochemical and optical biosensors for in situ sensing that are sensitive and cost effective, with a simple protocol and wide linear range. Despite the abundance of articles in this field, we assessed and checked out various basic features of MOFs as porous compounds that include clusters or ions, and some of the ligands connected to these clusters have a variety of useful properties. Afterward, we also assessed various electrochemical and optical sensing assays, which have recently gathered interest because of their potential applications for recognizing certain compounds in the environment. Their operation and approaches are dependent on their structures, the materials and component types used, and the substances they are targeting.



1. INTRODUCTION

Environmental contamination is one of the most severe problems humans are now facing. It is generally recognized that most heavy metals, particularly d-block metals, are hazardous to human health.[1−5] Heavy metals are found in several different environments, caused by industrial waste and soil pollution and various kinds of human activities which potentially contaminate water sources. Heavy-metal ions, such as Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, and Ni^{2+}, pose a significant threat to water resources because they are not biodegradable and accumulate in human bodies, environments, and living organisms primarily through the food web. They are all equally toxic, even in trace amounts. It is concerning that these metal ions, with their toxicity and carcinogenicity, are present in drinking water, even if only present in trace quantities. The identification and removal of these potentially dangerous species from the water supply and food systems must be effective and financially manageable.[6−9]

Metal–organic frameworks (MOFs) have great potential for the detection of heavy-metal cations as metals, and other nanoparticles can be deposited on these substrates. Cells and tissues can also be identified with better accuracy using modified MOFs. The biosensing properties of MOFs include low toxicity, excellent water stability, good biodegradability, and biocompatibility. There has been much interest in MOFs, owing to their well-structured organization, excellent electrical conductivity, and unusual catalytic activity. Studies have shown that MOFs can be utilized to produce biosensors that can detect a wide variety of small molecules in complex mixtures, relying upon their preferred properties. Therefore, MOFs have had a significant impact on the development of optical biosensors.[10]

Numerous efforts have been made to identify heavy-metal ions remaining in water and environmental samples. Multiple techniques, including high-performance liquid chromatography (HPLC), chemiluminescence, anodic stripping voltammetry (IASV), X-ray absorption spectroscopy (XRD), ICP-atomic emission spectrometry (ICP-AES),[11] ICP mass spectrometry (ICP-MS),[12] and atomic absorption spectrophotometry (AAS),[13] are available for detecting toxic ions.[12,14−16] However, their large-scale application is severely limited by their complexity, stringent requirements, high cost, and high skill demand. Therefore, new effective methods capable of

Special Issue: Nanobiomaterials for Biosensing and Biodegradation

Received: August 25, 2022
Revised: December 2, 2022
Accepted: December 5, 2022
Published: December 19, 2022

https://doi.org/10.1021/acs.iecr.2c03011
Ind. Eng. Chem. Res. 2023, 62, 4611−4627

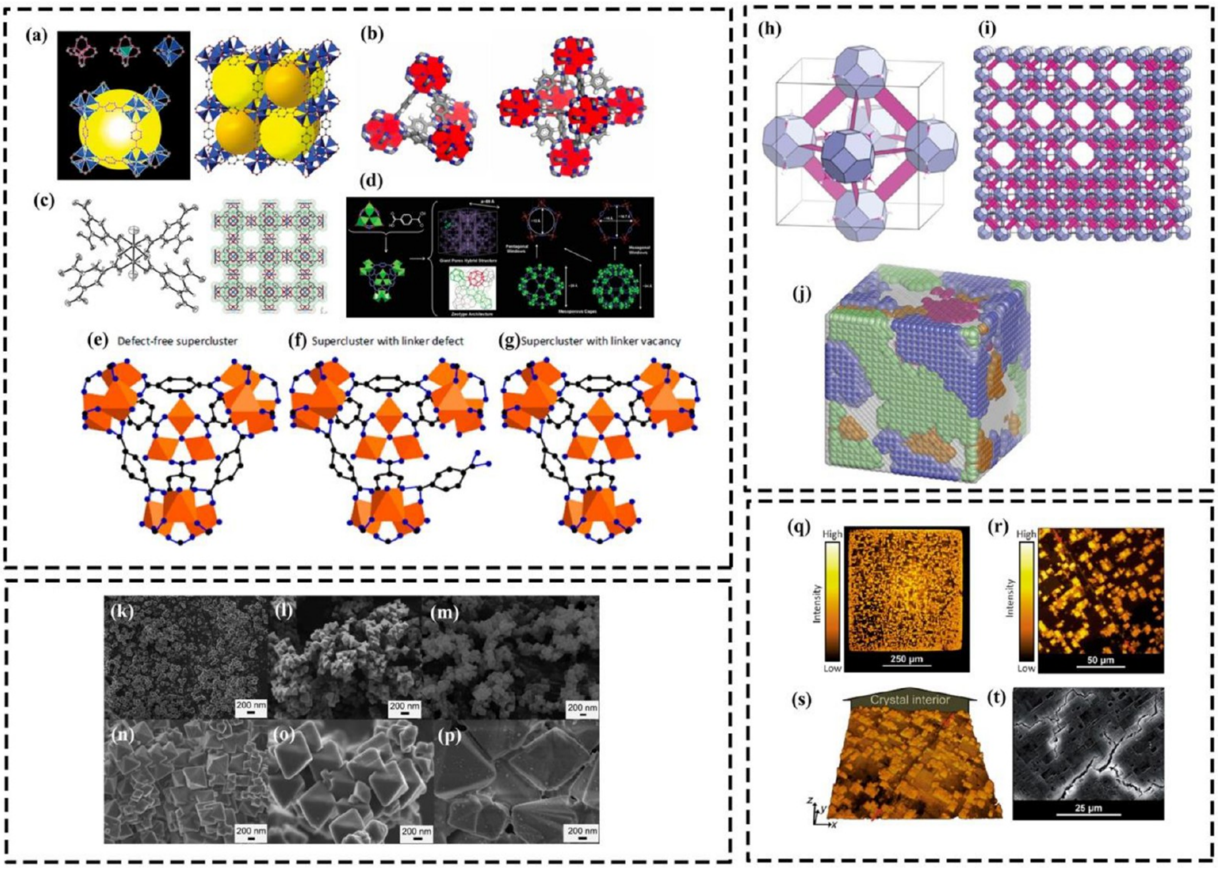


Figure 1. Crystal structures of MOFs: (a) cubic MOF-5: (b) tetrahedral or octahedral UiO-66, (c) structure of HKUST-1, (d) tetrahedral or octahedral MIL-101, (e) defect-free MIL-101(Cr) supercluster, (f) dangling linker MIL-101(Cr) supercluster, (g) MIL-101(Cr) supercluster with linker vacancy. (h) Polyhedral illustration of a single-unit cell of UiO-66. (i) Illustration of the part of the atomistic model from which a simulated diffraction pattern is made. (j) UiO-66, the defect concentration and domain size characteristics that have been obtained experimentally may be utilized to build atomistic representations of defect nanoregions in the material (Hf), (k) Scanning electron microscopy (SEM) images of UiO-66 grown for 2 h, (l) 4 h, (m) 8 h, (n) 24 h, (o) 48 h, and (p) 72 h. (q) Overview fluorescence micrograph of the outer surface of a large cubic MOF-5 crystal. (r) More detailed fluorescence micrograph of the crystal facet. (s) Three-dimensional (3D) representation of the fluorescence data presented in the panel. (t) Electron micrograph of a similar MOF-5 crystal illustrating the large irregular cracks formed upon drying. Reproduced with permission from ref 28. Copyright 2017, Elsevier.

identifying and detecting heavy-metal ions in water and environmental samples must be developed. These techniques must be simple to operate, fast to respond to, and highly sensitive and selective.[17−21]

Biosensors provide a technique that is both efficient and rapid for the detection of heavy metals. For this reason, many nanobiosensors, both optical and electrochemical, have been recommended.[22−24] Aspects such as ease of use, high sensitivity, and adaptability to a wide range of sample types (solid, liquid, or gas), which are particularly useful in this context, are beneficial for optical biosensors. Detectors of cancer markers,[25,26] antibiotics, heavy-metal ions,[27] and further analyses have been performed using MOF-based biosensors.[28] DNA strands can also be immobilized to produce biosensors on cation-based MOFs.[29,30]

One of the subclasses of coordination polymers, MOFs, is a polymer with a specific function composed of metal ions or clusters bound together by polytopic organic ligands. A mixture of MOFs with different shapes, sizes, and functional characteristics can be assembled into more than 20,000 configurations.[10,31] Highly porous structures with variable pore diameters, a range of functional groups, changeable chemical functionality, low bulk density, and the capacity to capture substances in both the chemisorption and physisorption phases are all characteristics of MOFs.[32−34] Porous MOFs have been employed in a broad range of applications, such as in the collection of radioactive waste,[35,36] release of medications,[36−38] detection of heavy-metal ions,[39,40] magnetism and catalysis, sensors, and optoelectronics.[41−44] Furthermore, when the reaction conditions are favorable, MOFs exhibit remarkable thermal and chemical stabilities resulting from the robust chemical bonds generated between the metal and linkers.[45] Metal−organic framework research is focused on the development of new techniques for mixing various types of MOFs to create hybrids.

Bimetallic MOFs have greater framework hydro-stability than single-parent MOFs.[46] Manufacturing of bimulti-metallic MOFs using various methods, including postsynthesis,[47] transmetalation,[48] and ligand-oriented bifunctional methods,[49] has been effective in the past because of their exceptional compatibility with different metal species. Using a formerly produced MOF to produce another MOF through lattice matching on the substrate of the MOF matrix is one method for creating epitaxially grown core−shell MOF-on-MOF hybrids. When developing these hybrids to create two-dimensional (2D) hybrid MOFs, the MOF-on-MOF technique may be used.[50]

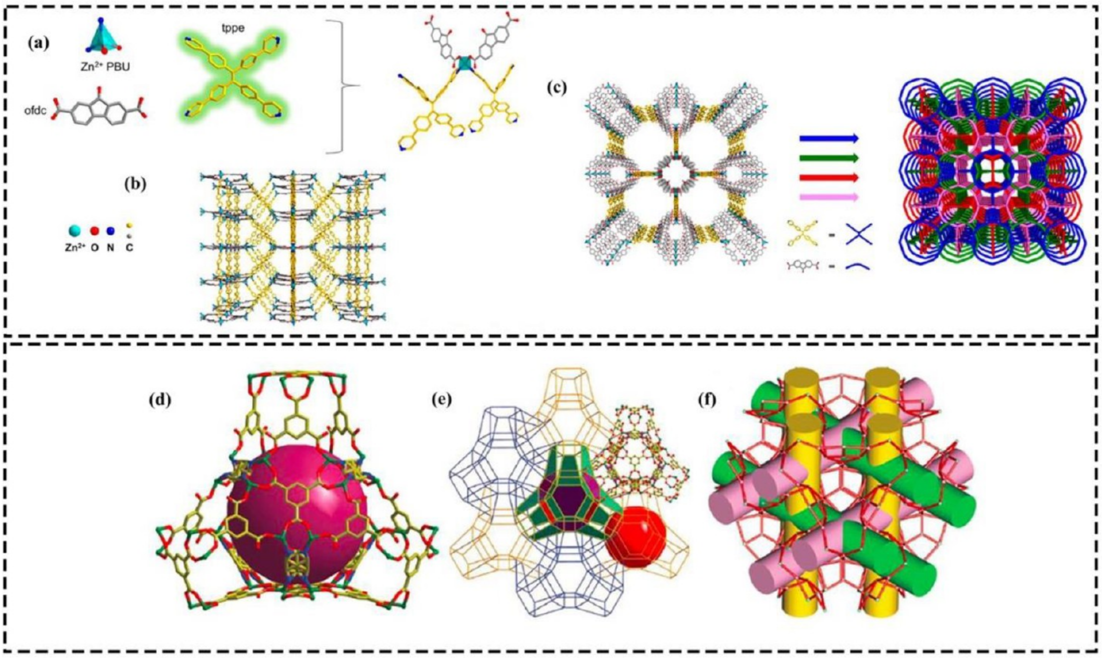


Figure 2. MOF scaffolding structure: (a) PBU (1-phenyl-3-butenyl) of luminescent MOF-261 (LMOF-261), (b) observable along *b*-axis is an individual LMOF-261 net with one-dimensional (1D) edge-sharing pentagonal and rhombohedral channels, (c) edge-sharing octahedral and cylindrical channel net displayed along the *c*-axis and simplified LMOF-261 showing 4-fold interpenetration. (d) Tetrapodal cage Zn_{48}(1,3,5-benzenetricarboxylic-1)$_{12}$(1,3,5-benzenetricarboxylic)$_8$(pyrolytic carbon)$_6$. (e) Packing of tetrapodal cages. (f) Three-dimensional (3-D) channel net running along the a, b, and c directions. Reproduced with permission from ref 65. Copyright 2019, Elsevier.

Throughout this review article, the advancement and direction of research on MOF-based sensing and biosensors for the determination and control of heavy metals have been discussed. We examined the outcomes of previous significant initiatives in this field following our results. Developing portable and complex systems based on these particles will supply more information, while simultaneously allowing researchers to undertake new research. Thus, the identification of novel applications and basic features of MOFs, their modifications, and their many uses in sensing and biosensing methods in the environment is simplified in this review. Furthermore, the impact of changes on the efficiencies of MOFs was thoroughly described, and corresponding issues were investigated. Within the scope of this investigation, key ideas and applications for the modifications and uses of MOFs in sensing methods for upcoming applications have been demonstrated.

