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A review of covalent organic frameworks for metal ion fluorescence sensing

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ABSTRACT

The concentration of metallic elements is closely associated with overall health. However, the discharge of untreated industrial wastewater can lead to metal-containing pollutants entering the human body through the food chain, disrupting the organism's homeostasis and posing a risk to human health. Covalent organic framework materials (COFs) have emerged as a novel porous material for detecting or adsorbing metal ions due to their unique pore structure, topological structure and flexible design. This paper summarizes the role, toxicity, and sources of metal ions related to human health, as well as the design, synthesis and performance of COFs fluorescent materials for detecting these elements. The interaction mechanism of different fluorescent COFs and metal ions are discussed. Additionally, the remaining challenges and prospects of COFs fluorescence sensors are provided. We believe this review will be useful in directing the development of fluorescent COFs towards metal ions.

1. Introduction

The abundance of different metallic elements in the environment is closely linked to their proportion in the human body. Macronutrients such as K, Na, Ca, and Mg, which are required in quantities greater than 100 mg per day, play a crucial role in regulating acid-base balance, neuromuscular excitability, intracellular and extracellular osmotic pressure balance, and enzyme activation in the human body [1]. Trace elements, including Fe, Mn, Co, Zn, Cu, *etc*., are essential for the human body and have vital functions in physiological regulation. They are closely associated with human immunity, growth and development, and even the occurrence of cancer [2]. Iron is the most abundant transition metal element in the human body, with a content of 4.2-6.1 g. As an important component of hemoglobin and myoglobin, iron plays an important role in energy conversion, respiration and metabolism of organisms [3]. However, the concentration of Fe^{3+} has a significant impact on biological systems. The lack or excess of Fe^{3+} can lead to various physiological disorders, including anemia, liver and kidney damage, heart failure, and diabetes [4]. Copper and zinc are frequently used as active centers for many enzymes. In normal mammals, approximately 96% of circulating copper in the blood exists in the form of an oxidase-like transporter-plasma ceruloplasmin, with each protein molecule containing 6 (or 1) copper atoms [5]. Zinc is present in about 18 zinc metalloenzymes and nearly 14 zinc ion-activating enzymes in the body. It can be function as a strong Lewis acid catalyst and can also stabilize the tertiary and quaternary structures of proteins [6]. However, excessive amounts of them in the body can cause equally serious damage to the organism [7]. Certain toxic metallic elements, such as mercury, arsenic, and cadmium, can cause severe toxicity and harm even in trace amounts when they enter the human body. The outbreak of Minamata disease in Japan serves as an example of the damage caused by organic mercury, which disrupts the metabolic balance of the body. Due to the environmental pollution caused by mercury-containing wastewater from industrial and agricultural production, organic mercury can enter the blood-brain barrier of the human body through bioaccumulation, causing damage to nerve cells, enzyme activity, and cell tissues [8]. The World Health Organization has prioritized cadmium as a food pollutant. Additionally, cadmium is listed as the first of twelve hazardous chemicals proposed by the United Nations Environment Programme [9]. Sewage irrigation and the use of cadmium-containing fertilizers have become the main sources

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of cadmium pollution in rice. In 1995, cadmium-contaminated rice and water caused a Itai-Itai Disease characterized by bone pain in Kandori River Basin, Fuji Prefecture, Japan [10]. Cadmium pollution can inhibit plant respiration, affect root growth, and impair the absorption of calcium and phosphorus. When absorbed by the human body, it can also affect the hematopoietic system and kidney function (Fig. S1 in Supporting information). The concentration of these metal ions is of crucial importance as they are essential trace elements for the human body. Even a slight overconsumption may lead to various detrimental effects and harm to the body. Thus, it is imperative to devise efficient techniques for monitoring and detecting trace metal ions present in food and water.

Various methods are available for detecting metal ions, including atomic absorption spectrometry (AAS) [11], atomic fluorescence spectrometry (AFS) [12], inductively coupled plasma (ICP) [13], inductively coupled plasma mass spectrometry (ICP-MS) [14], *etc*. These methods offer the benefits of high sensitivity and low detection limits. However, they can be costly and complex to operate, often requiring specialized pretreatment and trained professionals for accurate detection and identification of metal analytes. Electrochemical, fluorescence and some detection methods based on biological matrix, such as enzyme analysis [15], immunoassay [16], DNA-specific sensing methods [17], are also available for the detection of various metal ions. However, biomass-based sensors may not be suitable for rapid on-site detection due to the need for precise control, harsh conditions, and high costs [18,19]. While electrochemical sensing is a low-cost and simple alternative, it may not be adaptable for detecting metal ions in solid or suspended media due to the toxicity of interface materials [20]. Fluorescence sensing is a highly sensitive and rapid method of potential sensing, which holds significant potential for widespread application. This method utilizes the interaction between the analyte and the fluorescent probe to generate signal changes that facilitate quantitative detection [21]. The efficiency of fluorescence sensing is largely dependent on the properties of the fluorescent probes, such as quantum yield, specificity, and stability. At present, there are many fluorescent probes for metal ions, such as quantum dots [22], carbon dots [23], metal organic frameworks (MOFs) [24], metal nanoparticles [25] and some small molecule fluorescent probes [26]. The challenges of poor stability, low fluorescence intensity and difficult separation are often faced by them. Hence, it is of great significance for the large-scale application of fluorescence detection to find new organic molecular recognition carriers with high selectivity and design new fluorescent probes for metal ion detection [27].

