Indium metal–organic frameworks based on pyridylcarboxylate ligands and their potential applications

Bin Zhang,a,b Weize Wang,a Bo Liu and Lei Hou

Indium metal–organic frameworks (In-MOFs) based on pyridylcarboxylate ligands represent a subclass of MOFs featuring diverse structures, a high stability, and various properties. This review discusses the different aspects of In-MOFs including their design, synthesis and structures as well as their typical potential applications in adsorption and separation, catalysis, and chemical sensors. Importantly, the effect of pyridine on the properties and stability of frameworks has been carefully studied. The introduction of a pyridine group not only significantly enriches clusters of In^{3+} ions, but also enables flexible, controllably synthesized ionic or neutral frameworks to be fabricated. Based on this, we suggest that this type of In–metal organic framework (MOF) should receive more attention in the field of MOF design.

1. Introduction

Metal–organic frameworks (MOFs) featuring structural flexibility and high component tunability in terms of porosity and surface functionality, have become one of the most attractive hybrid materials in the field of chemistry. They are constructed from inorganic nodes (metal ions or clusters) and organic linkers to create abundant multifunctional structures.1–3 Over the past decade, the areas of application of MOFs, as excellent platforms, have been expanding, ranging from gas storage and separation, chemical sensing to drug delivery, heterogeneous catalysis, water harvesting and so on.4–10 Some MOFs have recently been found to outperform some traditional materials in hydrocarbon separation, for example, Chen and co-workers took advantage of ultramicroporous MOFs to address one-step C_{2}H_{2} purification with a low energy consumption for regeneration using synergistic sorbent separation technology, as it is too challenging for classical physisorbents to simultaneous separate C_{2}H_{2}, C_{2}H_{6}, and other trace impurities from C_{2}H_{4}.11

In the early stages of research into inorganic nodes, divalent metal cations (Zn^{2+}, Cu^{2+}) were predominantly used in the process of construction,12 and yet the lability of M(II)–carboxyligic ligands (M–L) coordination bonds accelerate the development of MOFs based on M(II/III), owing to the inherent robustness of the M(II/III)-carboxylate bonds.11 Since then, a series of famous and stable MOFs (MIL, UiO, PCN) have emerged, and shown high thermal and chemical stability, expanding the working environments of MOFs.14,15 Indium metal–organic frameworks (In-MOFs), representing a special subset of MOFs with the main group element In as a metal center, are increasingly becoming a research focus owing to their distinct advantages including: (i) the sturdy bonds (In–O) and high coordination numbers provide support to form stable MOFs; (ii) compared with MOFs built using other metals(II/III) (Zr^{4+}, Hf^{4+}, Fe^{3+}, Cr^{3+}, Al^{3+}, Ga^{3+}, etc.), which are synthesized with strongly acidic modulators or competing monotopic ligands because of the kinetic inertness of their metal–ligand bonding, the larger ionic radius of the In^{3+} ion (0.940 Å) increases the kinetic lability in the complex and accelerates the ligand exchange rate, improving the possibility of obtaining single crystals for structural determination; (iii) owing to the hard–soft (Lewis) acid–base (HSAB) classification of the oxyphilic coordination of In^{3+} ion, its abundant coordination capabilities endow it with binding affinities toward softer donors; and (iv) the accessible high level p-orbitals of the unsaturated In^{3+} center enable it to easily receive electrons in various Lewis acidic reactions.16–20

Since 2002, recent years have seen the exponential development of the chemistry of indium MOFs, and a few representative In-MOFs (MIL-96, InOF-8, InPF-110) have been extensively studied.21–23 However, In-MOFs based on bifunctional pyridyl-carboxylate ligands (Scheme 1) are still in their infancy in contrast to carboxylate ligands, and papers on these represent a small percentage of the total number of In-MOFs papers reported thus far. In addition, pyridylcarboxylate ligands often play a pivotal role in the self-assembly process of MOFs, for