2. MOFS: STRUCURE, CHARACTERISTICS, APPLICATIONS, AND VARIOUS TYPES

2.1. Structure. MOFs have a highly porous structure with variable pore sizes and functions, making them attractive choices for pollutant sorption. A new class of materials has emerged: inorganic and hybrid organic materials that exhibit inorganic and organic characteristics. These materials have not been observed before and represent a significant advancement in material science.[51−53] To build them, metals, such as Zn^{2+}, Cu^{2+}, and Mn^{2+}, and other elements, such as Ca^{2+}, Al^{3+}, Zr^{4+}, Ti^{3+}, Co^{2+}, and Cd^{2+}, were used. Square, pyramidal, trigonal, bipyramidal, tetrahedral, and octahedral geometric shapes were observed in MOF synthesis (Figure 1).[54] Organic molecules react directly with metals under certain conditions to construct MOF structures using a bottom-up approach, resulting in oriented growth. Layer-by-layer growth and various synthesis routes, including solvothermal (dissolving reactants in a warm solvent followed by a heating step in a pressurized condition), hydrothermal (dissolving reactants in an aqueous solution and using a heating step in a pressurized condition), ultrasonic (using ultrasonic waves to carry out the reaction), mechanochemical (using a mechanical force like hand grinding to carry out the reaction), electrochemical (using electrochemical cells and reactions with different electrodes), and microwave synthesis (using microwaves to carry out the reaction), are utilized to make the majority of MOFs.[55]

With the help of the porous structures of MOFs, pollution may be transported to the active sites more quickly, resulting in faster utilization, greater functionality of functional groups, and rapid adsorption rate adjustments. Inorganic anionic pollutants can be eliminated from the environment by utilizing a pseudo-ion exchange technique that only weakly binds organic ligands, which are subsequently replaced by the next pollutant.[56,57] Rather than using covalent connections to remove encapsulated organic contaminants, scientists now turn to noncovalent connections, including hydrogen, van der Waals, and hydrophobic contacts. If the chemical and physical frameworks of the node and binding MOFs are correctly designed, more covalent interaction sites can be created.[58]

2.2. Characteristics. Owing to the potential applications of MOFs and porous coordination polymers (PCP) in a variety of sectors and the possibility of their use to form porous crystalline polymeric metal complexes,[37,59−64] many researchers are interested in the unusual structural characteristics of these materials (Figure 2).[65]

MOFs can be applied several times for different cycles of reactions which can have rates over 90%.[55] These materials have great characteristics for types of applications like adjustable and uniform structure, thermal stability, high specific surface area, high porosity and nanoscale cavities, tunable pore size, adaptable particle dimensions, accessible cages and tunnels, specific

Table 1. Recent Advances in Electrochemical Sensing Assays for Sensitive Determination of Various Heavy Metals Using MOF Components

Recognition elements	LOD[f] (μg L^{-1})	Adsorption capacity (mg L^{-1})	Analyte	Method	Ref
Ca-MOF	0.6	–	Hg^{2+}	ASV[a]	6
2DMA(Ca-MOF)	640–1400	522	Pb^{2+}	ASV	120
2DMA(Ca-MOF)	640–1400	220	Cd^{2+}	ASV	120
trGNO/Fc-NH_2-UiO-66	85×10^{-4}	–	Cd^{2+}	Ratiometric detection	121
trGNO/Fc-NH_2-UiO-66	6×10^{-4}	–	Pb^{2+}	Ratiometric detection	121
trGNO/Fc-NH_2-UiO-66	8×10^{-4}	–	Cu^{2+}	Ratiometric detection	121
Zn-MOF/GO	6×10^{-2}	–	As^{3+}	DPASV[b]	122
Ln-MOF ZJU-27	228	–	Cd^{2+}/Pb^{2+}	SWASV[c]	123
UiO-66-EDA	–	243.90	Pb^{2+}	–	124
UiO-66-EDA	–	217.39	Cd^{2+}	–	124
UiO-66-EDA	–	208.33	Cu^{2+}	–	124
GA-UiO-66-NH_2	–	9×10^{-3}	Cd^{2+}	CV[d]/EIS[e]	125
GA-UiO-66-NH_2	–	1×10^{-3}	Pb^{2+}	CV/EIS	125
GA-UiO-66-NH_2	–	8×10^{-3}	Cu^{2+}	CV/EIS	125
GA-UiO-66-NH_2	–	9×10^{-4}	Hg^{2+}	CV/EIS	125
UiO-66-NH_2@PANI	3×10^{-1}	–	Cd^{2+}	DPASV	126
Au/SWNTs@MOF-199	25×10^{-6}	–	Pb^{2+}	CV	127

[a] ASV: Anodic stripping voltammetry. [b] DPASV: Differential pulse anodic stripping voltammetry. [c] SWASV: Square wave anodic stripping voltammetry. [d] CV: Cyclic voltammetry. [e] EIS: Electrochemical impedance spectroscopy. [f] LOD: Limit of detection.

adsorption sympathy, the presence of in-pore functionality and outer-surface modification, etc. Remarkably, one of the MOF applications based on these characteristics is detection of underground water pollutants by fluorescent detection methods which is one of the optical detection methods.[66] Based on the named advantages of MOFs, these are reliable substances for different utilizations. Detection, gas storage, separation, biomedical imaging, drug delivery, and catalysis are some of these applications.[67]

Owing to the extra interactions between the adsorbates and the adsorbents of MOFs that make them comparable to other porous adsorbents for the exclusion of toxic materials, the central metal[68−71] acts as a functionalized linker,[72−77] coordinated unsaturated site,[71,72,78−80] and loaded active species.[70,81] These interactions of MOFs, including π-complexation, H-bonding,[72,82] coordination with open metal sites, host–guest interactions, and acid–base interactions,[83] lead to the development of higher adsorption processes.

2.3. Various Types and Applications. Metal–organic frameworks containing organic groups have been suggested as proof-model adsorbents for a range of purification techniques[37,84−87] owing to their strong affinity for heavy-metal ions. As another classification of MOFs, they can be categorized as either isoreticular (IRMOFs) or microporous (MMOFs). Moreover, MOFs and zeolites can be combined. The structure may simply form at low temperatures in MOFs due to the weaker interactions between the solvents and the framework, which commonly maintains the framework's integrity and quickly provides a considerable and easily accessible porosity. Another noteworthy feature of MOFs is the broad diversity of cations that may be present. Metal–organic frameworks can take almost all of the cations in the categorizations. This presents several potentials for the creation of unique MOFs. This number has greatly increased because of the large variety of functionalized organic linkers that may be utilized in combination with inorganic components. The linker's actions include either O or N donors. When it comes to O, they are primarily mono- or polycarboxylates or mono- or polyphosphonates, and very seldom sulfonates. They all have different possibilities for bonding with inorganic cations, even when combined. Luckily, MOFs provide a significant advantage in reducing the range of possible structural kinds. Similar to how inorganic zeolitic solids accept group substitutions while retaining their topology, the functionalized linker may be replaced by larger ones as long as the connection with the inorganic compounds is preserved. A range of "isoreticular" solids (IRMOFs) are being generated, which are the reason for the possibilities of loss. But it causes an increase in the pores size of the solid and length of the ligand.[65]

Isoreticular MOFs can be developed by simply changing the length of the ligand for the identical metal species, which has a pore size dependent on its length.[88] Metal–organic frameworks have a range of uses, including recognition,[89,90] separation,[91−93] sensing,[94] gas storage,[95−97] biomedical imaging,[98] drug delivery,[99,100] and catalysis.[101−103] Because of their many structural variations and distinct characteristics, MOFs are well suited for analytical applications.[104] Using innovative MOF-based biosensors, it is now feasible to detect cancer,[25] heavy-metal ions,[27] antibiotics, and other analytes.[28]

Using centrifugation, it is possible to remove heterogeneous catalysts, such as MOFs, from the reaction mixture. In addition, their catalytic properties remain intact even after several cycles of recovery and reuse. Organic processes involving the condensation of substances benefit from the use of MOFs as catalysts, and this is especially true in the creation of C–C bonds and C–X (N–O–S) bonds. Additionally, certain homochiral MOFs may be used to catalyze enzymatically selective activities which is difficult to achieve with homogeneous catalysts.[105] This is partly due to the inherent features of lanthanide ions and the transfer of energy across ligands and their respective lanthanide centers, which leads certain Ln-MOFs to have strong luminous capabilities.[106] For instantaneous and colorimetric luminescent applications, it is vital to examine the use of the obtained information based on visible luminescent color changes caused by the presence of targeted analytes. Ln-MOFs, which can be utilized as sensors because of their strong and distinct red and green emissions, are often produced using Eu^{3+} and Tb^{3+} ions.[107] It has been demonstrated that MOFs may be used as sorbents for sampling,[108,109] solid-phase microextraction,[110−112]

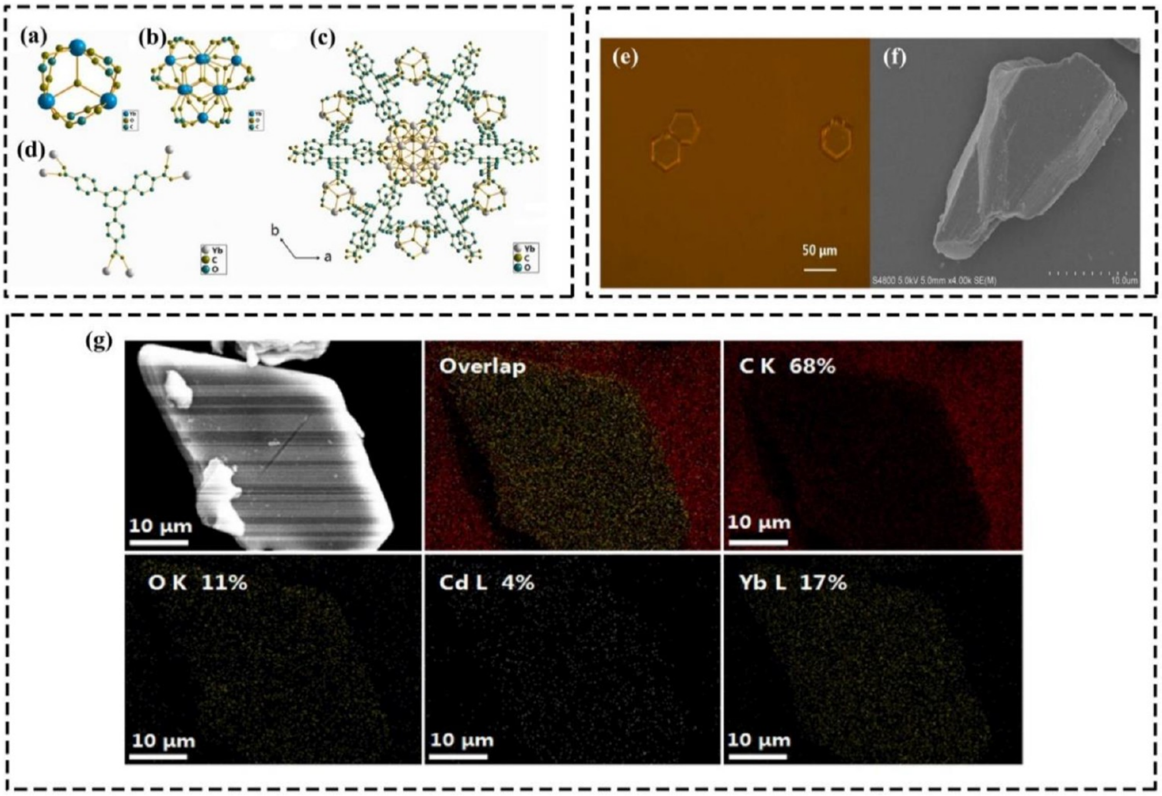


Figure 3. Lanthanide−MOF cluster and microscopy images: (a) two secondary building units of the trinuclear cluster, (b) nonanuclear cluster, (c) the ligand H_3BTB, and (d) structural depiction of ZJU-27. (e) Fluorescence microscopic image of ZJU-27. (f) Field emission scanning electron microscope (FE-SEM) image of ZJU-27. (g) Energy dispersive X-ray spectroscopy (EDS) element mapping of ZJU-27/GCE after deposition of Cd^{2+}. Reproduced with permission from ref 123. Copyright 2020, Elsevier.

solid-phase extraction (SPE),[113,114] as stationary phases for gas chromatography (GC),[115] and as stationary phases for liquid chromatography (LC).[116] The MOF adsorption technique has also been utilized to remove hazardous environmental elements. Special functional groups are commonly found within the organic linkers in MOFs. In the presence of negatively charged nucleic acid sequences, these functional groups may act as a source of potential stacking, hydrogen bonding, and electrostatic contact. Consequently, MOFs have the potential to be used as biosensors to detect trace amounts of heavy-metal ions or nucleic acid molecules in their surroundings.[117−119]

3. MOF-BASED DETERMINATION

3.1. Electrochemical-Based Sensing Assays. Biosensing elements and physical−chemical transducers are necessary for the development of biosensors. Electrochemical detectors are a viable technology because they are simple and low-cost substitutes for complex machinery. Various types of MOFs may be used as electrochemical biosensor matrices, either for the covalent or physical attachment of particular bioreceptor components or for amplifying optical, chemical, or electrical signals, as explained below.[10]

Using Ca-MOF as an electrode modifier, Kokkinos et al.[6] created an innovative 3D-printed lab-in-a-syringe device for Hg^{2+} analysis and demonstrated that it is an optimum Hg^{2+} sorbent with fast sorption kinetics. Water and soil samples were analyzed for the presence of Hg^{2+} using anodic stripping voltammetry (ASV). Voltammetric devices with improved electroanalytical features were created for the first time using 3D printing and an MOF electrode as a modifier. Hg^{2+} detection improved due to the high sorption capacity of Ca-MOF, which resulted in an LOD of 0.6 μg L^{-1}, comparable to or lower than that of traditional sensors, including plastic 3D-printed, gold, and MOF-based electrodes. Regarding Hg^{2+} detection, the Ca-MOF sensor solves the constraints of gold and MOF-based electrodes in terms of cost, manufacturing, and ease of operation, owing to the fact that it is both long lasting and malleable (see Table 1).

Pournara et al.[120] showed Ca-MOF to be capable of removing heavy-metal ions from aqueous environments and determined their concentration through voltammetry. The Pb^{2+} sorption capacity of Ca-MOF ($\simeq$522 mg g^{-1}) and Cd^{2+} sorption capacity of Ca-MOF ($\simeq$220 mg g^{-1}) were among the highest recorded for MOFs. One of the most significant findings is that the wastewater simulant solution filled with competitive ions removed Pb^{2+} (100 ppb) using a column packed with Ca-MOF (1 wt %) particles mixed in silica sand (99 wt %). The sorption capacity of Ca-MOF for Cd^{2+}, Ni^{2+}, and Zn^{2+} was considerable and was maintained even in the presence of several competing cations.

The concentrations of Cd^{2+}, Pb^{2+}, Cu^{2+}, and Zn^{2+} in aqueous solutions at mg L^{-1} levels were assessed using ASV with a straightforward ready-to-use electrochemical detector based on the modified graphite paste Ca-MOF. The results showed that the structures of Ni^{2+}-, Zn^{2+}-, and Cu^{2+}-loaded materials were quite similar to the crystalline $[Ni(H_4L)(H_2O)_4]\cdot 2DMF$ (DMF = dimethylformamide). In addition, it was found that the Pb^{2+}-loaded material shared structural properties with the $[Pb_2(H_2L)]\cdot 2H_2O$ molecule. The remarkable heavy-metal ion sorption capabilities of Ca-MOF prompted scientists to design a