Covalent organic frameworks (COFs), which are linked by strong covalent bonds, possess a range of desirable features, such as low mass density, excellent stability, large specific surface area, and adjustable pore structure [28–33]. Furthermore, they are particularly promising as fluorescent sensing materials due to their excellent histocompatibility and composition of non-toxic light elements [34,35]. Many COFs covalently assemble different functional blocks with monomers with large π-conjugated planes to construct highly ordered 2D or 3D frameworks with strong fluorescent luminescence, which play an important detection ability for metal ions [36,37]. As such, their systematic design and guided synthesis have drawn much attention, making it feasible to create a multifunctional system (Fig. 1).

As compared to other fluorescent detection probes such as metal organic frameworks (MOFs), the covalent bonds that form the backbone of COFs are more robust than the metal-ligand bonds in MOFs, affording them great luminescent properties and broadening their detection applications [38]. Moreover, COFs do not necessitate intricate pre-treatments or harsh conditions, allowing for faster application to water testing procedures than DNAzymes that need mild incubation circumstances and time during the testing process [39]. This review discusses the types, structures, fluorescence properties, and interaction mechanisms of these COFs with different metal ions, as well as their application status in metal ion detection. The synthesis method and quenching mechanism of COFs are introduced, followed by a discussion of the detection limit and application range of COFs with different structures and functional groups for metal ion detection. Finally, the challenges and development directions of these COFs materials in the field of metal ion detection are explored, providing researchers with design ideas for developing more efficient and excellent COFs for metal ion detection.

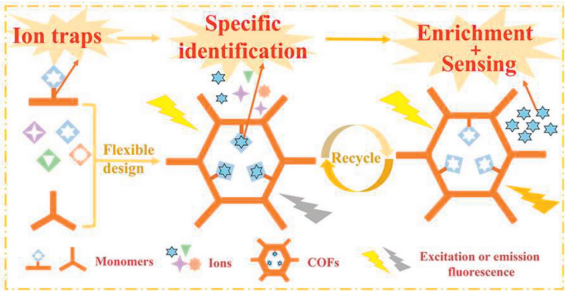

Fig. 1. Flexible design of fluorescent COFs for specific recognition, sensing and enrichment of metal ions.

2. Synthesis and fluorescence of COFs

Many COFs typically employ aromatic derivatives with rigid planar structure as monomers, which have excellent photoluminescence ability due to the extended π-conjugated electrons and ordered stacking structure in their skeletons [36]. Different block units can be designed to form highly ordered frameworks stacked by different kinds of covalent bonds. There are several covalent bonds employed in synthesizing COFs, such as boron-oxygen bonds, imine bonds, double bonds, hydrogen bonds, benzofuran rings [40–44]. Bonding styles play a key role in the construction of COFs as fluorescent probes, as they determine the stability of the probes. Among them, imine-linked COFs have been extensively utilized in fluorescence detection due to their reversible Schiff base reaction and comparatively simple synthesis conditions. However, an ideal fluorescence sensor requires not only a strong photoluminescence ability, but also a good stability to ensure that the error in the detection process is within a controllable range. The low stability of imine bond-linked COFs greatly affects their application as fluorescent sensing substrates. Banerjee and his team utilized the Schiff base reaction of 1,3,5-triformylresorcinol (Tp) and *p*-phenylenediamine (Pa-1) to transform the reversible enolimine into an irreversible ketone-enamine structure, which significantly improved its stability based on the formation of imine bonds. On this basis, the application of imine COFs in the field of fluorescent sensors has been quickly explored deeply [45,46]. In addition, the linked bonds formed by irreversible reaction were beneficial to improve the applicability of COFs as fluorescent sensors in complex environments, such as carbon-carbon double bonds, 1,4-dioxin bonds [47], benzofuran rings [42,48], They exhibit good stability to harsh conditions (high acidity, alkalinity and high temperature), although the bonding methods generally require long reaction times and complex reaction conditions. Recently, some new bonding methods such as hydrogen bond [43] and piperazine bond [49] have been reported. Their exceptional proton transfer, energy storage, and catalytic capabilities provide valuable insights and ideas for designing more ideal fluorescent COFs.