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a College of Chemistry & Pharmacy, Northwest A&F University, Yangling 712100, P. R. China. E-mail: chemliubo@nwsuaf.edu.cn
b Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of the Ministry of Education, College of Chemistry & Materials Science, Northwest University, Xi’an 710069, P. R. China
example: (i) ligand-directed synthesis, it is feasible to target the heterometallic cluster-based MOFs with a specific structure and function by using the different affinity of the two binding sites of pyridyl-N and carboxyl-O atoms for metals; (ii) the synthesis of positively charged metal–organic frameworks (P-MOFs), owing to the different charge contributions of the neutral pyridyl-N and negative carboxyl-O atoms to frameworks, adjusting the coordination ratios of the N and O atoms could facilitate the controlled assembly of P-MOFs, especially in the \([M_3O(RCOO)_6L_3]^+\) cluster; (iii) construction of novel MOFs, the pyridyl-N could be utilized to change the symmetry of the ligand, which produces unique clusters and special structures; and (iv) modification of frameworks, the bare pyridyl-N and carboxyl-O atoms can serve as functional sites.24–30 Based on these considerations, our group has carried out a series of explorations on the fabrication of In-MOFs by employing In\(^{3+}\) ions and pyridylcarboxylate ligands with different coordination modes, and concrete results have been produced (Scheme 2). Therefore, it is profitable to develop the coordination chemistry of In\(^{3+}\) ions with the assistance of pyridylcarboxylate ligands. In this review, we will present an overview of the recent work published in the area of In-MOFs based on pyridylcarboxylate ligands, aiming to provide readers with interesting ideas about the design principles.

2. Synthesis and structures of the In-MOFs

2.1. Synthetic methods

Similar to most MOFs, solvothermal synthesis is the main method used to prepare In-MOFs at present.31–33 The appropriate solvent, pH and reaction temperature are crucial to obtaining single crystals of In-MOFs. Owing to these factors, the role of solvents in the synthesis is very complicated because they may act as ligands, guests, templates or maybe even play two of these roles. A series of amide solvents, \(N,N\)-dimethylformamide (DMF), \(N,N\)-dimethylacetamide (DMA), \(N\)-methylformamide (NMF), \(N,N\)-diethylformamide (DEF), are frequently employed in the synthesis of In-MOFs (Scheme 3). Primarily, amides can increase the solubility of ligands, and will slowly decompose at elevated temperatures to form an amine base and a carboxylic acid, initiating self-assembly. Secondly, different solvents can act as templates to influence the self-assembly owing to the exceptional host–guest properties of the MOFs, inducing the formation of the desired structures. Furthermore, the addition of acidic modulators (HF, HNO\(_3\), HCl, HCOOH, CH\(_3\)COOH) is imperative, as they sometimes facilitate the crystallization of products. The optimal reaction temperature is another key factor for the self-assembly, In-MOFs in general are prepared from organic solutions (DMF, DMA) at 80–150 °C.