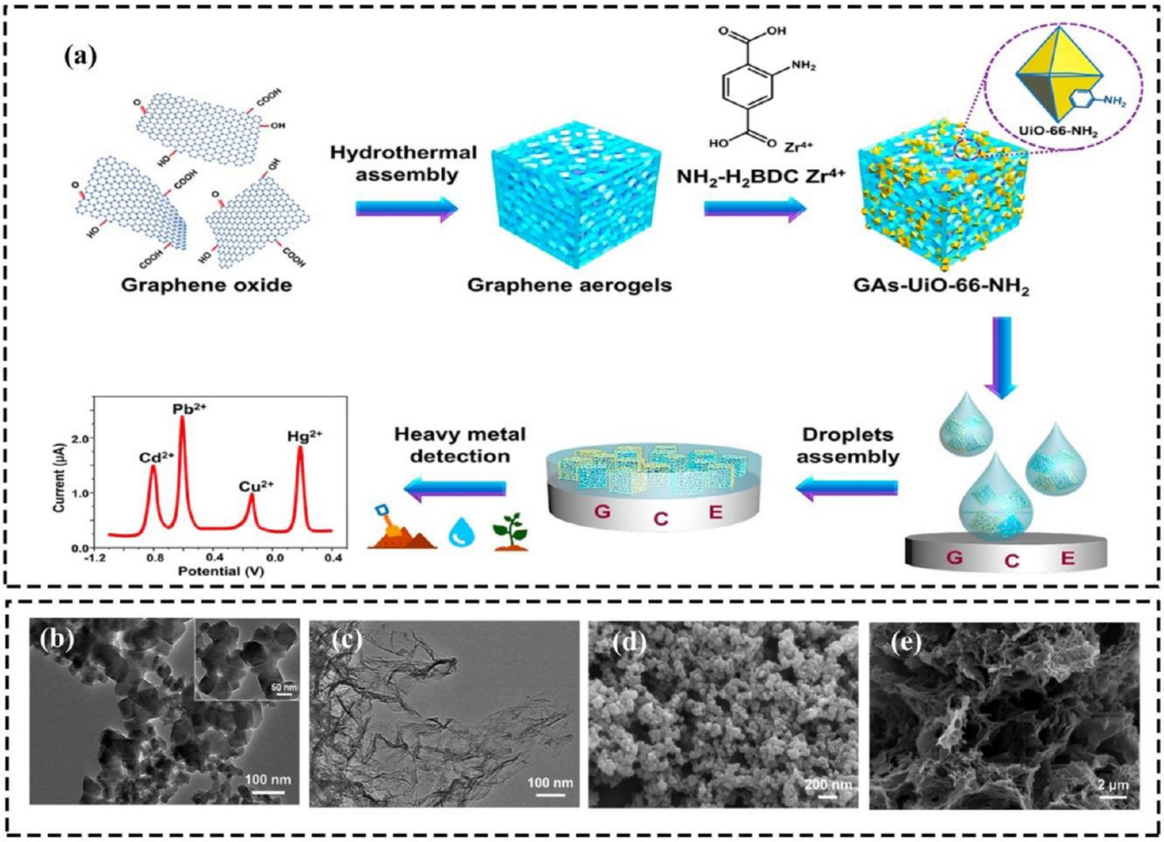


Figure 4. Graphene aerogel-based MOFs: (a) How the graphene aerogel network was grown on the UiO-66-NH_2 crystal in situ and how the GAs-UiO-66-NH_2-improved electrode was used to identify heavy-metal ions. (b) Scanning electron microscopy image of graphene aerogels. (c) Scanning electron microscopy image of UiO-66-NH_2. (d) Transmission electron microscopy (TEM) image of graphene aerogels. (e) Transmission electron microscopy image of UiO-66-NH_2. Reproduced with permission from ref 125. Copyright 2019, American Chemical Society.

simple, ready-to-use electrochemical detector using graphite paste modified with Ca-MOF. Using the ASV method, this sensor detected Pb^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} ions with a low LOD of 0.64−1.4 mg L^{-1}.[120]

The ferrocenecarboxylic acid-functionalized MOF and thermally reduced graphene oxide (trGO/Fc-NH_2-UiO-66) was created by Wang et al.[121] as a functionalized MOF composite. Utilizing a ratiometric electrochemical sensing approach based on the Fc-NH_2-UiO-66 molecule, it was discovered that it could simultaneously detect Cd^{2+}, Pb^{2+}, and Cu^{2+} ions. The porous structure of NH_2-UiO-66 and its large specific surface area make it an excellent material for the adsorption and preconcentration of heavy-metal ions. To achieve ratiometric detection, which may greatly minimize signal and noise variations caused by variable research conditions, it was demonstrated that covalently linked Fc enhances the conductivity of the material while simultaneously serving as an internal reference. The electrochemical properties of the material were improved using trGO as the substrate. The unique structural features and superior electrochemical performance of the sensing platform make it feasible to concurrently detect Pb^{2+}, Cd^{2+}, and Cu^{2+} with high sensitivity. The LODs (limits of detection) of the ratiometric electrochemical detector were calculated to be 0.8 nM for Cu^{2+}, 0.6 nM for Pb^{2+}, and 8.5 nM for Cd^{2+}.

Baghayeri et al.[122] detected As^{3+} with an LOD of 0.06 ppb by combining zinc-based MOFs with graphene oxide (GO) nanosheets to create a new nanocomposite substance, which is lower than the standard of the U.S. Environmental Protection Agency (EPA). The enhanced conductivity of reduced GO is a preferred alternative for electrode surface modification. The differential pulse anodic stripping voltammetry (DPASV) approach detected As^{3+} when the closed-circuit mode was established. These results reveal that this sensor has exceptional electrochemical functionality, with a linear range from 0.2 to 25 ppb ($\mu g\ L^{-1}$), an extremely low LOD ($S/N = 3$) of 0.06 ppb, and strong repeatability with a relative standard deviation (RSD) value of 2.1%. Additionally, the proposed sensor demonstrated excellent anti-interference capabilities and outstanding repeatability for As^{3+} detection. The GO-MOF sensor was also successfully employed to analyze trace quantities of As^{3+} released in actual water samples. Using a solvothermal approach, Ye et al.[123] created a new Ln-MOF: ZJU-27. Since their discovery, hexagonal sheet-like MOFs seem to be promising for developing electrochemical sensors for heavy-metal ion detection based on ZJU-27-modified glassy carbon electrodes (GCE). ZJU-27/GCE and SWASV were used to concurrently measure trace amounts of Cd^{2+} and Pb^{2+} under the optimum conditions. The strong conductivity and outstanding sorption capacity of ZJU-27/GCE for heavy-metal ions may be ascribed to the sensitivity, selectivity, and anti-interface ability of the sensor for Pb^{2+} and Cd^{2+} measurements in aqueous solutions. The LOD of 0.228 ppb defines the sensitivity of the sensor to Pb^{2+} (Figure 3).

Ethylenediamine (EDA) is a two-amine ligand coordination agent. Many EDA-functionalized substances have been employed for gas adsorption and water pollution remediation. The capacity of EDA to form coordination complexes with heavy-metal ions is a key factor for its wide range of uses in water purification. Therefore, EDA provided us with an ideal option for functionalizing adsorbent materials to assist in the removal of different heavy metals from wastewater. Using an EDA-functionalized Zr-based MOF (UiO-66-EDA) as the parent MOF, Ahmadijokani et al.[124] investigated the ability of the MOF to absorb heavy-metal ions from water glycidyl methacrylate (GMA) and EDA through the addition process. Pb^{2+}, Cd^{2+}, and Cu^{2+} metal ions were successfully removed from water using UiO-66-EDA (an EDA-modified version of UiO-66). The effectiveness of UiO-66-EDA for removing Pb^{2+}, Cd^{2+}, and Cu^{2+} metal ions was fully examined using parameters, such as agitation duration, pH, adsorbent amount, starting metal ion concentration, temperature, and the presence of other metal ions. An approximate second-order model was used to model Pb^{2+}, Cd^{2+}, and Cu^{2+} interactions with UiO-66-EDA. Pb^{2+}, Cd^{2+}, and Cu^{2+}were adsorbed at 243.90, 217.39, and 208.33 mg g^{-1}, respectively, in the Langmuir isotherm model, which accurately matched the experimental adsorption isotherm. Electron exchange, electron sharing, electrostatic and covalent interactions between the metal ions, and the presence of multiple functional groups on the surface of UiO-66-EDA all impacted the adsorption of Pb^{2+}, Cd^{2+}, and Cu^{2+} ions onto UiO-66-EDA.

The Fe-MOF core−shell nanostructured composite and mFe_3O_4@mC have an ordered mesoporous opening structure and inner cavity, which are unique characteristics (known as Fe-MOF@mFe_3O_4@mC) produced by Zhang et al.[134] The Fe-MOF@mFe_3O_4@mC nanocomposite was used as a sensing platform for the determination of heavy metals. The manufacture of the aptasensing assay based on Fe-MOF@mFe_3O_4@mC was comprised of a three-step process: (I) fabrication of Fe-MOF@mMn_3O_4@mC, (II) immobilization of the aptamer strands, and (III) formation of a biorecognition association between heavy-metal ions and aptamer strands to identify heavy metals (Pb^{2+} and As^{3+}). The mFe_3O_4@mC nanocapsules were manufactured by first removing the SiO_2 core from the SiO_2@Fe_3O_4@C spheres and then using a hydrothermal technique in the presence of $FeCl_3$ as a precursor and 2-amino-terephthalic acid as an organic linker to form hollow Fe_3O_4@mC nanocapsules. This is highly desirable and promising because the core−shell Fe-MOF@mFe_3O_4@mC has an extraordinarily large surface area and excellent dispersion and electrochemical efficiency. Owing to hydrogen bonding interactions and supramolecular stacking, strong binding may produce a considerable immobilizing force for aptamer strands among the Fe-MOF and aptamer strands. Before being used to determine hazardous heavy-metal ions, the as-prepared Fe-MOF@mFe_3O_4@mC nanocomposite was constructed to incorporate the catalytic properties, excellent biocompatibility, environmental friendliness, high stability, and high surface area of Fe_3O_4, carbon, and MOFs. According to electrochemical studies, there is evidence that the Fe-MOF@mFe_3O_4@mC nanocomposite's unique structure has a special selectivity for sensing As^{3+} and Pb^{2+} in natural water sources and human blood serum. The porosity and bioaffinity of the newly created nanocomposite are equally impressive. When the manufactured aptasensor was used to evaluate the presence of heavy-metal ions, such as Pb^{2+} and As^{3+}, it demonstrated a sensitivity with a low LOD of 2.27 and 6.73 pm, respectively, in a wide concentration range from 0.01 to 10.0 nm. Additionally, the manufactured aptasensor demonstrated high specificity and selectivity, renewability, strong stability, and adequate repeatability.

Lu et al.[125] developed electrochemical techniques based on graphene aerogel (GA) and MOF composites to detect several heavy-metal ions in aqueous-phase solutions (Figure 4). The MOF UiO-66-NH_2 crystals were grown in situ on a GA matrix to create GA-MOF (GA-UiO-66-NH_2) composites. Although GA acts as the primary structural component of UiO-66-NH_2, it also enhances its conductivity by accelerating the flow of electrons in its matrix. Owing to the incorporation of GAs into the structure, GA-modified GCEs exhibited high conductivity using CV and EIS electrochemical performance analysis. Further research has shown that the modified electrode can detect Pb^{2+}, Cd^{2+}, Hg^{2+}, and Cu^{2+} in aqueous solutions with high sensitivity and selectivity when used under the ideal conditions. Simultaneous detection of various metal ions has a LOD of 0.9 nM for Hg^{2+}, 8 nM for Cu^{2+}, 1 nM for Pb^{2+}, and 9 nM for Cd^{2+}. The detection of Cd^{2+}, Pb^{2+}, Cu^{2+}, and Hg^{2+} in river water and soil and vegetable leaching solutions further proves that the described technique can be used to identify a wide range of metal ions precisely and consistently in real-world samples. In addition, Cd^{2+}, Pb^{2+}, Cu^{2+}, and Hg^{2+} were recovered at rates ranging from 86.7% to 104.7%.

In a one-pot hydrothermal process, Guo et al.[135] synthesized innovative nanoscale MOFs, named nanoplate Ni-based MOFs (Ni-MOFs), which use 2-aminobenzene dicarboxylic acid as an organic linker. They employed a nanoplate Ni-MOF-modified glassy carbon electrode (Ni-MOF-GCE) as a detector to increase the preconcentration and sensing of Pb^{2+} ions using SWASV to build a novel electrochemical sensor capable of sensitive metal ion detection. The Ni-MOF-modified Pb^{2+} detection electrode demonstrated high selectivity and immutability. Operational parameters such as deposition potential, pH, and deposition duration were modified to measure the trace levels of metal ions. The optimal deposition potential was −0.9 V. The optimal pH value was 5.8, and the best deposition time was 300 s.

The conductive polyaniline (PANI) polymer was polymerized around the MOF (UiO-66-NH_2) with a core structure by a simple hydrothermal technique followed by PANI coatings, as shown by Wang et al.[126] to effectively create an electrochemical sensor: UiO-66-NH_2@PANI. The modified UiO-66-NH_2@PANI composite-modified electrode was used to detect trace quantities of Cd^{2+} ions by DPASV under optimal experimental conditions. Compared to other Cd^{2+} ion sensors, a broader linear range, improved repeatability, and a lower LOD of 0.3 μg L^{-1} were found in the UiO-66-NH_2@PANI-modified electrode. Core and shell materials must have excellent electrode properties, and their new properties, incorporating the features of each component, must improve sensor quality. Real samples were used to demonstrate the practical applicability of Cd^{2+} determinations. The photocatalyst adsorbent and acid−base catalyst demonstrated their potential uses. UiO-66-NH_2 was chosen for this purpose because of its excellent water and chemical stability and the number of amine groups in the material. The ability of PANI to accelerate electron and ion diffusion into and out of the matrix material results in an increase in the conductivity of hybrid materials. The adsorption sites on UiO-66-NH_2 are numerous and have large surface areas, making it an excellent candidate for use as the PANI backbone. Gold nanoparticles and single-walled carbon nanotube (SWCNT) nanocomposite-incorporated copper benzene tricarboxylate (MOF-199) (Au/SWNTs@MOF-199) were utilized by Shen et al.[127] to achieve the selective and sensitive detection of Pb^{2+} ions. They reported successful completion of the solvothermal synthesis of Au/SWNTs@MOF-199. It was discovered that the sensor exhibited excellent selectivity for Pb^{2+} ions exclusively when cross-analyte sensing was performed with numerous heavy-metal ions. Using error bar diagrams, they determined the electrochemical response of Au/SWNTs@MOF-199 toward Pb^{2+} to be highly sensitive, selective, repeatable, and reproducible, with an LOD of 25 pM L^{-1} and a response time of a few seconds.

3.2. Optical-Based Sensing Assays. Metal−organic framework-based biosensors can also use optical approaches to sense targeted components. Table 2 summarizes the recent analytical features of optical sensing platforms for determination of various heavy-metal compounds. For example, to detect trace Hg^{2+} levels in water, Wan et al.[128] developed and synthesized Zn-TPTC (TPTC = [2,2′:6′,2″-terpyridine]-4,4′,4″-tricarboxylic acid). The radiation intensity of Zn-TPTC is directly related to the concentration of Hg^{2+}, which ranges from 10^{-4} to 10^{-6} M. Zn-particular TPTC identification of Hg^{2+} is mostly due to the strong affinity of the ligand for Hg^{2+} and N. The LOD was found to be as low as 3.67 nM due to the small pore size, many N sites, and anionic framework (Figure 5).

Table 2. Advances in Optical Sensing Assays for the Determination of Heavy Metals in Various Real Samples

Sensor	LOD (M)	Analyte	Method	Ref
Zn-TPTC	3.67×10^{-9}	Hg^{2+}	Fluorescence	128
Cd-lMOF	–	Fe^{3+}/Ag^{+}	Fluorescence	129
Tb-MOF	10^{-7}	Pb^{2+}	–	130
Zn-MOF	10^{-8}	Hg^{2+}	Fluorescence	131
Ni-MOF	–	Hg^{2+}	–	44
Eu-MOF	$(2.48 \pm 0.014)\times10^{-7}$	Eu^{3+}	Fluorescence	66
Zn-MOF	2×10^{-8}	Fe^{3+}	Fluorescence	132
Zn-MOF	5×10^{-8}	Cd^{2+}	Fluorescence	132
Ln-MOFs	0.46 (μg L^{-1})	Pb^{2+}	FAAS[a]	133
Ln-MOFs	0.265 (μg L^{-1})	Cu^{2+}	FAAS	133

[a] FAAS: Flame atomic absorption spectroscopy.