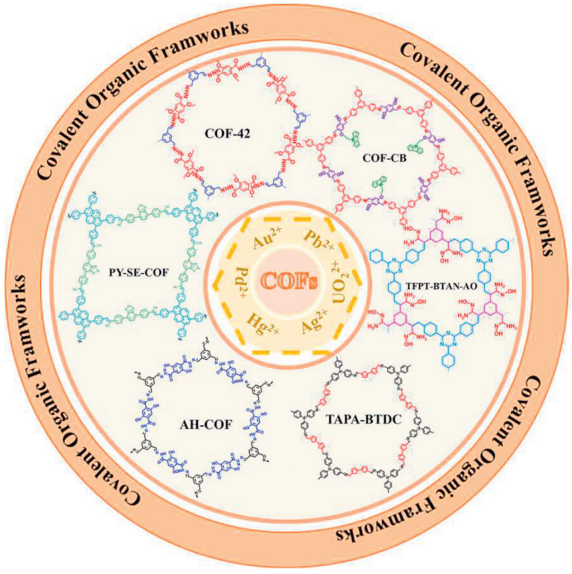

Fig. 2. A pie chart summarizing the application of COFs for metal ion detection. Reprinted with permission [31,88,91,97,104,122]. [31] Copyright 2022, Elsevier Inc. [88] Copyright 2018, The Royal Society of Chemistry. [91] Copyright 2021, The Royal Society of Chemistry. [97] Copyright 2020, Elsevier B.V. [104] Copyright 2022, Springer Nature. [122] Copyright 2020, Nature.

In addition, any slight alterations, whether at the electronic or atomic level, can affect the photoluminescence ability of COFs. For example, Wang *et al.* synthesized two COFs to investigate the influence of flexible planar monomers with aggregation-induced emission (AIE) effect and rigid planar monomers with non-twistable structures on the photoluminescence performance of COFs [50]. It was demonstrated that the rigid structures present in COF monomers and the degree of spin within the molecule have a significant impact on the luminescent ability of COFs. This can be explained from two perspectives: the electronic and atomic perspectives. From the atomic perspective, the photoluminescence ability of COFs is affected by the type of synthesis monomers and the degree of stacking. Different monomers can introduce different band structures and electronic states, thereby affecting the photoluminescent performance. Additionally, the stacking arrangement of COFs can also regulate their optical properties [34,51,52]. From the electronic perspective, the photoluminescence ability of COFs is also related to the structural characteristics of COF monomers. COFs with rigid planar monomers exhibit strong π-conjugation structures within the molecules, which facilitate electronic conjugation and spin coupling, thereby enhancing the luminescence effect. On the other hand, COFs with flexible planar monomers may exhibit AIE effect, where weak or no luminescence is observed in solution but strong luminescence appears in the solid state. The presence of such flexible structures limits the π-conjugation and spin coupling within the molecule, thus restricting the luminescence ability [53,54].

Metal ions are commonly utilized as fluorescence quenchers, possessing the capability to either accept or donate electrons. The mechanisms for fluorescence quenching generally include static quenching, dynamic quenching, fluorescence resonance energy transfer, internal filtering effect, electron transfer, intramolecular charge transfer, among others [55–57]. Currently, a diverse range of fluorescent COFs has been developed to facilitate the specific recognition and detection of metal ions (Fig. 2). They mainly coordinate with metal ions through photoinduced electron transfer (PET) [29], absorption competition inhibition (ACQ) [58], intramolecular charge transfer (ICT) [59], *etc*. to establish an effective detection platform.