2.2. Typical types of inorganic building units

The structural richness of MOFs is dominated by secondary building units (SBUs) or clusters and organic ligands. The different geometries and connectivity of the clusters significantly increase their diversity, and thus enrich the chemical and physical properties of the frameworks.34–36 Recently, clusters based on In\(^{3+}\) ions have received special attention owing to the nuances of the coordination affinity between the pyridyl-N and carboxyl-O atoms in directing the assembly.
Three kinds of In$^{3+}$ clusters are generally generated, including: (i) mononuclear clusters, (ii) a rod-shaped [In–OH–In] chains, and (iii) trinuclear clusters, with types (i) and (iii) more commonly observed, in which the In$^{3+}$ ion shows relatively higher coordination numbers (6, 7, or 8-coordinated). Some representative clusters for the construction of bifunctional pyridylcarboxylate ligands and In$^{3+}$ ions are shown in Fig. 1. Xiang and co-workers synthesized two anionic MOFs ([FJU-16, FJU-17] based on typical mononuclear [In(COO)$_2$N$_2$] clusters. Every In$^{3+}$ ion is coordinated by eight carboxyl-O atoms from four ligands, and can be described as a 4-connected node. In particular, mononuclear In$^{3+}$ clusters are likely to coordinate with carboxyl-O, as well as pyridyl-N atoms, to maintain the framework charge balance. A mononuclear [In(COO)$_8$N]$^{-}$ unit-based MOF was reported by Zhang and co-workers. Structural analysis revealed that the In$^{3+}$ centers are all in a heptacoordinated environment completed by six carboxyl-O atoms and a pyridyl-N atom. Liu and co-workers prepared three indium-organic frameworks ([JLU-Liu8, 9, 10]). Three compounds were constructed from the same ligand, but templated using three different anions (NO$_3^-$, HCOO$^-$, and Cl$^-$), and they exhibit three different 3-connected neutral mononuclear clusters ([In(COO)$_2$N$_2$(NO$_3$)(DMA)], [In(COO)$_2$N$_2$(HCOO)(H$_2$O)], [In(COO)$_2$N$_2$Cl]). Eddaoudi and co-workers reported the first example of an M$_6$L$_{12}$ metal–organic octahedron, which was assembled using 2,5-pyridinedicarboxylic acid and [In(COO)$_6$N]$^{2-}$ clusters. Our group reported two stable In-MOFs in the orthorhombic space group C222$_1$ and the monoclinic space group P2$_1$/c (1, 2). For 1, each In$^{3+}$ ion is bonded to six O atoms from four different ligands and two μ$_2$-OH$^-$ groups, forming an octahedral coordination geometry, and duplicate In$^{3+}$ ions are linked through the μ$_2$-OH$^-$ groups to form an infinite extended zigzag [In–OH–In]$_n$ chain. For 2, adjacent In$^{3+}$ ions are connected by carboxylates and two μ$_2$-OH$^-$ anions to give a trinuclear [In$_3$(COO)$_6$N$_2$(OH)$_2$]$^{2-}$ linear cluster, in which the positions at both ends are occupied by the pyridyl-N atoms. The first heterometallic (In, Cu) cluster-based framework was reported by Hong and co-workers, in this framework 6-coordinated In$^{3+}$ ions link the carboxylate groups of ligands to constitute a 6-connected [In$_3$O(COO)$_6$(H$_2$O)$_3$]$^{+}$ cluster, while N-affinitive Cu(i)-based units bind only to the pyridyl N-centers with the help of the ligand-oriented method. Additionally, in the trinuclear indium cluster, pyridyl-N not only balances the framework charge, but also hinders the coordination of the other terminal atoms. Bu and co-workers proposed an effective approach to synthesize stable positively charged metal–organic frameworks, where one common feature in the 9-connected [In$_3$(O(COO)$_2$N$_3$)$^+$ clusters is the presence of ideal all-M$^{3+}$ conditions, negative carboxylate groups (cluster-forming module) and neutral pyridyl groups (preemptive coordination module), precluding the attachment of neutralizing anions. It is difficult to control the charge of the framework using only multicarboxylate ligands.

### 2.3. Types of organic ligands

The rational selection or design of organic ligands is another important factor for the construction of In-MOFs in addition to metal clusters. These bifunctional pyridylcarboxylate ligands fall into two types: (i) pyridyl-N atoms that may take part in coordination; (ii) pyridyl-N atoms that can be protected. Some representative ligands are summarized in Scheme 4.

### 2.4. Stability of framework structures

Normally, an ideal MOF not only exists steadily in a variety of conditions, but is also recyclable, maintaining a steady performance after multiple uses. However, in the initial stages of the synthesis of MOFs, their lability (thermal and chemical) is a negative property, and is thought to be extremely fatal in practical applications. Previous studies indicate the lability is largely determined by the strength of coordination bonds (as guided by HSAB theory) and ligand rigidification. For the above-mentioned considerations, stable MOFs based on highly charged metal In and carboxylate ligands have been reported, for instance, In$_2$(OH)[btc](Hbtc)$_{0.4}$(L)$_{0.6}$·3H$_2$O exhibits an exceptional thermal (300 °C) and chemical stability, especially in water or acidic media (0.01 M HCl). The nature of this stability can be attributed to the sturdy bonds (In–O) and high coordination numbers of the In$^{3+}$ ion. For the pyridylcarboxylate ligands, it is inevitable that the strength of the coordination bonds is reduced if the pyridyl-N atom takes part in the coordination. Amazingly, the pyridyl group can serve as a preemptive coordination module, sometimes hindering the attachment of solvent molecules to generate highly connected clusters. However, the pyridyl group contributes to form rigid ligands advancing the complexity, as well as the stability of the backbone, and can also form unique ligands with irregular coordination modes to match the low symmetric clusters, boosting the stability. On the whole, In-MOFs based on the pyridylcarboxylate ligands present a good thermal and water stability (Fig. 2), which is comparable with some famous Zr-MOFs. The good stability of the frameworks offers promise for future practical applications and good cycling stability.