Cd-LMOF $\{[Cd_2(BPDPE)_2(chdc)_2(H_2O)_2]4H_2O\}n$ (BPDPE = 4,4′-bis(pyridyl)diphenyl ether, H_2chdc = 1,4-cyclohexanedicarboxylic acid) was produced in three dimensions by Hu et al.[129] using a hydrothermal method. The findings revealed that $\{[Cd_2(BPDPE)_2(chdc)_2(H_2O)_2]\cdot4H_2O\}n$ (complex **1**) had great selectivity and sensitivity for detecting nitroaromatic explosives 2,4,6-trinitrophenol (TNP) and metal ions Fe^{3+} or Ag^{+}. Furthermore, it is worth emphasizing that complex **1** demonstrated very sensitive and selective fluorescence-quenching activities for the metal ions TNP, Fe^{3+}, and Ag^{+}, with quenching constants reaching 2.794×10^5 M^{-1}, 2.893×10^4 M^{-1}, and 1.483×10^4 M^{-1}, respectively. Because of its high recyclability for TNP identification, complex **1** was easily recreated in DMF using a single wash step. According to these findings, it is possible to rationally design LMOFs with improved performance by adding the appropriate ligands and metal ions to the mechanism.[129] Pb^{2+} ion detection was achieved using a novel lanthanide MOF, $[Tb(L)\ (H_2O)_5]n$, which is extremely selective and ultrasensitive (Figure 6). Only a few studies have described Tb-MOFs with single crystals larger than 6 mm. The ligands in Tb-MOFs have significant antenna characteristics that produce green light. The lack of interaction between Pb^{2+} ions and the oxygen Lewis structures on the Tb-MOFs may explain the high sensing sensitivity of the material. Tb-MOF is a dependable and simple light sensor that can be used in pollution tracking because of its good linear connection with the concentration of Pb^{2+} ions. It is the only millimeter-level bright MOF detector that has such a high LOD for detecting minuscule levels of Pb^{2+} (10^{-7} M).[130]

Xiao et al.[131] successfully achieved 3D printing of Zn-MOFs with nitrogen-rich channels and vivid blue fluorescence

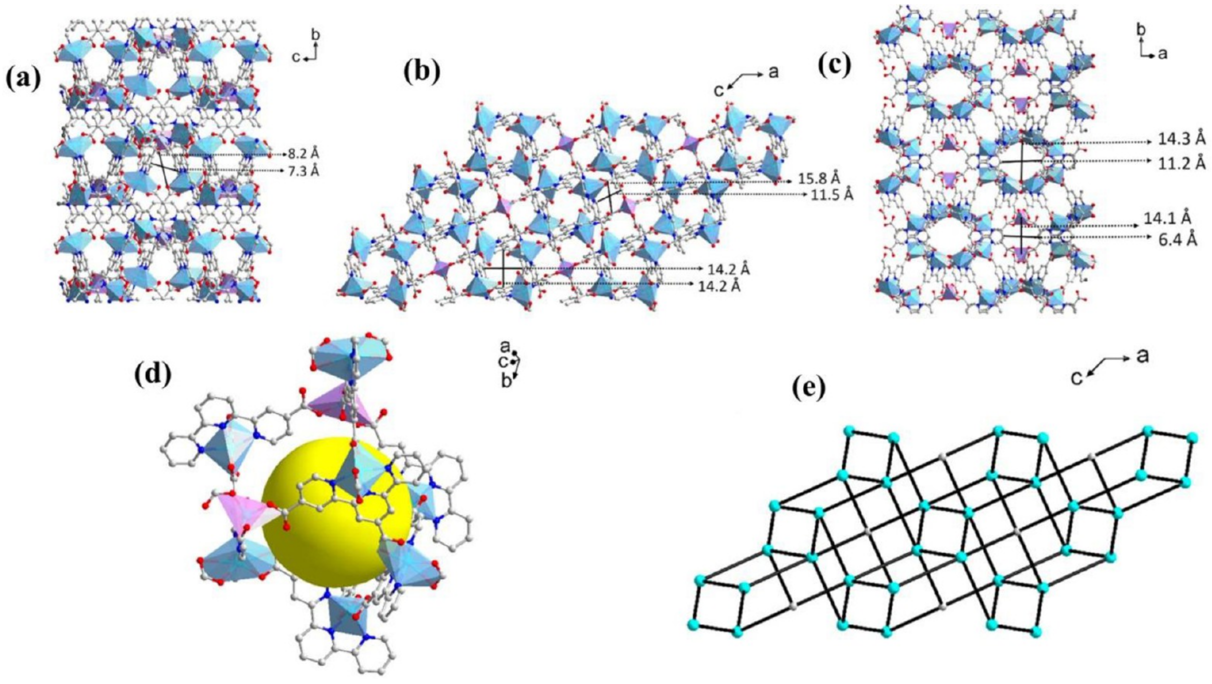


Figure 5. Structure of Zn-TPTC in view of the (a) *a* axis, (b) *b* axis, and (c) *c* axis. Zn_3-SBUs are illustrated in purple, and Zn_1-SBUs and Zn_2-SBUs are shown in blue. (d) Largest cage in Zn-TPTC. (e) Simplified topology of Zn-TPTC. The blue ball represents $ZnC_{18}H_8N_3O_5$, and the gray ball represents ZnO_4. Reproduced with permission from ref 128. Copyright 2018, Elsevier.

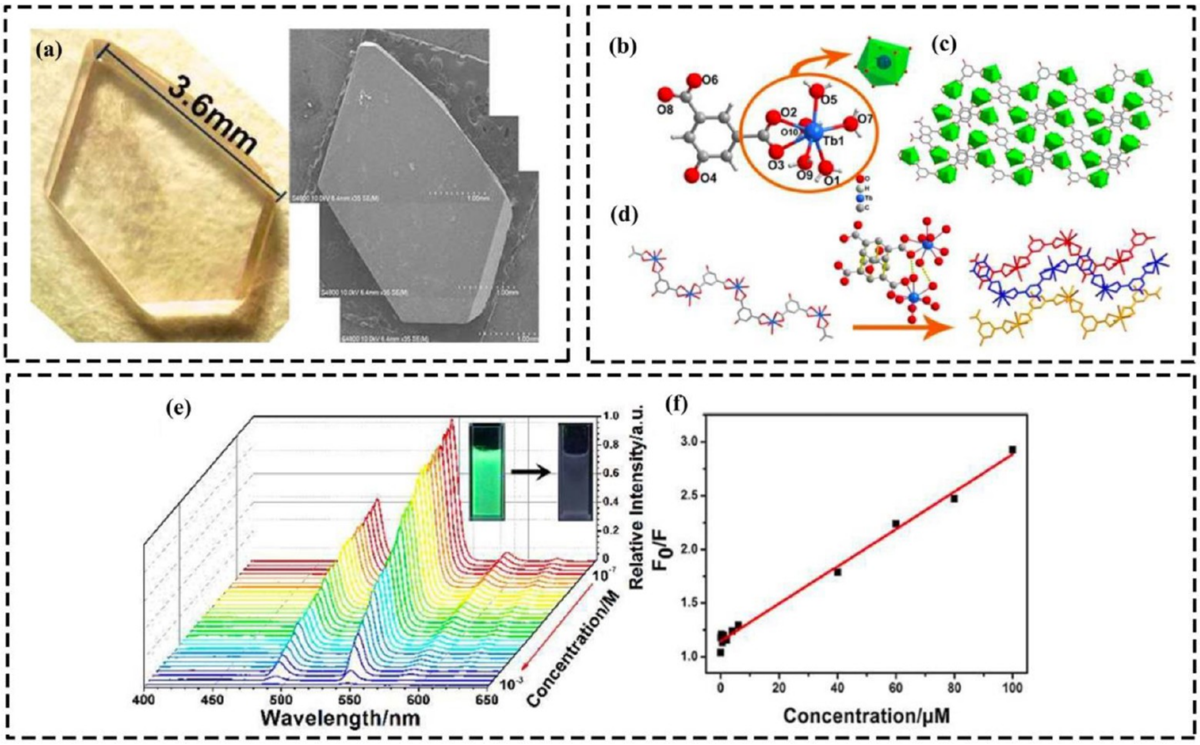


Figure 6. Optical aspects of Tb-MOF: (a) scanning electron microscopy images (right) and the optical (left) of the prepared Tb-MOF. (b) Coordinated environments of Tb (III). (c) 2-D inorganic layer of Tb-MOF formed by Tb (III) ions. (d) Three views of Tb−π-stacking interactions and hydrogen bonds that connect MOF to form a 2-D molecular model (right) and a zigzag-shaped chain molecular model (left). The strong π-stacking interactions and hydrogen bonds are represented by yellow broken lines (middle). (e) Fluorescence spectra of Tb-MOF and (f) the calibration plot. Reproduced with permission from ref 130. Copyright 2017, Royal Society of Chemistry.

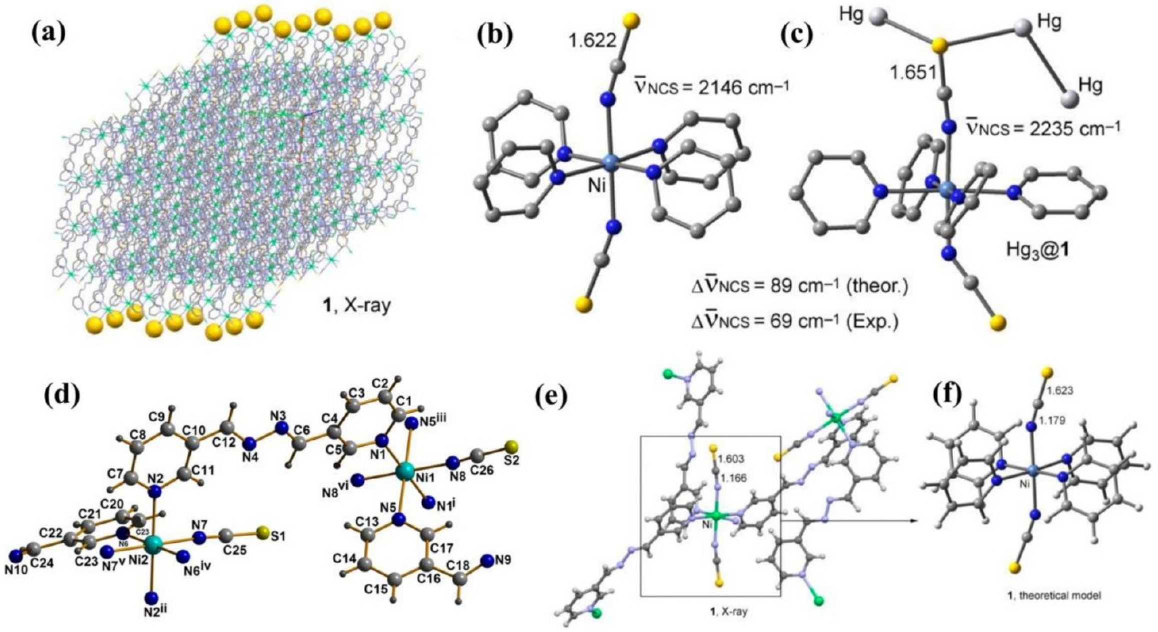


Figure 7. (a) The 3 × 3 × 3 packing of compound **1**, showing the in wire frame separated from the external S atoms in space-filling format. (b) Theoretical model of compound **1**. (c) Theoretical model of compound **1** interacting with three Hg atoms. (d) Representation of the asymmetric unit of **1**. Symmetry codes: (I) 1-x, -y, -z, (II) 1-x, - y, -z, (III) 1-x, -y, 1-z, (IV) 2-x, 1-y, -z, (V) 3-x, 1-y, 1-z, and (VI) 1-x, -y, -z. (e) X-ray of complex **1**. (f) Minimalistic theoretical model of *1*. Reproduced with permission from ref 44. Copyright 2017, Royal Society of Chemistry.

emission. Ligands containing three pyridine-ring carboxylates were discovered to have an unusual luminescent output when coupled with Zn^{2+}. Currently, metal ions may survive in the uncoordinated nitrogen atoms of the channel, resulting in regenerable ratiometric reactions with Hg^{2+} or high selectivity and sensitivity for the CrO_4^{2-} and $Cr_2O_7^{2-}$ aqueous oxidants in media with a broad linearity range. Zn-MOF, as a fluorescence sensor for Hg^{2+}, CrO_4^{2-}, and $Cr_2O_7^{2-}$ in aqueous solution, also

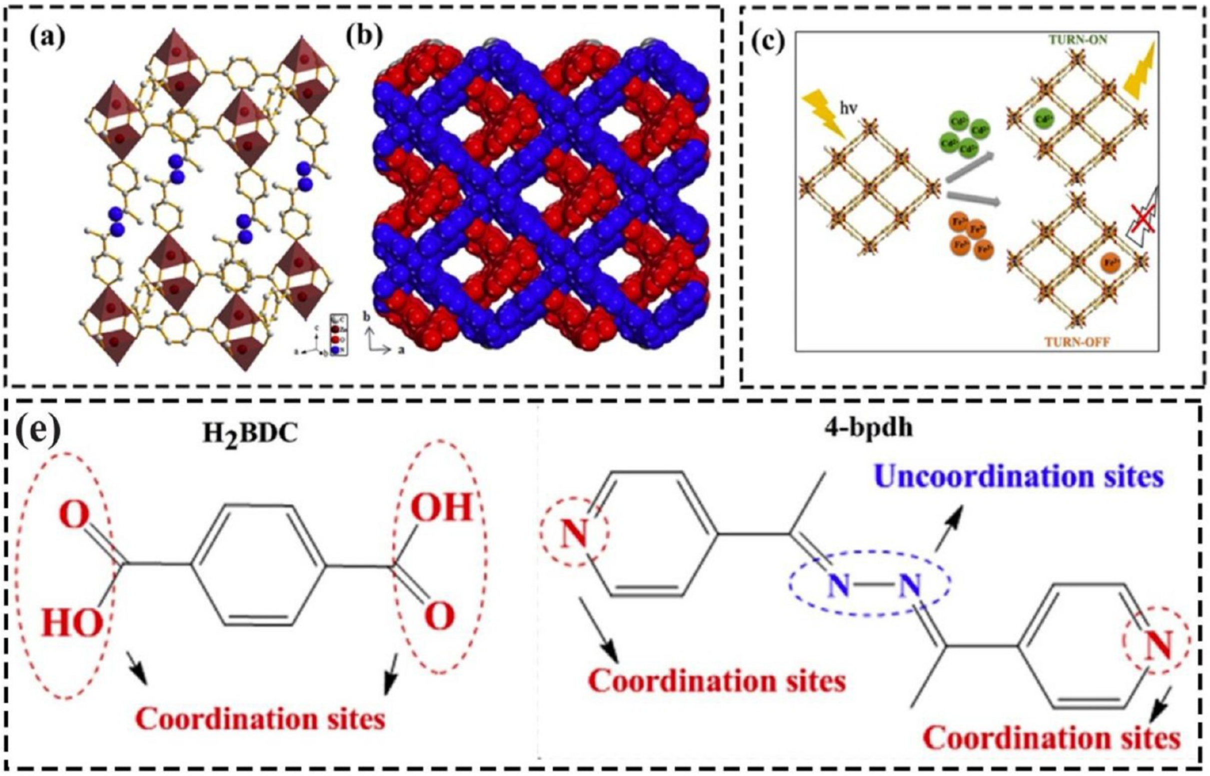


Figure 8. Structure of TMU-16: (a) elongated primitive cubic net of TMU-16, (b) 2-fold interpenetration TMU-16, and (c) fluorescence quenching and enhancement of TMU-16 by Fe^{3+} and Cd^{2+} ions. (e) Molecular structures of H_2BDC and 4-bpdh. Reproduced with permission from ref 132. Copyright 2019, Elsevier.

has outstanding photoluminescence and chemical durability. The MOF-based Hg^{2+} fluorescence probe changes color from blue to brilliant green. Despite this, the present Cr(VI) research shows that CrO_4^{2-} and $Cr_2O_7^{2-}$ have the lowest LODs. Halder et al.[44] detected and removed Hg^{2+} ions from water using a nickel-based MOF synthesized under ambient conditions, $[Ni(1,4\text{-bis}(3\text{-pyridyl})\text{-}2,3\text{-diaza-}1,3\text{-butadiene})_2(NCS)_2]$ (Figure 7). According to $[NCS_2]_n$, N-atoms are connected to the hexa-coordinated metal center by two thiocyanate moieties, whereas the sulfur end remains uncoordinated. In addition, both model's (component **1** and component with three Hg atoms) theoretical IR spectrum has evaluated and SCN's IR band attracted more attention which is around 2100 cm^{-1}. Being complexed with Hg atoms results in an increase in the wavenumber of this bond up to 89 cm^{-1} in theoretical aspect and 69 cm^{-1} in real experiments. It can be concluded that in the complex generation reaction between these two reagents SCN is participating.