3. Metal ion detection of COFs

3.1. Trace metal elements detection

3.1.1. Fe^{3+} detection

Fe^{3+} is a key component of biological systems, thus necessitating the development of a highly sensitive Fe^{3+} sensor for the purpose of aiding in the diagnosis of blood, visceral and other related diseases [60]. Most of the COFs are designed with a series of fluorescent sensors based on the principle of electron transfer with Fe^{3+}, which is due to the empty d-orbitals of Fe^{3+}, being a good electron acceptor [61,62]. PI-COF 201 and PI-COF 202 were first used to detect Fe^{3+} by Wang *et al.,* which was synthesized by pyromellitic dianhydride (PMDA) and naphthalene tetracarboxylic dianhydride (NTDA) with melamine (MA) under nitrogen atmosphere (Fig. S2a in Supporting information). The strong absorption band of Fe^{3+}-incorporated PI-COF 201 implies an effective energy transfer from the emission level of PI-COF 201 to the unoccupied d-orbital of Fe^{3+}, leading to a fluorescence quenching, which enables a sensitive and selective sensing for Fe^{3+} in turn-off mode. Moreover, the coordination interaction between Fe^{3+} and N atoms of the COF pore walls, along with the high electron-deficiency and electron-affinity of Fe^{3+}, probably contribute to the fluorescence quenching. However, PI-COF 201 was significantly interfered by Ni^{2+} while the specificity of PI-COF 202 was interfered by Ca^{2+}, Mg^{2+} and Cu^{2+}. In the emission range of PI-COF 201, no absorption peak was observed for all of the metal ion incorporated PI-COF 201 suspensions except for Fe^{3+}, indicating that there was no energy transfer from the excitation state of PI-COF 201 to the energy levels of these metal ions. The luminescence quenching caused by the other ions was due to the aggregation-induced quenching (AIQ) effect [63]. Xue's group combined melamine (MA) with squaric acid (SA) to form a new triazine-based covalent organic framework, ST-COF-1, for the detection of Fe^{3+} and nitro explosives (Fig. S2b in Supporting information). The energy transfer between ST-COF-1 and Fe^{3+} leads to fluorescence quenching due to the formation of electron defect regions. Furthermore, the photoexcited electrons of ST-COF-1 can be transferred from the skeleton donor to the electron-deficient nitroaromatic compounds for the qualitative detection of nitroaromatic compounds [64]. COF-TTPE, a bifunctional COF constructed by Cui *et al.* based on tetraphenylethylene Schiff base, can simultaneously detect and adsorb Fe^{3+}. It not only has a good detection effect on Fe^{3+} (detection limit 3.07 μmol/L), can also be used as a gas storage adsorbent and volatile organic compound (VOC) capture agent, providing a powerful platform for organic vapor adsorption and fluorescence sensors (Fig. S2c in Supporting information). The quenching of metal ions detected by the TTPE-COF is likely due to electron transfer. Fe^{3+} with d orbitals are able to accept electrons provided by TTPE-COF under the excitation of light, and this electron transfer leads to energy transfer, which results in fluorescence quenching [59].

However, due to the susceptibility of electron transfer quenching caused by Fe^{3+} to interference from ions with similar electron acceptors, establishing an efficient and specific detection system has proven challenging. Absorption competitive quenching (ACQ) is a fluorescence phenomenon in which a competition for energy transfer occurs between a fluorescent ligand and a guest molecule (metal ion). To this end, Wang's group synthesized four Fe^{3+}-sensitive fluorescent COFs (TaTa, DhaTab, TRITER-1 and TzDa) with similar structure and explored the effects of triazine ring structure and hydroxyl side chain on the fluorescence excitation ability and Fe^{3+} affinity of COFs (Fig. S3a in Supporting information). Interestingly, by comparing the quenching phenomena of other metal ions such as Cu^{2+}, Al^{3+} and Pb^{2+}, it exhibited a good Fe^{3+} selectivity (Figs. S3b–e in Supporting information). In order to understand the quenching mechanism between them clearly, fluorescence res-