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**Fig. 1** Representative SBUs in In-MOFs. Color scheme: Dark green: indium, gray: carbon, red: oxygen, blue: nitrogen, light green: fluorine. Hydrogen atoms are omitted for clarity.
3. Potential applications

MOFs are structurally diverse with adjustable pore walls, and thus have broad prospects in many applications, especially in storage and separation, chemical sensing as well as catalysis, which can be attainable via the custom-design of functional organic ligands and appropriate clusters. Therefore, a significant strategy for building multifunctional MOFs from pyridylcarboxylate ligands has already been well demonstrated in previously published literature, in which its potential active sites are conducive to an improved performance, increasing interactions between MOFs and the entering guests. Furthermore, coordination developments of the In$^{3+}$ ion bring new opportunities to perform modifications on stable MOF platforms. In the following sections, some important works will be presented in detail.

3.1 Adsorption and separation

3.1.1 Gas adsorption and separation. CH$_4$, as a clean and efficient energy, has attracted increasing attention owing to the aggravation of environmental pollution caused by fossil fuel energy. However, impurities such as CO$_2$ and C$_2$-hydrocarbons often exist in CH$_4$ production. Therefore, complete removal of impurities is the key to improving the fuel quality of CH$_4$. Liu and co-workers developed a stable MOF [NO$_3$][In$_3$OL$_3$]-4DMF·3H$_2$O (JLU-Liu18) based on pyridine-3,5-bis(phenyl-4-carboxylic acid) (H$_2$L). JLU-Liu18 displays a high adsorption for small gases without any open metal sites (OMSs) and Lewis base sites, especially CO$_2$ (129 and 63 cm$^3$ g$^{-1}$ at 273 and 298 K, respectively, under 1 bar). Furthermore, the adsorption enthalpy of JLU-Liu18 is 24.9 kJ mol$^{-1}$, indicating strong interactions between the CO$_2$ molecules and host framework. It also possesses a commendable selectivity for CO$_2$ and C$_2$H$_6$ over CH$_4$. At 298 K and 1 bar, the selectivities of CO$_2$ over CH$_4$ for JLU-Liu18, according to the experimental data, are 5.4 and 4.5, respectively, and the obtained value of the resulting selectivity of C$_2$H$_6$ over CH$_4$ for equimolar mixtures is 13.1 (Fig. 3).