Che et al.[66] used a new Eu-MOF to detect F^- and Eu^{3+} in water with high sensitivity and selectivity. 2-Aminoterephthalic acid and $Eu(NO_3)_3{\cdot}6H_2O$ were used to prepare Eu-MOF for the first time. The aggregation action of Eu^{3+}, coupled with the amino-functional groups disclosed on Eu-MOF dramatically reduced the Eu-MOF signal at 425 nm blue-violet fluorescence in the presence of Eu^{3+}. The LOD for Eu^{3+} was determined as $(2.481 \pm 0.014) \times 10^{-7}$ M. In particular, fluoride added to the amino group caused the recovery of the fluorescence, with the LOD of fluoride being $(1.145 \pm 0.019) \times 10^{-6}$ M. Typical interfering ions have little effect on Eu^{3+} detection. The invention of Eu-MOF logic detectors and paper sensors has significantly improved the detection of Eu^{3+} and fluoride ions in groundwater.

Wang et al.[136] created a new water-stable MOF$[Zn_3(DDB)(DPE)]{\cdot}H_2O$, by combining a stiff carboxylate ligand 3,5-di(2′,4′-dicarboxylphenyl) benzoic acid (H_5DDB) with a flexible bis(pyridyl) linker 1,2-di(4-pyridyl)ethylene (DPE). $[Zn_3(DDB)(DPE)]{\cdot}H_2O$ in aqueous solution is highly stable. With great selectivity and sensitivity, it may be employed as a new luminous probe to identify the harmful pesticide 2,6-dich-4-NA and heavy-metal oxy-anions and cations. Zn-MOF has a three-dimensional structure with six nuclear groups and excellent water and pH stability. Resonance energy transfer, the poor affinity of nitrogen atoms, and photoinduced electron transfer have been proposed as possible processes for luminescence quenching. Copper 2-aminobenzene-1,3,5-tricarboxylate ($Cu_3(NH_2BTC)_2$) was explored by Rubin and coworkers to identify metal ions. In addition to identifying alkaline metals, fluorescence quenching can be used to detect $Cu_3(NH_2BTC)_2$. The ligand NH_2BTCH_3 is a good fluorescent probe because of its high fluorescence in solution and in MOFs. The DMF dispersion of the MOF was used to conduct fluorescence studies by applying various metal cations to the MOF. Metal−organic framework amines and carboxylate receptors of the linker and open coordination regions of Cu^{2+} in the MOF may be utilized to quench fluorescence by divalent metals such as Mn^{2+}, Pb^{2+}, and Fe^{2+}. Another method, namely, metal-ion monitoring, proved to be very rapid and sensitive (1.55 ppm for Fe^{2+}) within minutes. The CO_3^{2-} anions would also cause total fluorescence quenching$^-$, moreover, OAc^-, and $Cr_2O_7^{2-}$, which may bind to the free amine in the ligand structure. Dimethyl formamide detected toxic dichromate at a concentration of 1.65 ppm. Even in MOFs with free and accessible functional handles (such as amines), fluorescence turn-off reactions may result from more than one route,

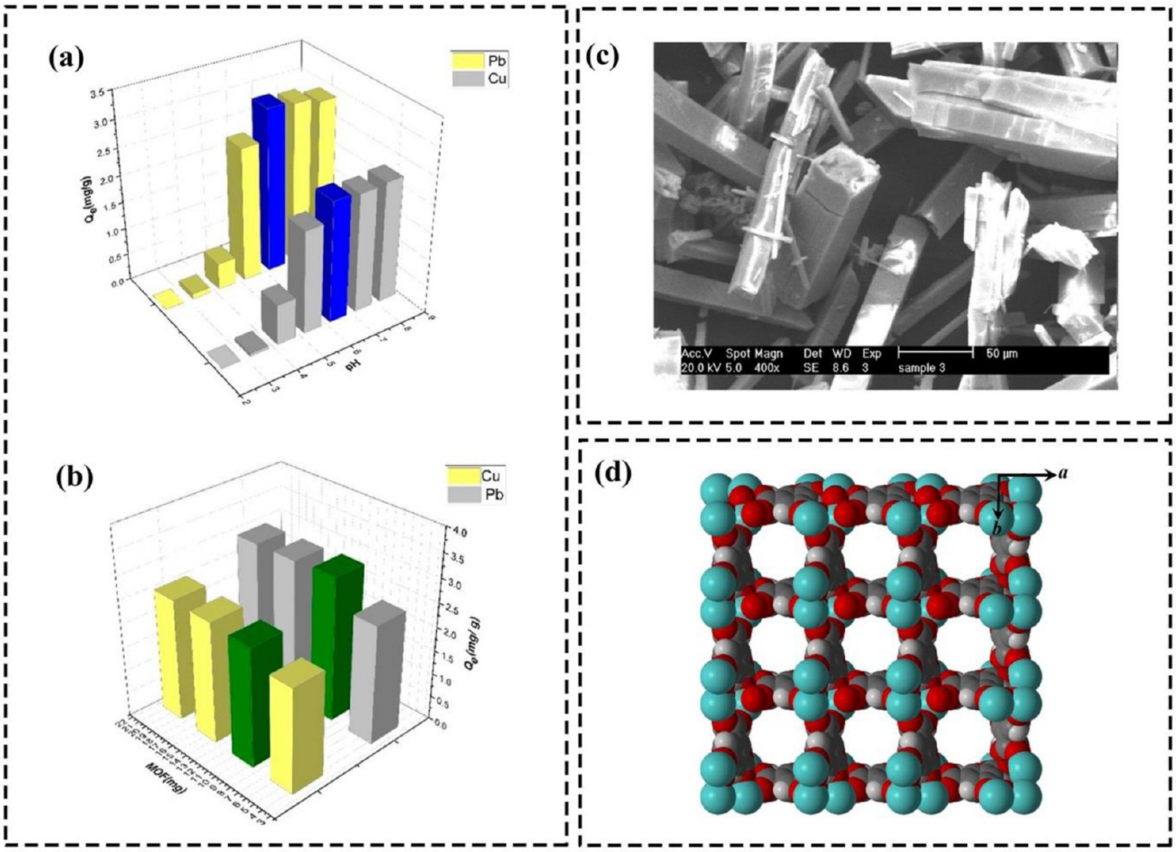


Figure 9. Extraction rate and microscopy images: (a) impact of pH on the functionality of extraction (blue bar represents the optimum pH). Extraction conditions: sample solution of 50 mL of 1 mg L^{-1} target metal ions, MOF, and extraction time of 15 min and (b) effect of MOF amount (green bar represents the optimum amount of MOFs). (c) Scanning electron microscopy image of dysprosium-based MOF. (d) Representation of pores of lanthanide MOFs (hydrogen atoms, white; oxygen atoms, red; carbon atoms, gray; lanthanides, cyan). Reproduced with permission from ref 133. Copyright 2016, Royal Society of Chemistry.

depending on the specific analyte. Metal ions can be linked to free amines using the carboxylates of the ligand.[13]

On the other hand, an ion-exchange process employing Ni-MOF as a template was used to create Fe-Ni-MOFs with variable Fe concentrations by Wang et al.[137] Peroxidase-like activity in Fe-Ni-MOF has been demonstrated in kinetic studies, allowing it to catalyze the oxidation of 3,3′,5,5′-tetramethylbenzidine (TMB) to form blue-colored oxidized TMB (oxTMB). The Fe-Ni-MOF has proven to be a peroxidase-mimetic MOF with effective and stable catalysis. It has been used to develop a highly sensitive colorimetric test for Sn^{2+} ions. Based on the redox interaction, it is hypothesized that Sn^{2+} ions might reduce the activity of the Fe-Ni-peroxidase-like MOF by reducing the Sn^{2+} ion concentration, resulting in a lighter oxTMB color and reduced absorbance at 652 nm. The UV−vis spectrometer can accurately measure Sn^{2+} ions concentrations in linear ranges from 0.01 to 1.0 mM and 1.0 to 4.0 mM. The process of action of Sn^{2+} in MOFs is as follows: it is possible to modify the shape of Fe-Ni-MOFs by etching a template of Ni-MOF. The resulting Fe-Ni-MOFs have a lower Michaelis constant (K_m), stronger peroxidase-like catalytic activity, better durability, and high sensitivity and selectivity. Using a bipyridyl ligand with a bridging azine group, Farahani et al.[132] produced a Zn(II) MOF, $[Zn_2(BDC)_2(4\text{-bpdh})]_3DMF$ (TMU-16; H_2BDC141,4-benzene dicarboxylate, 4-bpdh14 2,5-bis(4-pyridyl)-3,4) under solvothermal conditions. Fluorescence measurements were performed to investigate the sensitivity of TMU-16 to different metal ions (Figure 8). TMU-16 is a luminous substance that can be used to identify metal ions and small molecules with high sensitivity. The fluorescence intensity of this MOF decreased significantly when Fe^{3+} was added, whereas the luminescence intensity increased when Cd^{2+} and CH_2Cl_2 were added. According to the calculations, LODs for Fe^{3+} and Cd^{2+} are 0.02 and 0.05 μM, respectively. Both Fe^{3+} and Cd^{2+} ion identification procedures have strong anti-interference capabilities.

Jamali et al.[133] used a solvothermal approach to prepare lanthanide MOFs ($Ln(BTC)(H_2O)(DMF)1.1$, where Ln = Tb, Dy, Er, and Yb). These MOFs have a large surface area and donor atoms, making them ideal for detecting trace quantities of heavy-metal ions such as Pb^{2+} and Cu^{2+} (Figure 9). According to the adsorption isotherms, the oxygen-containing compounds in the MOF govern the Lewis acid−base interactions that result in the sorption of the target ions. As a novel type of material for adsorption and preconcentration applications, Dy-MOFs are simple, have a large surface area, reduce organic wastewater, are highly dispersible, and have a broad pH range stability. It is feasible to enrich a high volume of target ions in a short period of time using the suggested method for the extraction and preconcentration of heavy-metal ions because of the low sorbent requirement and short diffusion path. The improved processes have a linearity of 1−120 μg L^{-1}, with LODs of 0.46 μg L^{-1} for Pb^{2+} and 0.265 μg L^{-1} for Cu^{2+}.

4. READINESS OF MOF-BASED BIOSENSORS

Over the past 20 years, MOFs have become well known in the chemical literature. This class of materials initially attracted interest because of their high surface area and porosity. These materials may be defined as metal ion networks or clusters bound together by organic ligands. Such features indicate potential future applications in gas storage, separation, and catalysis, along with a wide range of chemical functionalization possibilities. Research has advanced to the point where a wide range of intriguing options are now available for integration into systems found in the real world. The prospective capabilities of these materials have been frequently mentioned in grant proposals and academic articles. There are valid assertions that MOF-based tools can fix major problems including the catalytic breakdown of hazardous species, gas storage with low pressure for fuels with transporting potential (particularly pertinent for a workable hydrogen economy), and carbon capture as a way of restricting climate change. However, an increasing number of critics claim that MOFs are overpromising and underdelivering and that there are insurmountable obstacles in implementing meaningful MOF-based solutions to these issues. Following prominent papers in *Science* and *Nature* in 1999, the chemical corporation BASF developed interest in MOFs through the development of a MOF-based natural gas storage system, which has been examined in a fleet of demonstration vehicles since 2013. Methane fuels may not be currently favored, owing to economic strains, but signs point to the potential of this technology for the market.

Decco announced that TruPick, a tool for managing the freshness of fruits and vegetables after harvest, was registered with the U.S. Environmental Protection Agency. At the fifth International Conference on MOF & Open Framework Compounds in California, specifics about the product were publicized. The product employs an MOF as an efficient adsorbent for the release and storage of 1-methyl cyclopropane, a competitive inhibitor of the ethylene receptor presents in certain fruits. Ethylene, which is emitted by ripening fruit in large storage facilities, accelerates the ripening of nearby fruits and can result in notable issues with premature aging. The period in which the fruit may be properly preserved can be greatly extended by up to nine months because of the strong binding of 1-MCP. Apples harvested in September may be consumed in March of the following year, with the help of TruPick. Turkey has already registered and other nations are anticipated to follow. To date, MOF Technologies is working to increase the mechanochemical manufacturing capacity of a wide range of MOFs (100 kg per week).

NuMat Technologies produced a fully integrated MOF solution that was prepared for the market, rather than acting as an MOF supplier. The debut of a system for the storage of dangerous gases, which are often utilized in the electronics sector, was also announced by NuMat at MOF2016.

The maturity of MOF research has reached a vital developmental stage, with at least two businesses already bringing goods to market. Even if there are still many obstacles to overcome, the early steps taken by MOF innovators in the very competitive field of technology commercialization will undoubtedly open the door for other researchers to follow suit. Furthermore, experts should persuade organizations and private financiers to support this field by developing MOF-enabled products that may bring genuine social benefits, in addition to the sustainability that comes with commercial revenue.

5. CONCLUSION, CHALLENGES, AND FUTURE OUTLOOK

The pollution of ecosystems is one of the most serious issues that humanity is now confronted with. Heavy metals may be found in a variety of diverse contexts, such as industrial waste and soil contamination, as well as other types of human activity, all of which have the potential to poison water supplies in the future. Metal ions are extremely poisonous at trace levels in water. Several attempts have been made to detect heavy-metal ion residues in various water and environmental samples, with mixed results. Multiple methods are available for identifying hazardous ions, including HPLC, optical detection, chemiluminescence, X-ray absorption spectroscopy, ICP-MS, ASV, ICP-AES, ICP-MS, and AAS.

MOFs have various features, including highly porous frameworks with varied pore sizes, different functional groups, low bulk densities, and abilities to capture substances in both chemisorption and physisorption phases. Porous MOFs have been used for various purposes, including collection of radioactive waste, identification of heavy-metal ions, magnetism, catalysis, and application in sensors. Porous MOFs have also been used to produce nanoparticles. When comparing various kinds of MOFs, it is often observed that bimetallic MOFs have stronger framework hydro-stability than the single parent. To fabricate epitaxially grown MOF-on-MOF hybrids, one approach is to use an existing MOF to generate another MOF via lattice matching with the substrate of an MOF network. When creating epitaxial grown core−shell MOF-on-MOF hybrids to construct 2-D hybrid MOFs, the MOF-on-MOF method may be employed in conjunction with other techniques. All MOF synthesis techniques can be divided into direct aqueous and nonaqueous syntheses. The second is the synthesis of aqueous and nonaqueous media in a predefined ratio. MOFs are one of the most intriguing and promising areas of study in coordination chemistry and have the potential to revolutionize the field.