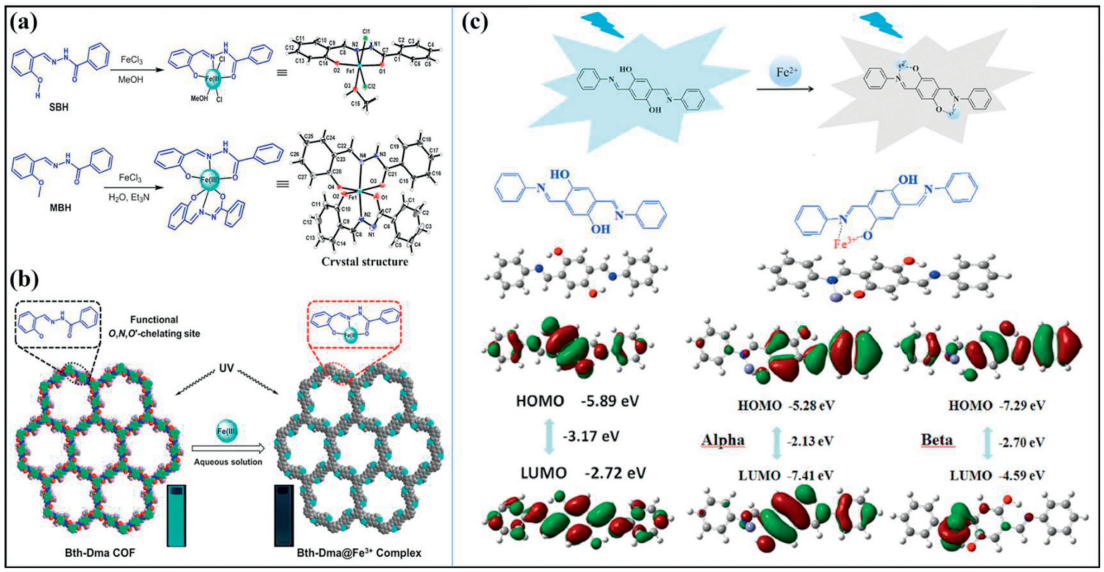

Fig. 3. (a) The coordination of salicylaldehyde benzoyl hydrazone (SBH) and *o*-methoxybenzaldehyde benzoyl hydrazone (MBH) with Fe(III) through O,N,O' chelating sites. (b) Schematic illustration of the sensing mechanism of Bth-Dma COF containing O,N,O 'chelating sites towards Fe^{3+}. Reprinted with permission [66]. Copyright 2019, American Chemical Society. (c) Optimized ground-state geometries and frontier orbital shapes of a free model compound of TT-COF and its complex with Fe^{3+} ion. Color code: C (gray), N (blue), H (white), O (red), and Fe (cordurablue). Reprinted with permission [58]. Copyright 2021, Elsevier Ltd.

onance energy transfer (FRET) mechanism between them was first ruled out by the fact that the fluorescence emission of COFs does not overlap with the UV absorption of Fe^{3+} (Figs. S3f and g in Supporting information). However, the UV–vis absorption spectra of all these COFs are overlapped with Fe^{3+}, and the overlap of the absorption spectra follows the order of DhaTab > TaTa > TRITER-1 > TzDa, which is consistent with the order of the quenching coefficient (KSV). Thus, it is demonstrated that the effective fluorescence quenching between these COFs and Fe^{3+} is due to the occurrence of ACQ, which is an important reference value for the design and study of Fe^{3+}-specific COFs [65].

Nevertheless, the interaction mechanism between the recognition sites or coordination space of COFs and Fe^{3+} remains largely unexplored, representing a crucial breakthrough in the development of more stable and feasible COFs as Fe^{3+} sensors. It has been reported that Fe(III) forms a strong coordination complex with salicylaldehyde benzoyl hydrazone (SBH), through an O,N,O′-Fe(III)-chelating mechanism. Furthermore, a hydrothermal reaction of *o*-methoxybenzaldehyde benzoyl hydrazone (MBH) with the Fe(III) ion resulted in a novel Fe(III) complex, which was characterized by two SBH ligands that were generated *in situ via* demethylation (Fig. 3a). Given the similar binding motif between the O,N,O′-chelating ligand and Fe(III) center from both SBH and MBH, Chen *et al.* were able to synthesize two pre-designed hydrazone-linked COFs (Bth-Dha and Bth-Dma, Fig. 3b) containing O,N,O' chelating sites through a Schiff base condensation reaction. Bth-Dma-COF has demonstrated excellent selectivity towards Fe^{3+} and highly sensitive fluorescence quenching in aqueous solution, making it a valuable Fe^{3+} fluorescent probe [66]. Moreover, the interaction mechanism between N-O chelating sites and iron ions is still deepening. Zhang's group has also developed a covalent organic framework (TT-COF) using 2,5-dihydroxyterephthalaldehyde and 1,3,5-tris(4-aminophenyl)benzene as raw materials. The synergistic effect of N and O chelating sites and the special pore structure of TT-COF give it a highly selective coordination effect on Fe^{3+} (Fig. 3c). DFT calculations have further confirmed the complexation process of TT-COF with Fe^{3+}. The fluorescence intensity of TT-COF at 425 nm showed a good linear relationship with the concentration of Fe^{3+} in the range of 2–20 μmol/mL, with a detection limit of 8.4×10^{-5} mol/L [58]. Li *et al.* have also synthesized a novel covalent organic framework Tfpa-Mth based on the coordination recognition of N and O chelating sites of hydrazone bonds with Fe^{3+}, which can be used as a fluorescence sensor for Fe^{3+} in ethanol solvent. Additionally, they have prepared a novel quartz crystal microbalance (QCM) sensor based on COF by *in-situ* growth of Tfpa-Mth COF on an amino-modified QCM chip. This COF-based QCM sensor has a uniform surface and can selectively monitor Fe^{3+} in real-time based on the change of Tfpa-Mth COF film thickness. This is the first report of a COF-based QCM sensor for metal ion detection [67].