As coordinatively unsaturated metal ions, OMSs can serve as Lewis acids to preferentially anchor and activate specific molecules, in particular for gas storage/separation applications. In addition to OMSs, Lewis basic/acidic sites can also form interactions with unsaturated hydrocarbons. In order to introduce Lewis base metals and Lewis acids into MOFs, Trikalitis and co-workers utilized the palladated ligand, trans-[bis(3,5-dicarboxypyridyl)palladium(II)] chloride (H$_2$L) and In$^{3+}$ to synthesize the first heterobimetallic In(III)/Pd(II)-based MOF with a square-octahedron (soc) topology. After successful activation using supercritical CO$_2$, high-resolution microporous analysis revealed the presence of small micropores (5.8 Å) with a Brunauer–Emmett–Teller (BET) area of 795 m$^2$ g$^{-1}$ and a total pore volume of 0.35 cm$^3$ g$^{-1}$. The activated solid shows high gravimetric (92.3 cm$^3$ g$^{-1}$) and volumetric (120.9 cm$^3$ cm$^{-3}$) CO$_2$ uptake at 273 K and 1 bar, as well...
as high CO$_2$/CH$_4$ (15.4 for a 50 : 50 molar mixture), with moderate $Q_a$ for CO$_2$ (29.8 kJ mol$^{-1}$). This behavior can be mainly ascribed to the combination of the Lewis base Pd(II)--CO$_2$ and Lewis acid In(III)--CO$_2$ interactions in the pore surface (Fig. 4a). Feng and co-workers reported a novel design concept for a pore-partition agent by demonstrating a symmetry-guided pathway to develop a large variety of clusters for use as a pore-partition agent. A type of pacs material prepared using the novel pore space partition was presented, and the pyridyl functionality was located on the acs framework made from 3,5-dicarboxylpyridine (pydc), and a metal ion (Ag$^+$) capable of adopting a C$_3$-symmetric coordination geometry was used as a pore-partition agent (Fig. 4b). The wide range of new compositions and structures provides a high degree of tunability in gas sorption properties. Recently, our group reported two pyridyl-functionalized MOFs with 2,5-bis(2′,5′-dicarboxylphenyl)pyridine (H$_4$L) and In$_3^+$ ions; the materials showed preferential binding with C$_2$H$_2$ and a high C$_2$H$_2$ adsorption performance (91, 65 cm$^3$ g$^{-1}$, 298 K, 1 bar). In particular, they can selectively trap C$_2$H$_2$ over CH$_4$ (22, 18, 298 K, 1 bar). The high selectivities could be tentatively attributed to the polar pore environment, in which OH$^-$, [Me$_2$NH$_2$]$^+$, and free pyridyl-N sites generate a high polar pore environment and then strengthen the affinity between the skeleton and quadrupolar molecules (Fig. 5).

### 3.1.2 Dyes adsorption and separation

As common industrial materials, organic dyes are widely used in many industrial fields, such as inks, medicine and textiles, owing to their diverse colors and high stability. However, it was not predicted that the toxicity of organic dyes could cause irreversible damage to the ecological environment and human health. As promising dye adsorbents, ionic MOFs are known as powerful tools to adsorb and separate charged molecules by an exchange-based process. A flexible and stable interpenetrated anionic MOF, [NH$_2$(CH$_3$)$_2$][In(L)$_2$]·2.5DMF·5H$_2$O (1), was successfully constructed by our group. Compound 1 not only possesses an exceptional stability under water and harsh circumstances, it also shows a high adsorption selectivity and capacity for methyl blue in aqueous solution (410 mg g$^{-1}$). Notably, cationic frameworks are much rarer than anionic or neutral ones, because negative ligand groups always make the overall charge of the frameworks neutral or negative. Bu et al. proposed a concept, preemptive coordination (PC), for targeting P-MOFs. Under ideal all-M$^{4+}$ conditions and the incursion of neutral pyridyl-N groups, they showed that this PC concept is an effective approach for developing P-MOFs that possess a high stability, porosity, and anion-exchange capability, allowing immobilization of anionic nucleotides and coenzymes, in addition to the charge and size-selective capture or separation of organic dyes. Ion exchange studies of differently charged organic dyes were performed with CPM-85-In. The results showed ion exchange only occurs between hosts and guests of opposite charge and size-dependent ion exchange kinetics (Fig. 6).
3.1.3 Capture of metal ions. Another non-negligible environmental problem has developed regarding the pollution emanating from nuclear waste and industrial effluents containing toxic heavy metals, excessive amounts of some transition metal ions and radionuclide metals. Considering their rapid diffusion ability in natural water systems, some functionalized MOFs are designed to capture toxic metal ions to solve this problem.71–74 Diwu and co-workers reported an anionic layered compound (NC4H12)(NC2H8)2[In3(pydc)6]·13.1H2O (SZ-6; pydc = 2,5-pyridinedicarboxylic acid) with the potential remediation ability towards radioactive Sr2+ from seawater.75 This material exhibits excellent β- and γ-radiation resistance both in air and in aqueous solutions. In addition, the results of the adsorption experiment show that SZ-6 exhibits a superior Sr2+ removal capability over a wide pH range from 4 to 12 with fast adsorption kinetics and a high selectivity. The effective removal of 90Sr from real seawater was demonstrated as well. In addition to the anionic features, the XPS spectra indicate that the absorbed Sr2+ ions were associated with the bare pyridyl-N and carboxyl-O atoms located on the framework (Fig. 7). Li and co-workers synthesized a 3D framework [In6([ipbp])2[μ2-OH] (μ2-O)3] based on the zwitterionic ligand 1-(3,5-dicarboxyphenyl)-4,4′-bipyridinium bromide ([H2(ipbp) Br]).76 It can efficiently capture Cr(vi) due to the surface electrostatic interaction between the crystal surface and Cr(vi) in the aqueous system. A maximum amount of adsorption of 74.4 mg g−1 in the aqueous system was achieved and the residual amount of Cr(vi) was found to be far below the EU and USA standards for safe drinking water, suggesting the potential for use as adsorption materials (Fig. 8).