Many different forms of MOFs can be used in biosensor matrices with several applications, e.g., potential use of modified MOFs to improve the precision with which cells and tissues can be recognized, use of the ASV technique for Hg^{2+} analysis using a Ca-MOF electrode modifier on an innovative 3-D printed lab-in-a-syringe device, identification of As^{3+} utilizing a combination of zinc-based MOFs and GO nanosheets, synthesis of novel nanoscale Ni-based MOFs, and use of a nanoplate Ni-MOF-GCE as a sensor to increase the preconcentration and identification of Pb^{2+} ions using SWAS. Furthermore, optical techniques have been used to detect the presence of Pb^{2+} ions using a novel lanthanide-based MOF that is extremely selective and ultrasensitive. The production of 3-D Zn-MOFs with nitrogen-rich channels and vivid blue fluorescence emission is an example of using MOF-based sensors in optical approaches. Besides a huge amount of research about MOFs, a number of exciting new routes have been provided by researching about MOF obstacles to overcome in the area of environmental governance to investigate the following. Hysteretic isotherms result from structural transitions between the presence and absence of guests. By gaining insight into the mechanisms, we may manipulate the adsorption and desorption hysteresis features. The ideal scenario would be met if substances could be provided by improved hysteresis behavior to suit certain uses.

It is important to note that MOFs' usages are not limited to their structural features alone, but nevertheless entail their electric and magnetic ones. There is a clear relationship between electrical states and spatial structures; together, they generate a wide range of responses to chemical or physical stimuli. One of the ways in which the area of MOFs may advance significantly would be via the study and manipulation of the dynamic phenomena that occur in the pores of such frameworks. Properties like electrical conductivity are all the result of intense interaction between the guests in the pores and the framework. Charge transfer interactions between guests and MOFs substrate play a crucial role because they create magnetic spins resulting in distinctive physical features. It is desirable for guest storage that the open/closed pores in a MOF may be controlled by various external effects like photons or heat. Moreover, to precisely manage a reaction, a nanospace filled with tunable characteristics of soft porous crystals is an ideal possibility. The molecules in the pores may be arranged by the soft porous crystal's dynamic guest space. This adaptability is crucial for achieving high-quality molecule identification and effective transformation which is enabled even for gas molecules.[37]

■ AUTHOR INFORMATION

Corresponding Authors

Alireza Khataee − *Research Laboratory of Advanced Water and Wastewater Treatment Processes, Department of Applied Chemistry, Faculty of Chemistry, University of Tabriz, 51666-16471 Tabriz, Iran; Department of Environmental Engineering, Gebze Technical University, 41400 Gebze, Turkey;* orcid.org/0000-0002-4673-0223; Email: a_khataee@tabrizu.ac.ir

Yeojoon Yoon − *Department of Environmental and Energy Engineering, Yonsei University, Wonju 26493, Republic of Korea;* orcid.org/0000-0001-9346-8849; Email: yajoony@yonsei.ac.kr

Authors

Hessamaddin Sohrabi − *Department of Analytical Chemistry, Faculty of Chemistry, University of Tabriz, 51666-16471 Tabriz, Iran*

Shahin Ghasemzadeh − *Department of Analytical Chemistry, Faculty of Chemistry, University of Tabriz, 51666-16471 Tabriz, Iran*

Sama Shakib − *Department of Analytical Chemistry, Faculty of Chemistry, University of Tabriz, 51666-16471 Tabriz, Iran*

Mir Reza Majidi − *Department of Analytical Chemistry, Faculty of Chemistry, University of Tabriz, 51666-16471 Tabriz, Iran*

Amir Razmjou − *School of Engineering, Edith Cowan University, Perth, WA 6027, Australia; Centre for Technology in Water and Wastewater, University of Technology Sydney, New South Wales 2007, Australia;* orcid.org/0000-0002-3554-5129

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.iecr.2c03011

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are thankful to the University of Tabriz and Yonsei University Mirae Campus for the support.

■ REFERENCES

(1) Zhou, H. C.; Long, J. R.; Yaghi, O. M. Introduction to Metal-Organic Frameworks. *Chem. Rev.* **2012**, *112*, 673−674.

(2) Dang, S.; Zhang, J. H.; Sun, Z. M. Tunable Emission Based on Lanthanide(Iii) Metal-Organic Frameworks: An Alternative Approach to White Light. *J. Mater. Chem.* **2012**, *22* (18), 8868−8873.

(3) Dang, S.; Zhang, J.-H.; Sun, Z.-M.; Zhang, H. Luminescent Lanthanide Metal-Organic Frameworks with a Large SHG Response. *Chem. Commun.* **2012**, *48* (90), 11139−11141.

(4) Eliseeva, S. v.; Pleshkov, D. N.; Lyssenko, K. A.; Lepnev, L. S.; Bünzli, J. C. G.; Kuzmina, N. P. Highly Luminescent and Triboluminescent Coordination Polymers Assembled from Lanthanide β-Diketonates and Aromatic Bidentate O-Donor Ligands. *Inorg. Chem.* **2010**, *49* (20), 9300−9311.

(5) White, K. A.; Chengelis, D. A.; Zeller, M.; Geib, S. J.; Szakos, J.; Petoud, S.; Rosi, N. L. Near-Infrared Emitting Ytterbium Metal-Organic Frameworks with Tunable Excitation Properties. *Chem. Commun.* **2009**, No. 30, 4506−4508.

(6) Kokkinos, C.; Economou, A.; Pournara, A.; Manos, M.; Spanopoulos, I.; Kanatzidis, M.; Tziotzi, T.; Petkov, V.; Margariti, A.; Oikonomopoulos, P.; Papaefstathiou, G. S. 3D-Printed Lab-in-a-Syringe Voltammetric Cell Based on a Working Electrode Modified with a Highly Efficient Ca-MOF Sorbent for the Determination of Hg(II). *Sens Actuators B Chem.* **2020**, *321*, 128508.

(7) Carvalho, C. M. L.; Chew, E. H.; Hashemy, S. I.; Lu, J.; Holmgren, A. Inhibition of the Human Thioredoxin System: A Molecular Mechanism of Mercury Toxicity. *J. Biol. Chem.* **2008**, *283* (18), 11913−11923.

(8) Clarkson, T. W.; Magos, L. The Toxicology of Mercury and Its Chemical Compounds. *Critical Reviews in Toxicology.* **2006**, *36*, 609−662.

(9) Stern, A. H. A Review of the Studies of the Cardiovascular Health Effects of Methylmercury with Consideration of Their Suitability for Risk Assessment. *Environmental Research* **2005**, *98*, 133−142.

(10) Pashazadeh-Panahi, P.; Belali, S.; Sohrabi, H.; Oroojalian, F.; Hashemzaei, M.; Mokhtarzadeh, A.; de la Guardia, M. Metal-Organic Frameworks Conjugated with Biomolecules as Efficient Platforms for Development of Biosensors. *TrAC - Trends in Analytical Chemistry* **2021**, *141*, 116285.

(11) Lv, R.; Li, H.; Su, J.; Fu, X.; Yang, B.; Gu, W.; Liu, X. Zinc Metal-Organic Framework for Selective Detection and Differentiation of Fe(III) and Cr(VI) Ions in Aqueous Solution. *Inorg. Chem.* **2017**, *56* (20), 12348−12356.

(12) Bansod, B. K.; Kumar, T.; Thakur, R.; Rana, S.; Singh, I. A Review on Various Electrochemical Techniques for Heavy Metal Ions Detection with Different Sensing Platforms. *Biosensors and Bioelectronics* **2017**, *94*, 443−455.

(13) Rubin, H. N.; Reynolds, M. M. Amino-Incorporated Tricarboxylate Metal-Organic Framework for the Sensitive Fluorescence Detection of Heavy Metal Ions with Insights into the Origin of Photoluminescence Response. *Inorg. Chem.* **2019**, *58* (16), 10671−10679.

(14) Kanayama, N.; Takarada, T.; Maeda, M. Rapid Naked-Eye Detection of Mercury Ions Based on Non-Crosslinking Aggregation of Double-Stranded DNA-Carrying Gold Nanoparticles. *Chem. Commun.* **2011**, *47* (7), 2077−2079.

(15) Bernaus, A.; Gaona, X.; Esbrí, J. M.; Higueras, P.; Falkenberg, G.; Valiente, M. Microprobe Techniques for Speciation Analysis and Geochemical Characterization of Mine Environments: The Mercury District of Almadén in Spain. *Environ. Sci. Technol.* **2006**, *40* (13), 4090−4095.

(16) Chen, X.; Han, C.; Cheng, H.; Wang, Y.; Liu, J.; Xu, Z.; Hu, L. Rapid Speciation Analysis of Mercury in Seawater and Marine Fish by Cation Exchange Chromatography Hyphenated with Inductively Coupled Plasma Mass Spectrometry. *J. Chromatogr A* **2013**, *1314*, 86−93.

(17) Samanta, P.; Desai, A. v.; Sharma, S.; Chandra, P.; Ghosh, S. K. Selective Recognition of Hg2+ Ion in Water by a Functionalized Metal-Organic Framework (MOF) Based Chemodosimeter. *Inorg. Chem.* **2018**, *57* (5), 2360−2364.

(18) An, J.; Farha, O. K.; Hupp, J. T.; Pohl, E.; Yeh, J. I.; Rosi, N. L. Metal-Adeninate Vertices for the Construction of an Exceptionally Porous Metal-Organic Framework. *Nat. Commun.* **2012**, *3*, 604.

(19) Qian, H.; Wang, J.; Yan, L. Synthesis of Lignin-Poly(N-Methylaniline)-Reduced Graphene Oxide Hydrogel for Organic Dye and Lead Ions Removal. *Journal of Bioresources and Bioproducts* **2020**, *5* (3), 204−210.

(20) Khataee, A.; Sohrabi, H.; Arbabzadeh, O.; Khaaki, P.; Majidi, M. R. Frontiers in Conventional and Nanomaterials Based Electrochemical Sensing and Biosensing Approaches for Ochratoxin A Analysis in Foodstuffs: A Review. *Food Chem. Toxicol.* **2021**, *149*, 112030.

(21) Soozanipour, A.; Sohrabi, H.; Abazar, F.; Khataee, A.; Noorbakhsh, A.; Asadnia, M.; Taheri-Kafrani, A.; Majidi, M. R.; Razmjou, A. Ion Selective Nanochannels: From Critical Principles to Sensing and Biosensing Applications. *Adv. Mater. Technol.* **2021**, *6* (10), 2000765.

(22) Yoo, S. M.; Lee, S. Y. Optical Biosensors for the Detection of Pathogenic Microorganisms. *Trends in Biotechnology* **2016**, *34*, 7−25.

(23) Ahmed, A.; Rushworth, J. v.; Hirst, N. A.; Millner, P. A. Biosensors for Whole-Cell Bacterial Detection. *Clin Microbiol Rev.* **2014**, *27* (3), 631−646.

(24) Sanvicens, N.; Pastells, C.; Pascual, N.; Marco, M. P. Nanoparticle-Based Biosensors for Detection of Pathogenic Bacteria. *TrAC - Trends in Analytical Chemistry* **2009**, *28*, 1243−1252.

(25) Huang, X.; Liu, Y.; Yung, B.; Xiong, Y.; Chen, X. Nanotechnology-Enhanced No-Wash Biosensors for in Vitro Diagnostics of Cancer. *ACS Nano* **2017**, *11*, 5238−5292.

(26) Saad, E. M.; Elshaarawy, R. F.; Mahmoud, S. A.; El-Moselhy, K. M. New Ulva Lactuca Algae Based Chitosan Bio-Composites for Bioremediation of Cd(II) Ions. *Journal of Bioresources and Bioproducts* **2021**, *6* (3), 223−242.

(27) Zhao, J.; Wang, Y. N.; Dong, W. W.; Wu, Y. P.; Li, D. S.; Zhang, Q. C. A Robust Luminescent Tb(III)-MOF with Lewis Basic Pyridyl Sites for the Highly Sensitive Detection of Metal Ions and Small Molecules. *Inorg. Chem.* **2016**, *55* (7), 3265−3271.

(28) Ren, J.; Ledwaba, M.; Musyoka, N. M.; Langmi, H. W.; Mathe, M.; Liao, S.; Pang, W. Structural Defects in Metal-Organic Frameworks (MOFs): Formation, Detection and Control towards Practices of Interests. *Coord. Chem. Rev.* **2017**, *349*, 169−197.

(29) Zhou, N.; Su, F.; Guo, C.; He, L.; Jia, Z.; Wang, M.; Jia, Q.; Zhang, Z.; Lu, S. Two-Dimensional Oriented Growth of Zn-MOF-on-Zr-MOF Architecture: A Highly Sensitive and Selective Platform for Detecting Cancer Markers. *Biosens Bioelectron* **2019**, *123*, 51−58.

(30) Wang, G. Y.; Song, C.; Kong, D. M.; Ruan, W. J.; Chang, Z.; Li, Y. Two Luminescent Metal-Organic Frameworks for the Sensing of Nitroaromatic Explosives and DNA Strands. *J. Mater. Chem. A Mater.* **2014**, *2* (7), 2213−2220.

(31) Sohrabi, H.; Javanbakht, S.; Oroojalian, F.; Rouhani, F.; Shaabani, A.; Majidi, M. R.; Hashemzaei, M.; Hanifehpour, Y.; Mokhtarzadeh, A.; Morsali, A. Nanoscale Metal-Organic Frameworks: Recent Developments in Synthesis, Modifications and Bioimaging Applications. *Chemosphere* **2021**, *281*, 130717.

(32) Roushani, M.; Valipour, A.; Saedi, Z. Electroanalytical Sensing of Cd2+ Based on Metal-Organic Framework Modified Carbon Paste Electrode. *Sens Actuators B Chem.* **2016**, *233*, 419−425.

(33) Pournara, A. D.; Tarlas, G. D.; Papaefstathiou, G. S.; Manos, M. J. Chemically Modified Electrodes with MOFs for the Determination of Inorganic and Organic Analytes via Voltammetric Techniques: A Critical Review. *Inorganic Chemistry Frontiers* **2019**, *6*, 3440−3455.

(34) Wang, D.; Ke, Y.; Guo, D.; Guo, H.; Chen, J.; Weng, W. Facile Fabrication of Cauliflower-like MIL-100(Cr) and Its Simultaneous Determination of Cd2+, Pb2+, Cu2+ and Hg2+ from Aqueous Solution. *Sens Actuators B Chem.* **2015**, *216*, 504−510.

(35) Jiang, D.; Deng, R.; Li, G.; Zheng, G.; Guo, H. Constructing an Ultra-Adsorbent Based on the Porous Organic Molecules of Noria for the Highly Efficient Adsorption of Cationic Dyes. *RSC Adv.* **2020**, *10* (11), 6185−6191.

(36) Sohrabi, H.; Khataee, A.; Ghasemzadeh, S.; Majidi, M. R.; Orooji, Y. Layer Double Hydroxides (LDHs)- Based Electrochemical and Optical Sensing Assessments for Quantification and Identification of Heavy Metals in Water and Environment Samples: A Review of Status and Prospects. *Trends in Environmental Analytical Chemistry* **2021**, *31* (June), No. e00139.