The fully conjugated sp^2 carbon covalent organic frameworks (COFs) are a network of C=C double bond linkages formed through irreversible Knoevenagel condensation. These COFs exhibit improved resistance to acids, alkalis, and radiation compared to those containing imine or hydrazone bonds, which are typically synthesized through Schiff base reactions. Currently, this innovative C=C double bond-linked COF, known as TFPPy-ThDAN, has only been reported by You *et al.* for the detection of Fe^{3+}. It boasts exceptional crystallinity, chemical stability, and fluorescence performance in pure water, making it a promising candidate for highly sensitive and selective recognition of Fe^{3+} [68]. Though there are limited reports on sp^2 carbon COF, its exceptional performance and potential applications warrant further exploration. The parameters of the COFs for detecting Fe^{3+} are listed in Table S1 (Supporting information).

The detection of Fe^{3+} in COFs is one of the most extensively studied methods for metal ion detection, but it also has a significant impact on the detection of other metal ions. There are several possible reasons, firstly, Fe^{3+} is an ion with empty d orbitals, which allows it to act as a good electron acceptor and alter the electron distribution of ligands. Secondly, nitrogen and oxygen are the basic elements in COFs synthesis, and they are typically present in the form of electron-rich functional groups such as hydroxyl, amino, and amide groups. However, these groups have a high affinity for Fe^{3+} due to their lone pair electrons, allowing them to coordinate well with Fe^{3+} and thus affecting the structure and fluorescence properties of COFs [69]. Therefore, the key to developing a specific COFs detection system for Fe^{3+} lies in explor-

ing spatial structural coordination models. For example, the O,N,O'-Fe(III) chelation mechanism mentioned earlier has been found to effectively recognize and coordinate with Fe^{3+} [66].

3.1.2. Cu^{2+} detection

The proliferation of metal-based electronics industries, including mining, metal processing, and machinery production, has resulted in Cu^{2+} pollution in the environment [70,71]. The United States Environmental Protection Agency (EPA) has set the maximum allowable content of copper in drinking water at 1.3 ppm [72]. Therefore, it is essential to develop advanced detection methods for effective Cu^{2+} detection ions in water [73]. Li's research team created a covalent organic framework (COF-JLU3) using 1,3,5-tris(3′-*tert*-butyl-4′-hydroxy-5′-formylphenyl) benzene and hydrazine hydrate as comonomers through solvothermal conditions (Figs. S4a–c in Supporting information). This framework was designed to function as a fluorescent probe for Cu^{2+} due to its strong crystallinity, unique porosity, and large specific surface area, which resulted in high sensitivity and selectivity. The good stability and fluorescence luminescence efficiency may be attributed to the fact that the hydroxyl groups in the skeleton form hydrogen bonds within the molecule, and the *tert*-butyl on the pore wall regulates the π-π interaction between the layers of COF-JLU3, which improves the luminescence efficiency of the material. Additionally, the azide bond in COF-JLU3 has numerous heteroatom activation sites that can act as an electron donor for Cu^{2+}, leading to significant fluorescence quenching. This work proves the practicability of crystal COFs in ion sensing for the first time, and provides valuable insights for the design of functional porous crystal materials [74]. Furthermore, Cui *et al.* developed a new hydroxyl and imine functionalized covalent organic framework (COFs-DT, Figs. S4d–f in Supporting information) that exhibits strong and stable fluorescence in isopropanol. Its extended π-conjugated skeleton, strong chemical and thermal stability, fluorescence characteristics, and unique bidentate coordination sites make it possible to construct a highly sensitive and selective fluorescent sensor for the detection of Cu^{2+}. The redox potential of Cu^{2+}/Cu^{+} was located between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of COFs-DT, which enabled efficient transfer of excited state electrons from COFs-DT to Cu^{2+}. This electron transfer process, facilitated by the coordination bonds between Cu^{2+} and the bidentate ligand sites of COFs-DT, resulted in a fluorescence quenching process through a photoinduced electron transfer (PET) with COFs-DT as the donor and Cu^{2+} as the acceptor [75].