3.2 Catalysis
To satisfy the energy needs for development, excessive reliance on fossil fuels has produced substantial emissions of CO2, which has triggered a rise in the sea-level and the greenhouse effect. It is proposed that the acid-catalyzed transformation of CO2 based on MOFs is a promising application and has actual value. MOFs with designable pores and intensive Lewis or Brønsted acidic sites can not only enhance the adsorption toward CO2, but also transform CO2 and epoxides into useful chemicals.77–79 In particular, unsaturated In3+ ions with high level p-orbitals features an intrinsic high Lewis acidity. With the help of a “bifunctional ligand directed strategy” and 5-(3′,5′-dicarboxyphenyl)nicotinic acid (H1DCPN), Liu and co-workers successfully integrated two types of unsaturated
monomeric In SBUs (neutral \([\text{In(OOC–)}_2\text{(-N–)}\text{H}_2\text{O})\text{X}]) and anionic \([\text{In(OOC–)}_2\text{(-N–)}\text{X}_2\text{)}^–\]) and trimeric In clusters \([\text{In}_3\text{O} (\text{OOC–})_6\text{(DMA)}_3]\)) into one framework.\(^{80}\) Then, they further tuned the channels by shifting the surface terminal substituents with different halogens, and formed three isostructural MOFs. By virtue of the diffusion facilitated nanotubular channels and synergism of the weak Lewis acidic and basic sites, the MOFs exhibited a high conversion and selectivity, especially for large-sized substrates, outperforming some top-performing MOF catalysts (Fig. 9).

### 3.3 Chemical sensor

Photoluminescence, an important property of MOFs, is broadly used to detect temperature, small organic molecules, gases, various metal ions and anions, and explosives in sensor probes. To meet the requirements of practice applications, a good sensitivity, reproducibility and selectivity are always key standards used to judge suitable sensor probes. Taking into account these factors, a common design strategy is to combine the metal ions (hard acids) with the carboxylate ligands (large conjugated double bond (\(\pi\) bond) system, rigid planar structure or substituents with electron-donating groups) to generate luminescent metal–organic frameworks (LMOFs). Specifically, to avoid steric repulsion between the aromatic protons, pyridine units can be used to form coplanar ligands. Moreover, Lewis base sites often play a central role in sensing analytes, by increasing the sensitivity for example. Owing to this, bifunctional pyridylcarboxylate ligands and In\(^{3+}\) ions have begun to receive attention in recent years.