(37) Horike, S.; Shimomura, S.; Kitagawa, S. Soft Porous Crystals. *Nat. Chem.* **2009**, *1*, 695−704.

(38) Sohrabi, H.; Arbabzadeh, O.; Khaaki, P.; Majidi, M. R.; Khataee, A.; Woo Joo, S. Emerging Electrochemical Sensing and Biosensing Approaches for Detection of Fumonisins in Food Samples. *Crit Rev. Food Sci. Nutr* **2022**, *62* (31), 8761−8776.

(39) Wen, L.; Zheng, X.; Lv, K.; Wang, C.; Xu, X. Two Amino-Decorated Metal-Organic Frameworks for Highly Selective and Quantitatively Sensing of HgII and CrVI in Aqueous Solution. *Inorg. Chem.* **2015**, *54* (15), 7133−7135.

(40) Xiang, Z.; Fang, C.; Leng, S.; Cao, D. An Amino Group Functionalized Metal-Organic Framework as a Luminescent Probe for Highly Selective Sensing of Fe3+ Ions. *J. Mater. Chem. A Mater.* **2014**, *2* (21), 7662−7665.

(41) Lin, Z. J.; Lü, J.; Hong, M.; Cao, R. Metal-Organic Frameworks Based on Flexible Ligands (FL-MOFs): Structures and Applications. *Chemical Society Reviews* **2014**, *43*, 5867−5895.

(42) Gao, W. Y.; Chrzanowski, M.; Ma, S. Metal-Metalloporphyrin Frameworks: A Resurging Class of Functional Materials. *Chemical Society Reviews* **2014**, *43*, 5841−5866.

(43) Halder, S.; Layek, A.; Ghosh, K.; Rizzoli, C.; Ray, P. P.; Roy, P. A Cd(Ii) Based Metal Organic Framework: A Photosensitive Current Conductor. *Dalton Transactions* **2015**, *44* (36), 16149−16155.

(44) Halder, S.; Mondal, J.; Ortega-Castro, J.; Frontera, A.; Roy, P. A Ni-Based MOF for Selective Detection and Removal of Hg2+ in Aqueous Medium: A Facile Strategy. *Dalton Transactions* **2017**, *46* (6), 1943−1950.

(45) Meilikhov, M.; Furukawa, S.; Hirai, K.; Fischer, R. A.; Kitagawa, S. Binary Janus Porous Coordination Polymer Coatings for Sensor Devices with Tunable Analyte Affinity. *Angewandte Chemie - International Edition* **2013**, *52* (1), 341−345.

(46) Song, X.; Kim, T. K.; Kim, H.; Kim, D.; Jeong, S.; Moon, H. R.; Lah, M. S. Post-Synthetic Modifications of Framework Metal Ions in Isostructural Metal-Organic Frameworks: Core-Shell Heterostructures via Selective Transmetalations. *Chem. Mater.* **2012**, *24* (15), 3065−3073.

(47) Qian, J.; Li, T. T.; Hu, Y.; Huang, S. A Bimetallic Carbide Derived from a MOF Precursor for Increasing Electrocatalytic Oxygen Evolution Activity. *Chem. Commun.* **2017**, *53* (97), 13027−13030.

(48) Bellarosa, L.; Brozek, C. K.; García-Melchor, M.; Dincă, M.; López, N. When the Solvent Locks the Cage: Theoretical Insight into the Transmetalation of MOF-5 Lattices and Its Kinetic Limitations. *Chem. Mater.* **2015**, *27* (9), 3422−3429.

(49) Qian, J.; Li, Q.; Liang, L.; Yang, Y.; Cao, Z.; Yu, P.; Huang, S.; Hong, M. A Photoluminescent Indium-Organic Framework with Discrete Cages and One-Dimensional Channels for Gas Adsorption. *Chem. Commun.* **2016**, *52* (58), 9032−9035.

(50) Gu, Y.; Wu, Y. N.; Li, L.; Chen, W.; Li, F.; Kitagawa, S. Controllable Modular Growth of Hierarchical MOF-on-MOF Architectures. *Angewandte Chemie - International Edition* **2017**, *56* (49), 15658−15662.

(51) Hoskins, B. F.; Robson, R. Design and Construction of a New Class of Scaffolding-like Materials Comprising Infinite Polymeric Frameworks of 3D-Linked Molecular Rods. A Reappraisal of the Zn(CN)2 and Cd(CN)2 Structures and the Synthesis and Structure of the Diamond-Related Frameworks [N(CH3)4][Cu1Zn11(CN)4]and CUI[4,4″4″,4″’-Tetracyanotetraphenylmethane] BF4 ∼ xC6H5NO2; *J. Am. Chem. Soc.* **1990**, *112*, 1546−1554.

(52) Kitagawa, S.; Kitaura, R.; Noro, S. I. Functional Porous Coordination Polymers. *Angewandte Chemie - International Edition* **2004**, *43*, 2334−2375.

(53) O'Keeffe, M.; Eddaoudi, M.; Li, H.; Reineke, T.; Yaghi, O. M. Frameworks for Extended Solids: Geometrical Design Principles. *J. Solid State Chem.* **2000**, *152* (1), 3−20.

(54) Long, J. R.; Yaghi, O. M. The Pervasive Chemistry of Metal-Organic Frameworks. *Chemical Society Reviews* **2009**, *38*, 1213−1214.

(55) Rani, L.; Kaushal, J.; Srivastav, A. L.; Mahajan, P. A Critical Review on Recent Developments in MOF Adsorbents for the Elimination of Toxic Heavy Metals from Aqueous Solutions. *Environmental Science and Pollution Research* **2020**, *27*, 44771−44796.

(56) Drout, R. J.; Otake, K.; Howarth, A. J.; Islamoglu, T.; Zhu, L.; Xiao, C.; Wang, S.; Farha, O. K. Efficient Capture of Perrhenate and Pertechnetate by a Mesoporous Zr Metal-Organic Framework and Examination of Anion Binding Motifs. *Chem. Mater.* **2018**, *30* (4), 1277−1284.

(57) Sohrabi, H.; Arbabzadeh, O.; Khaaki, P.; Majidi, M. R.; Khataee, A.; Woo Joo, S. Emerging Electrochemical Sensing and Biosensing Approaches for Detection of Fumonisins in Food Samples. *Crit Rev Food Sci Nutr.* **2022**, *62* (31), 8761−8776.

(58) Kato, S.; Otake, K. I.; Chen, H.; Akpinar, I.; Buru, C. T.; Islamoglu, T.; Snurr, R. Q.; Farha, O. K. Zirconium-Based Metal-Organic Frameworks for the Removal of Protein-Bound Uremic Toxin from Human Serum Albumin. *J. Am. Chem. Soc.* **2019**, *141* (6), 2568−2576.

(59) Kumar, P.; Pournara, A.; Kim, K. H.; Bansal, V.; Rapti, S.; Manos, M. J. Metal-Organic Frameworks: Challenges and Opportunities for Ion-Exchange/Sorption Applications. *Progress in Materials Science* **2017**, *86*, 25−74.

(60) Brozek, C. K.; Dincă, M. Cation Exchange at the Secondary Building Units of Metal-Organic Frameworks. *Chemical Society Reviews* **2014**, *43*, 5456−5467.

(61) Genna, D. T.; Wong-Foy, A. G.; Matzger, A. J.; Sanford, M. S. Heterogenization of Homogeneous Catalysts in Metal-Organic Frameworks via Cation Exchange. *J. Am. Chem. Soc.* **2013**, *135* (29), 10586−10589.

(62) Yu, J.; Cui, Y.; Wu, C.; Yang, Y.; Wang, Z.; O'Keeffe, M.; Chen, B.; Qian, G. Second-Order Nonlinear Optical Activity Induced by Ordered Dipolar Chromophores Confined in the Pores of an Anionic Metal-Organic Framework. *Angewandte Chemie - International Edition* **2012**, *51* (42), 10542−10545.

(63) Wang, Z.; Zhang, J. H.; Jiang, J. J.; Wang, H. P.; Wei, Z. W.; Zhu, X.; Pan, M.; Su, C. Y. A Stable Metal Cluster-Metalloporphyrin MOF with High Capacity for Cationic Dye Removal. *J. Mater. Chem. A Mater.* **2018**, *6* (36), 17698−17705.

(64) Tan, Y. X.; He, Y. P.; Zhang, J. Pore Partition Effect on Gas Sorption Properties of an Anionic Metal-Organic Framework with Exposed Cu2+ Coordination Sites. *Chem. Commun.* **2011**, *47* (38), 10647−10649.

(65) Gao, Q.; Xu, J.; Bu, X. H. Recent Advances about Metal-Organic Frameworks in the Removal of Pollutants from Wastewater. *Coord. Chem. Rev.* **2019**, *378*, 17−31.

(66) Che, H.; Li, Y.; Zhang, S.; Chen, W.; Tian, X.; Yang, C.; Lu, L.; Zhou, Z.; Nie, Y. A Portable Logic Detector Based on Eu-MOF for Multi-Target, on-Site, Visual Detection of Eu3+ and Fluoride in Groundwater. *Sens Actuators B Chem.* **2020**, *324*, 128641.

(67) Tahmasebi, E.; Masoomi, M. Y.; Yamini, Y.; Morsali, A. Application of Mechanosynthesized Azine-Decorated Zinc(II) Metal-Organic Frameworks for Highly Efficient Removal and Extraction of Some Heavy-Metal Ions from Aqueous Samples: A Comparative Study. *Inorg. Chem.* **2015**, *54* (2), 425−433.

(68) Canivet, J.; Fateeva, A.; Guo, Y.; Coasne, B.; Farrusseng, D. Water Adsorption in MOFs: Fundamentals and Applications. *Chemical Society Reviews* **2014**, *43*, 5594−5617.

(69) Hamon, L.; Serre, C.; Devic, T.; Loiseau, T.; Millange, F.; Ferey, G.; Weireld, G. D. Comparative Study of Hydrogen Sulfide Adsorption in the MIL-53(Al, Cr, Fe), MIL-47(V), MIL-100(Cr), and MIL-101(Cr) Metal-Organic Frameworks at Room Temperature. *J. Am. Chem. Soc.* **2009**, *131* (25), 8775−8777.

(70) Khan, N. A.; Jun, J. W.; Jeong, J. H.; Jhung, S. H. Remarkable Adsorptive Performance of a Metal-Organic Framework, Vanadium-Benzenedicarboxylate (MIL-47), for Benzothiophene. *Chem. Commun.* **2011**, *47* (4), 1306−1308.

(71) Grant Glover, T.; Peterson, G. W.; Schindler, B. J.; Britt, D.; Yaghi, O. MOF-74 Building Unit Has a Direct Impact on Toxic Gas Adsorption. *Chem. Eng. Sci.* **2011**, *66* (2), 163−170.

(72) Britt, D.; Tranchemontagne, D.; Yaghi, O. M. Metal-Organic Frameworks with High Capacity and Selectivity for Harmful Gases. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105* (33), 11623−11627.

(73) Haque, E.; Lee, J. E.; Jang, I. T.; Hwang, Y. K.; Chang, J. S.; Jegal, J.; Jhung, S. H. Adsorptive Removal of Methyl Orange from Aqueous Solution with Metal-Organic Frameworks, Porous Chromium-Benzenedicarboxylates. *J. Hazard Mater.* **2010**, *181* (1−3), 535−542.

(74) Ke, F.; Qiu, L. G.; Yuan, Y. P.; Peng, F. M.; Jiang, X.; Xie, A. J.; Shen, Y. H.; Zhu, J. F. Thiol-Functionalization of Metal-Organic Framework by a Facile Coordination-Based Postsynthetic Strategy and Enhanced Removal of Hg 2+ from Water. *J. Hazard Mater.* **2011**, *196*, 36−43.

(75) Khan, N. A.; Jhung, S. H. Adsorptive Removal of Benzothiophene Using Porous Copper- Benzenetricarboxylate Loaded with Phosphotungstic Acid. *Fuel Process. Technol.* **2012**, *100*, 49−54.

(76) Khan, N. A.; Jhung, S. H. Low-Temperature Loading of Cu+ Species over Porous Metal-Organic Frameworks (MOFs) and Adsorptive Desulfurization with Cu+-Loaded MOFs. *J. Hazard Mater.* **2012**, *237−238*, 180−185.

(77) Khan, N. A.; Jhung, S. H. Remarkable Adsorption Capacity of CuCl 2-Loaded Porous Vanadium Benzenedicarboxylate for Benzothiophene. *Angewandte Chemie - International Edition* **2012**, *51* (5), 1198−1201.

(78) Karra, J. R.; Walton, K. S. Effect of Open Metal Sites on Adsorption of Polar and Nonpolar Molecules in Metal-Organic Framework Cu-BTC. *Langmuir* **2008**, *24* (16), 8620−8626.

(79) Blanco-Brieva, G.; Campos-Martin, J. M.; Al-Zahrani, S. M.; Fierro, J. L. G. Effectiveness of Metal-Organic Frameworks for Removal of Refractory Organo-Sulfur Compound Present in Liquid Fuels. *Fuel* **2011**, *90* (1), 190−197.

(80) Huo, S. H.; Yan, X. P. Metal-Organic Framework MIL-100(Fe) for the Adsorption of Malachite Green from Aqueous Solution. *J. Mater. Chem.* **2012**, *22* (15), 7449−7455.

(81) Peterson, G. W.; Wagner, G. W.; Balboa, A.; Mahle, J.; Sewell, T.; Karwacki, C. J. Ammonia Vapor Removal by Cu 3(BTC) 2 and Its Characterization by MAS NMR. *J. Phys. Chem. C* **2009**, *113* (31), 13906−13917.

(82) Hamon, L.; Leclerc, H.; Ghoufi, A.; Oliviero, L.; Travert, A.; Lavalley, J. C.; Devic, T.; Serre, C.; Férey, G.; de Weireld, G.; Vimont, A.; Maurin, G. Molecular Insight into the Adsorption of H2S in the Flexible MIL-53(Cr) and Rigid MIL-47(V) MOFs: Infrared Spectroscopy Combined to Molecular Simulations. *J. Phys. Chem. C* **2011**, *115* (5), 2047−2056.

(83) Ahmed, I.; Hasan, Z.; Khan, N. A.; Jhung, S. H. Adsorptive Denitrogenation of Model Fuels with Porous Metal-Organic Frameworks (MOFs): Effect of Acidity and Basicity of MOFs. *Appl. Catal., B* **2013**, *129*, 123−129.

(84) Bradshaw, D.; Claridge, J. B.; Cussen, E. J.; Prior, T. J.; Rosseinsky, M. J. Design, Chirality, and Flexibility in Nanoporous Molecule-Based Materials. *Acc. Chem. Res.* **2005**, *38* (4), 273−282.

(85) Férey, G. Hybrid Porous Solids: Past, Present, Future. *Chem. Soc. Rev.* **2008**, *37* (1), 191−214.

(86) Farha, O. K.; Hupp, J. T. Rational Design, Synthesis, Purification, and Activation of Metal-Organic Framework Materials. *Acc. Chem. Res.* **2010**, *43* (8), 1166−1175.

(87) Zheng, S.; Wu, T.; Zhang, J.; Chow, M.; Nieto, R. A.; Feng, P.; Bu, X. Porous Metal Carboxylate Boron Imidazolate Frameworks. *Angewandte Chemie - International Edition* **2010**, *49* (31), 5362−5366.