The element Cu^{2+} is a transition metal with an unfilled d-orbital valence layer capable of forming complexes with electron donors. However, the specific recognition of Cu^{2+} can be easily disrupted by certain transition metal ions, such as Fe^{3+}, Co^{2+}, Ni^{2+}, which possess similar unfilled d orbitals. Therefore, the development of a highly specific copper ion fluorescence detection platform requires ongoing research and development. Yan and colleagues have addressed this issue by utilizing a surfactant-assisted strategy to improve the dispersion of COFs in aqueous solutions and finely adjust their sensitivity. They synthesized a sp^2 carbon conjugated COF (sp^2 TPE COF) for metal ion sensing, which incorporates an olefin-linked conjugated chain as a signal amplification transducer. The detection of trace copper ions is achieved through a photoinduced electron transfer (PET) mechanism. The cyano group uniformly distributed in sp^2-TPE-COF can be used as a recognition site for Cu^{2+}. This is due to the lone pairs of nitrogen atoms in the cyano group being able to chelate with copper ions, which possess partly full d orbitals, resulting in a photo-induced electron transfer (PET) process that displays a prominent quenching phenomenon. However, sp^2-TPE-COF is hydrophobic, leading to an aggregation effect when immersed in water. To address this, the bulk COFs were exfoliated into nanosheets (NSs) by a variable temperature gas exfoliation method and three representative surfactants, neutral F127, negative sodium dodecylbenzene sulfonate (SDBS) and positive cetyltrimethylammonium bromide (CTAB), were selected to dissolve COF NSs and to study their effects on heavy metal detection performance. The sensing system in SDBS solution was found to be around eight times more sensitive than in organic solvent DMSO. In contrast, the fluorescence intensity of sp^2-TPE-COF NSs in CTAB solution was almost unaffected by Cu^{2+} with a quenching efficiency of only 7.3%. Such high sensitivity of sp^2-TPE-COF NSs in SDBS solutions is likely due to the electrostatic attraction between the negative-charged surface of the sp^2-TPE-COF NSs, which is encapsulated by anionic SDBS, and the positive Cu^{2+}, resulting in an intensified local concentration of Cu^{2+} in the vicinity of the probes. The zeta potentials of sp^2-TPE-COF NSs in F127, CTAB, and SDBS solutions demonstrate this (-5.4, $+37.8$, and -56.9 mV). [76]. Similarly, Dong's group has designed and synthesized a new fluorescent NH_2-Th-Tfp-COF that accurately recognizes Cu^{2+} through the synergistic effect of O,N,O' chelating sites and free amines. This material contains abundant O,N,O' chelating sites and a large number of free amino groups. The introduction of free amino groups plays a crucial role in improving Cu^{2+} detection sensitivity and adsorption capacity, as demonstrated by better sensitivity (0.19 μmol/L) and higher adsorption capacity (153 mg/g) compared to the non-functionalized Th-Tfp-COF [77]. Q-graphene, also known as carbon quantum dots or nano-onion hot graphene materials, has been found to enhance the fluorescence intensity of COFs due to its high proportion of folded edges and surface defects. Studies have shown that multilayer graphene and hollow QG composed of different carbon allotropes are particularly effective in this regard [78]. Cai's research group has successfully synthesized a metal-free fluorescent COF using a QG scaffold through a one-step covalent condensation reaction of melamine, phenol, and paraformaldehyde. This COF exhibits strong Cu^{2+} absorption capacity and specific fluorescence quenching, making it a useful tool for detecting Cu^{2+} in blood and wastewater. The hollow QG scaffold-mediated synthesis route holds promise for creating various types of multifunctional metal-free COFs suitable for applications in biomedical sensing, environmental monitoring, and metal removal [79].

Currently, research on the sensing properties of COFs for metal ions other than Fe^{3+} and Cu^{2+} is limited. Hence, there is an urgent need to develop a highly fluorescent COFs for the efficient identification and detection of these metal ions [80,81]. The parameters of the COFs for detecting Cu^{2+} are listed in Table S2 (Supporting information).

3.1.3. Zn^{2+}, Co^{2+}, Ni^{2+}, Al^{3+} detection

A great deal of research has been conducted to identify Zn^{2+}, Co^{2+}, Ni^{2+} and Al^{3+} using COFs. Yin's group rationally designed a novel hydroxyl-functionalized fluorescent covalent organic framework DHTPz-Bt based on the reaction of 2,5-dihydroxyterephthaloyl hydrazide (DHTPz) with 1,3,5-benzenetricarbaldehyde (Bt). The coordination form of Zn^{2+} and the oxygen atom in the phenolic hydroxyl group was studied. The framework exhibits high sensitivity and excellent selectivity in the detection of Zn^{2+}, with a detection limit of 14.89 nmol/L (Fig. 4a) [82].