#### 3.3.1 Sensing organic molecules

Although some antibiotics and chemical precursors promote food production, the treatment of diseases and industrial development, their residues, if present in the environment, can cause a threat to food safety and human health. Therefore, it is important to know how to establish a framework for the detection of residues.\(^{31–34}\)

Two luminescent anionic In-MOFs \([\text{(Me}_2\text{NH}_2)]\text{[In(BCP)]-2DMF)}_n (\text{V101})\) and \([\text{(Me}_2\text{NH}_2)]\text{[In(BCP)]-2.5DEF)}_n (\text{V102})\) \((\text{BCP} = 5\text{-}2,6\text{-bis}\text{-}(4\text{-carboxyphenyl} \text{pyridin-4-yl}))\) were obtained by Zhao and co-workers (Fig. 10). Interestingly, luminescence investigations reveal that only V102, and not V101 can sensitively and selectively detect traces of nitrofurazone (NZF) in aqueous solution (detection limits: 0.2 ppm). The Stern–Volmer equation deviated from linearity and bent upwards at higher concentrations, these phenomena indicate the coexistence of dynamic and static quenching processes. Based on structural analysis, the luminescent difference between V101 and V102 mainly originates from the divergence of the interpenetration structures.\(^{85}\) The Zhao group then designed and constructed a luminescent indium-organic framework to detect colchicine for the first time using \([\text{(CH}_3\text{)}_2\text{NH}_2]\text{[In(L)]-9DMF (V105) [H}_4\text{L} = 4,4\text{,}4\text{,}4\text{‴-}(1,4\text{-phenylene-bis}[\text{pyridine-4,2,6 triyl}])\text{tetrabenzoic acid}].\) Luminescent experiments demonstrate that V105 can selectively detect colchicine with a high sensitivity in the water. The calculated Stern–Volmer quenching constant \((K_{sv})\) is equal to \(1.67 \times 10^5 \text{ M}^{-1}\) and the detection limit was calculated and found to be \(6.25 \times 10^{-7} \text{ M}\) (Fig. 11).\(^{86}\)

Zhang and co-workers reported a MOF-based material through a one-step fabrication by embedding \textit{in situ} nitrated HPTS into the channels of In\(\text{[III]}\)-MOF \([\text{In}_{\text{x}}\text{OL}_{\text{15}}\text{[H}_2\text{O}_{\text{30}}]\text{[NO}_3\text{-} (\text{DMA})_4\text{[CH}_3\text{CN}]}_{\text{10}}\text{[H}_2\text{O}_{\text{30}}]\) (FJU-10).\(^{87}\) FJU-10 and dye@FJU-10 all display a sensing ability towards aniline, and the \(K_{sv}\) constants for aniline are \(1.87 \times 10^4\) and \(5.82 \times 10^4 \text{ M}^{-1}\), respectively. In addition, the detection limits of FJU-10 and
InOF-23, suggesting that upon excitation, electrons are transferred from the conduction band of InOF-23 to the lowest unoccupied molecular orbitals (LUMOs) of nitroaromatics that will result in a fluorescence quenching effect.

Recently, our group reported a MOF \([\text{Me}_2\text{NH}_2][\text{CPTA}]_2\cdot\text{H}_2\text{O}\), which was synthesized from an undeveloped asymmetrical pyridylcarboxylate ligand 2-(2-carboxypyridin-4-yl)terephthalic acid (H₃CPTA) with In³⁺ ions using a solvothermal method. It displays a 3D anionic framework with a large void space, which contains open square channels with a cross section of 14.6 Å and the pore surface is decorated with carboxylic oxygen atoms. Under excitation at 334 nm, the complex exhibits a strong luminescence emission at 450 nm and shows detection capabilities for neonicotinoid pesticides. The detection limit of the complex for nitenpyram was calculated to be 4.25 μM (1.15 μg mL⁻¹). By calculating the frontier molecular orbitals of the pesticides and testing the UV-Vis absorption spectra, it was proved that the resonance energy transfer (FRET) and photo induced electron transfer (PET) may cause fluorescence quenching (Fig. 13).