(88) Jhung, S. H.; Khan, N. A.; Hasan, Z. Analogous Porous Metal-Organic Frameworks: Synthesis, Stability and Application in Adsorption. *CrystEngComm* **2012**, *14* (21), 7099−7109.

(89) Chen, B.; Xiang, S.; Qian, G. Metal-Organic Frameworks with Functional Pores for Recognition of Small Molecules. *Acc. Chem. Res.* **2010**, *43* (8), 1115−1124.

(90) Ravikumar, I.; Ghosh, P. Recognition and Separation of Sulfate Anions. *Chem. Soc. Rev.* **2012**, *41* (8), 3077−3098.

(91) Li, J. R.; Kuppler, R. J.; Zhou, H. C. Selective Gas Adsorption and Separation in Metal-Organic Frameworks. *Chem. Soc. Rev.* **2009**, *38* (5), 1477−1504.

(92) Cychosz, K. A.; Ahmad, R.; Matzger, A. J. Liquid Phase Separations by Crystalline Microporous Coordination Polymers. *Chemical Science* **2010**, *1*, 293−302.

(93) Li, J. R.; Sculley, J.; Zhou, H. C. Metal-Organic Frameworks for Separations. *Chem. Rev.* **2012**, *112*, 869−932.

(94) Kreno, L. E.; Leong, K.; Farha, O. K.; Allendorf, M.; van Duyne, R. P.; Hupp, J. T. Metal-Organic Framework Materials as Chemical Sensors. *Chem. Rev.* **2012**, *112*, 1105−1125.

(95) Suh, M. P.; Park, H. J.; Prasad, T. K.; Lim, D. W. Hydrogen Storage in Metal-Organic Frameworks. *Chem. Rev.* **2012**, *112*, 782−835.

(96) Zhao, Y.; Seredych, M.; Zhong, Q.; Bandosz, T. J. Superior Performance of Copper Based MOF and Aminated Graphite Oxide Composites as CO2 Adsorbents at Room Temperature. *ACS Appl. Mater. Interfaces* **2013**, *5* (11), 4951−4959.

(97) Li, J. R.; Ma, Y.; McCarthy, M. C.; Sculley, J.; Yu, J.; Jeong, H. K.; Balbuena, P. B.; Zhou, H. C. Carbon Dioxide Capture-Related Gas Adsorption and Separation in Metal-Organic Frameworks. *Coord. Chem. Rev.* **2011**, *255*, 1791−1823.

(98) della Rocca, J.; Liu, D.; Lin, W. Nanoscale Metal-Organic Frameworks for Biomedical Imaging and Drug Delivery. *Acc. Chem. Res.* **2011**, *44* (10), 957−968.

(99) Horcajada, P.; Serre, C.; Vallet-Regí, M.; Sebban, M.; Taulelle, F.; Férey, G. Metal-Organic Frameworks as Efficient Materials for Drug Delivery. *Angewandte Chemie - International Edition* **2006**, *45* (36), 5974−5978.

(100) Horcajada, P.; Gref, R.; Baati, T.; Allan, P. K.; Maurin, G.; Couvreur, P.; Férey, G.; Morris, R. E.; Serre, C. Metal-Organic Frameworks in Biomedicine. *Chem. Rev.* **2012**, *112*, 1232−1268.

(101) Masoomi, M. Y.; Morsali, A. Applications of Metal-Organic Coordination Polymers as Precursors for Preparation of Nano-Materials. *Coord. Chem. Rev.* **2012**, *256*, 2921−2943.

(102) Wang, Z.; Chen, G.; Ding, K. Self-Supported Catalysts. *Chem. Rev.* **2009**, *109*, 322−359.

(103) Ma, L.; Abney, C.; Lin, W. Enantioselective Catalysis with Homochiral Metal-Organic Frameworks. *Chem. Soc. Rev.* **2009**, *38* (5), 1248−1256.

(104) Gu, Z. Y.; Yang, C. X.; Chang, N.; Yan, X. P. Metal-Organic Frameworks for Analytical Chemistry: From Sample Collection to Chromatographic Separation. *Acc. Chem. Res.* **2012**, *45* (5), 734−745.

(105) Anastasiou, E.; Lorentz, K. O.; Stein, G. J.; Mitchell, P. D. Prehistoric Schistosomiasis Parasite Found in the Middle East. *The Lancet Infectious Diseases* **2014**, *14*, 553−554.

(106) Zhang, H.; Zhou, L.; Wei, J.; Li, Z.; Lin, P.; Du, S. Highly Luminescent and Thermostable Lanthanide-Carboxylate Framework Materials with Helical Configurations. *J. Mater. Chem.* **2012**, *22* (39), 21210−21217.

(107) Hao, J. N.; Yan, B. A Water-Stable Lanthanide-Functionalized MOF as a Highly Selective and Sensitive Fluorescent Probe for Cd2+. *Chem. Commun.* **2015**, *51* (36), 7737−7740.

(108) Ni, Z.; Jerrell, J. P.; Cadwallader, K. R.; Masel, R. I. Metal-Organic Frameworks as Adsorbents for Trapping and Preconcentration of Organic Phosohonates. *Anal. Chem.* **2007**, *79* (4), 1290−1293.

(109) Gu, Z. Y.; Wang, G.; Yan, X. P. MOF-5 Metal-Organic Framework as Sorbent for in-Field Sampling and Preconcentration in Combination with Thermal Desorption GC/MS for Determination of Atmospheric Formaldehyde. *Anal. Chem.* **2010**, *82* (4), 1365−1370.

(110) Chen, X. F.; Zang, H.; Wang, X.; Cheng, J. G.; Zhao, R. S.; Cheng, C. G.; Lu, X. Q. Metal-Organic Framework MIL-53(Al) as a Solid-Phase Microextraction Adsorbent for the Determination of 16 Polycyclic Aromatic Hydrocarbons in Water Samples by Gas Chromatography-Tandem Mass Spectrometry. *Analyst* **2012**, *137* (22), 5411−5419.

(111) Cui, X. Y.; Gu, Z. Y.; Jiang, D. Q.; Li, Y.; Wang, H. F.; Yan, X. P. In Situ Hydrothermal Growth of Metal-Organic Framework 199 Films on Stainless Steel Fibers for Solid-Phase Microextraction of Gaseous Benzene Homologues. *Anal. Chem.* **2009**, *81* (23), 9771−9777.

(112) Jia, Y.; Su, H.; Wang, Z.; Wong, Y. L. E.; Chen, X.; Wang, M.; Chan, T. W. D. Metal-Organic Framework@Microporous Organic Network as Adsorbent for Solid-Phase Microextraction. *Anal. Chem.* **2016**, *88* (19), 9364−9367.

(113) Chen, X.; Ding, N.; Zang, H.; Yeung, H.; Zhao, R. S.; Cheng, C.; Liu, J.; Chan, T. W. D. Fe3O4@MOF Core-Shell Magnetic Microspheres for Magnetic Solid-Phase Extraction of Polychlorinated Biphenyls from Environmental Water Samples. *J. Chromatogr A* **2013**, *1304*, 241−245.

(114) Gu, Z. Y.; Chen, Y. J.; Jiang, J. Q.; Yan, X. P. Metal-Organic Frameworks for Efficient Enrichment of Peptides with Simultaneous Exclusion of Proteins from Complex Biological Samples. *Chem. Commun.* **2011**, *47* (16), 4787−4789.

(115) Chen, B.; Liang, C.; Yang, J.; Contreras, D. S.; Clancy, Y. L.; Lobkovsky, E. B.; Yaghi, O. M.; Dai, S. A Microporous Metal-Organic Framework for Gas-Chromatographic Separation of Alkanes. *Angewandte Chemie - International Edition* **2006**, *45* (9), 1390−1393.

(116) Alaerts, L.; Kirschhock, C. E. A.; Maes, M.; van der Veen, M. A.; Finsy, V.; Depla, A.; Martens, J. A.; Baron, G. v.; Jacobs, P. A.; Denayer, J. F. M.; de Vos, D. E. Selective Adsorption and Separation of Xylene Isomers and Ethylbenzene with the Microporous Vanadium(IV) Terephthalate MIL-47. *Angewandte Chemie - International Edition* **2007**, *46* (23), 4293−4297.

(117) Chen, A.; Chatterjee, S. Nanomaterials Based Electrochemical Sensors for Biomedical Applications. *Chem. Soc. Rev.* **2013**, *42* (12), 5425−5438.

(118) Chen, L.; Zheng, H.; Zhu, X.; Lin, Z.; Guo, L.; Qiu, B.; Chen, G.; Chen, Z. N. Metal-Organic Frameworks-Based Biosensor for Sequence-Specific Recognition of Double-Stranded DNA. *Analyst* **2013**, *138* (12), 3490−3493.

(119) Cheng, K.; Sun, Z.; Zhou, Y.; Zhong, H.; Kong, X.; Xia, P.; Guo, Z.; Chen, Q. Preparation and Biological Characterization of Hollow Magnetic Fe 3O4@C Nanoparticles as Drug Carriers with High Drug Loading Capability, PH-Control Drug Release and MRI Properties. *Biomater Sci.* **2013**, *1* (9), 965−974.

(120) Pournara, A. D.; Margariti, A.; Tarlas, G. D.; Kourtelaris, A.; Petkov, V.; Kokkinos, C.; Economou, A.; Papaefstathiou, G. S.; Manos, M. J. A Ca2+ MOF Combining Highly Efficient Sorption and Capability for Voltammetric Determination of Heavy Metal Ions in Aqueous Media. *J. Mater. Chem. A Mater.* **2019**, *7* (25), 15432−15443.

(121) Wang, X.; Qi, Y.; Shen, Y.; Yuan, Y.; Zhang, L.; Zhang, C.; Sun, Y. A Ratiometric Electrochemical Sensor for Simultaneous Detection of Multiple Heavy Metal Ions Based on Ferrocene-Functionalized Metal-Organic Framework. *Sens Actuators B Chem.* **2020**, *310*, 127756.

(122) Baghayeri, M.; Ghanei-Motlagh, M.; Tayebee, R.; Fayazi, M.; Narenji, F. Application of Graphene/Zinc-Based Metal-Organic Framework Nanocomposite for Electrochemical Sensing of As(III) in Water Resources. *Anal. Chim. Acta* **2020**, *1099*, 60−67.

(123) Ye, W.; Li, Y.; Wang, J.; Li, B.; Cui, Y.; Yang, Y.; Qian, G. Electrochemical Detection of Trace Heavy Metal Ions Using a Ln-MOF Modified Glass Carbon Electrode. *J. Solid State Chem.* **2020**, *281*, 121032.

(124) Ahmadijokani, F.; Tajahmadi, S.; Bahi, A.; Molavi, H.; Rezakazemi, M.; Ko, F.; Aminabhavi, T. M.; Arjmand, M. Ethylenediamine-Functionalized Zr-Based MOF for Efficient Removal of Heavy Metal Ions from Water. *Chemosphere* **2021**, *264*, 128466.

(125) Lu, M.; Deng, Y.; Luo, Y.; Lv, J.; Li, T.; Xu, J.; Chen, S. W.; Wang, J. Graphene Aerogel-Metal-Organic Framework-Based Electrochemical Method for Simultaneous Detection of Multiple Heavy-Metal Ions. *Anal. Chem.* **2019**, *91* (1), 888−895.

(126) Wang, Y.; Wang, L.; Huang, W.; Zhang, T.; Hu, X.; Perman, J. A.; Ma, S. A Metal-Organic Framework and Conducting Polymer Based Electrochemical Sensor for High Performance Cadmium Ion Detection. *J. Mater. Chem. A Mater.* **2017**, *5* (18), 8385−8393.

(127) Shen, L.; Liang, S.; Wu, W.; Liang, R.; Wu, L. CdS-Decorated UiO-66(NH2) Nanocomposites Fabricated by a Facile Photodeposition Process: An Efficient and Stable Visible-Light-Driven

Photocatalyst for Selective Oxidation of Alcohols. *J. Mater. Chem. A Mater.* **2013**, *1* (37), 11473−11482.

(128) Wan, Y.; Zou, D.; Cui, Y.; Yang, Y.; Qian, G. A Zn Based Anionic Metal-Organic Framework for Trace Hg2+ Ion Detection. *J. Solid State Chem.* **2018**, *266*, 70−73.

(129) Hu, J.; Wu, K.; Dong, S.; Zheng, M. A Luminescent Cd(II)-MOF as Recyclable Bi-Responsive Sensor for Detecting TNP and Iron(III)/Silver(I) with High Selectivity and Sensitivity. *Polyhedron* **2018**, *153*, 261−267.

(130) Ji, G.; Liu, J.; Gao, X.; Sun, W.; Wang, J.; Zhao, S.; Liu, Z. A Luminescent Lanthanide MOF for Selectively and Ultra-High Sensitively Detecting Pb2+ Ions in Aqueous Solution. *J. Mater. Chem. A Mater.* **2017**, *5* (21), 10200−10205.

(131) Xiao, J.; Liu, J.; Gao, X.; Ji, G.; Wang, D.; Liu, Z. A Multi-Chemosensor Based on Zn-MOF: Ratio-Dependent Color Transition Detection of Hg (II) and Highly Sensitive Sensor of Cr (VI). *Sens Actuators B Chem.* **2018**, *269*, 164−172.

(132) Farahani, Y. D.; Safarifard, V. Highly Selective Detection of Fe3+, Cd2+ and CH2Cl2 Based on a Fluorescent Zn-MOF with Azine-Decorated Pores. *J. Solid State Chem.* **2019**, *275*, 131−140.

(133) Jamali, A.; Tehrani, A. A.; Shemirani, F.; Morsali, A. Lanthanide Metal-Organic Frameworks as Selective Microporous Materials for Adsorption of Heavy Metal Ions. *Dalton Transactions* **2016**, *45* (22), 9193−9200.

(134) Zhang, Z.; Ji, H.; Song, Y.; Zhang, S.; Wang, M.; Jia, C.; Tian, J.-Y.; He, L.; Zhang, X.; Liu, C.-S. Fe(III)-Based Metal-Organic Framework-Derived Core-Shell Nanostructure: Sensitive Electrochemical Platform for High Trace Determination of Heavy Metal Ions. *Biosens Bioelectron* **2017**, *94*, 358−364.

(135) Guo, H.; Zheng, Z.; Zhang, Y.; Lin, H.; Xu, Q. Highly Selective Detection of Pb2+ by a Nanoscale Ni-Based Metal-Organic Framework Fabricated through One-Pot Hydrothermal Reaction. *Sens Actuators B Chem.* **2017**, *248*, 430−436.

(136) Wang, X. Q.; Feng, D. D.; Tang, J.; Zhao, Y. di; Li, J.; Yang, J.; Kim, C. K.; Su, F. A Water-Stable Zinc(Ii)-Organic Framework as a Multiresponsive Luminescent Sensor for Toxic Heavy Metal Cations, Oxyanions and Organochlorine Pesticides in Aqueous Solution. *Dalton Transactions* **2019**, *48* (44), 16776−16785.

(137) Hu, Y.; Yue, C.; Wang, J.; Zhang, Y.; Fang, W.; Dang, J.; Wu, Y.; Zhao, H.; Li, Z. Fe-Ni Metal-Organic Frameworks with Prominent Peroxidase-like Activity for the Colorimetric Detection of Sn $^{2+}$ Ions. *Analyst* **2020**, *145* (19), 6349−6356.