3.3.2 Sensing ions. As the potential harm resulting from the use of some specific ions has been mentioned previously, we will not repeat this here. An unsymmetrical pyridyl-decorated dicarboxylic acid, 3-(2,5-dicarboxyphenyl)pyridine acid (H₂dcpy), was employed to synthesize a stable In-MOF \([\text{H}_2\text{O}]_2[\text{dcpy}]_2[\text{OH}]_2\cdot\text{DMF}·\text{H}_2\text{O}\), 1 by our group. In particular, 1 contains two types of dcpy²⁻ linkers, in which the pyridyl group in one participates in coordination with the In³⁺ ion, whereas that in the other is uncoordinated, but hangs in the inner sides of the channels as functionalized sites, which can selective recognition of Fe³⁺ ions in an aqueous system. Throughout the detection, the energy absorbed gives rise to fluorescence because of the conjugated organic ligand, Fe³⁺ ions possess unsaturated 3d orbitals to accept electrons. The

![Image](https://via.placeholder.com/150)

**Table 1** Quenching efficiencies, quenching constants, and detection limits of different NACs of InOF-23. Adapted from ref. 88 Copyright 2019 Wiley-VCH

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![Image](https://via.placeholder.com/150)
electrons were then moved to the lowest unoccupied molecular orbital (LUMO) of Fe\textsuperscript{3+} ions through a nonradiative path on the basis of excitation, leading to fluorescence quenching of the MOF. Notably, the uncoordinated pyridyl-N atom can also provide one lone pair of electrons to the Fe\textsuperscript{3+} ions, increasing the recognition efficiency. A fluorescence sensing system based on an In(III)-organic complex ([In(H\textsubscript{2}bpydc)(H\textsubscript{2}O)Cl\textsubscript{3}]·CH\textsubscript{3}CN·H\textsubscript{2}O, \( \textit{In}_2 \)), H\textsubscript{2}bpydc = 2,2'-bipyridine-5,5'-dicarboxylic acid) with \textit{in situ} Lewis acid sites has been constructed by Yang and co-workers, exhibiting a high sensitivity for the detection of Fe\textsuperscript{3+} ions with a low detection limit of 3.95 \( \mu \text{M} \) and a short response time of less than 10 s.\textsuperscript{90} Rarely, the central metal In\textsuperscript{3+} is six-coordinated by three chlorine atoms, one oxygen atom from a water molecule, and two nitrogen atoms in the form of chelation from the same H\textsubscript{2}bpydc ligand, and the reserved –COOH groups possess an applicable orientation towards the inside of the channels, playing vital roles in the unique sensing properties. Moreover, the chemical shift of the O 1s peak from 531.4 to 532.2 eV provided more direct evidence to support the strong bonding effects between Fe\textsuperscript{3+} and the –COOH groups (Fig. 14). It is worth noting that the quenched fluorescence of the Fe\textsuperscript{3+}-incorporated sample could be reopened linearly with an increase in the alkalinity.

4. Conclusions and future prospects

In this review, we provide an overview on the recent progress in the development of In-MOFs with pyridylcarboxylate ligands, including their synthesis, crystal structures, stability and potential applications. Along these lines, some representative In-MOFs are listed, and their structures and properties are briefly described. Significantly, for In-MOFs, the introduction of a pyridyl group not only maintains the stability of the backbones, but also enhances the performance in applications, mainly for gas adsorption and separation and chemical sensors. This result is traceable in part to the formation of large π-conjugated systems or highly connected clusters and the enhancement in the affinity between the skeleton and the molecules. Furthermore, one distinguishing feature is the advantage offered by In-MOFs in the crystallization process compared to other metals(II/IV).

Despite the encouraging and very real progress made in the field of In-MOFs, they cover a small fraction of the numerous reported MOFs. In addition, this research is concentrated on only a few applications. Thus, it would be beneficial to enrich the structural diversity and applications of stable In-MOFs with the assistance of smart pyridylcarboxylate ligands. With continuous efforts, we are optimistic that further investigation of these MOFs will provide significant potentials for materials design, and more specifically, developing novel stable MOFs with excellent performance characteristics.

Author contributions

Conceptualization, B. Zhang and B. Liu; Writing – original draft, B. Zhang and W. Wang; Writing – review and editing, B. Liu and L. Hou; Supervision, B. Liu.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are thankful for the support of this work by the National Natural Science Foundation of China (Grants 21601145 and 21871220) and Natural Science Foundation of Shaanxi Province (2021JM-084).

Notes and references