Cobalt plays a crucial role in the production of proteins and red blood cells, but excessive amounts of Co^{2+} can result in negative reactions such as asthma, lung disease, and vasodilation [83]. A recent study by Wang *et al.* has examined the detection of Co^{2+} using a novel 3D COF connected by bipyridine. The COF was polymerized through tetrakis(4-aminophenyl)methane (TAPM), 2,2′-bipyridine-5,5′-diamine (Bpy), and 4,4′-biphenyldialdehyde (BPDA) under solvothermal conditions and exhibited a good detection limit

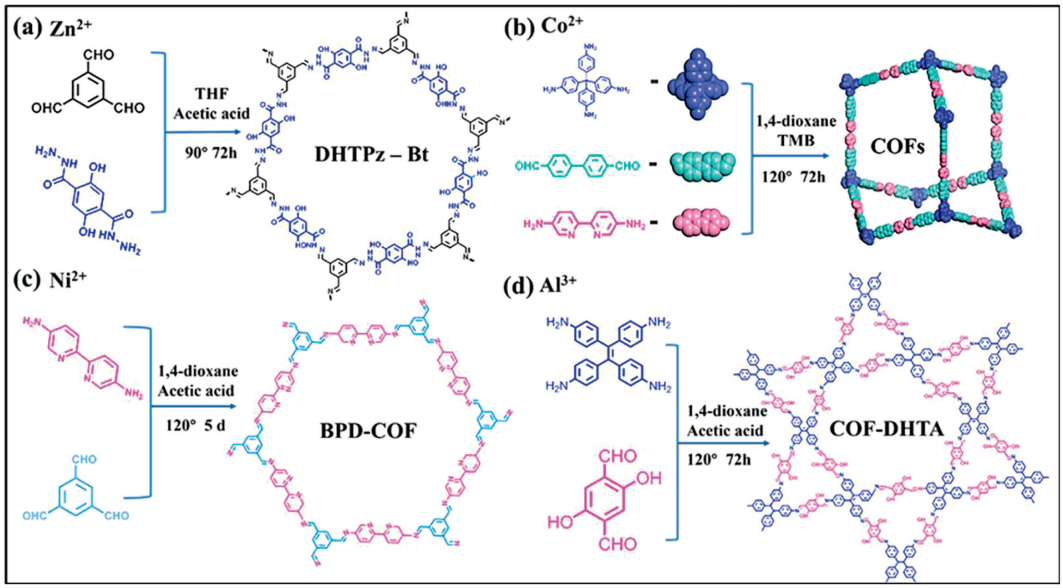

Fig. 4. The formation diagrams of COFs with different structures are used to detect different metal ions (a) Zn^{2+}, (b) Co^{2+}, (c) Ni^{2+}, (d) Al^{3+}. Reprinted with permission [82]. Copyright 2022, The Royal Society of Chemistry. Reprinted with permission [84]. Copyright 2021, Springer. Reprinted with permission [86]. Copyright 2021, Elsevier Inc. Reprinted with permission [87]. Copyright 2021, Elsevier B.V.

of 2.63 nmol/L with Co^{2+} (Fig. 4b). The method was successfully employed for the determination of Co^{2+} in complex samples such as shrimp and tap water, with a satisfactory recovery rate of 88.1%−109.7% [84].

Nickel is a transition metal widely used in industrial production, which is conducive to the stability and metabolic balance of hormones in the human body. However, excessive amounts of Ni^{2+} can cause respiratory diseases, dermatitis, allergies and even cancer. The World Health Organization (WHO) has set a drinking water safety exposure standard of 70.0 μg/L for Ni^{2+}, necessitating the development of convenient and feasible detection methods to measure its content [85]. Chen's group has reported the use of COFs for the fluorescence detection of Ni^{2+}. Specifically, they utilized 2,2′-bipyridine-5,5′-diamine and benzene-1,3,5-tricarbaldehyde as monomers to prepare BPD COFs with predesigned bipyridine recognition sites. BPD COFs possess a high specific surface area, regular pores, and a unique structure that confers outstanding fluorescence emission, ample space, and specificity to Ni^{2+} (Fig. 4c). By comparing the fluorescence sensing properties of BPD COFs and a corresponding small molecule model compound BPDB, the researchers found that BPD COFs had a wider concentration range ($4.20 \times 10^{-10} \sim 1.26 \times 10^{-6}$ mol/L) and a lower detection limit (6.80×10^{-11} mol/L). Moreover, the sensor demonstrated good detection ability for Ni^{2+} in actual samples, such as tea and chocolate, with a recovery rate exceeding 92%. These findings suggest that BPD COFs hold great promise as a sensitive and selective fluorescence sensor for Ni^{2+} detection [86].

Aluminum is not an essential element for the human body, but can be toxic to aquatic organisms and agricultural plants and damage their growth. There are few reports on COFs as Al^{3+} fluorescent sensors. Therefore, it is of great significance to identify and detect Al^{3+} in environment, medicine and food. Xie Yu's research group developed COF-DHTA using tetraphenylethene, which demonstrated exceptional thermal stability and crystallinity (Fig. 4d). The unique pore structure of COF-DHTA, coupled with the N, O chelating sites on the wall and Al^{3+}, resulted in excellent selectivity. In DMF, the fluorescence intensity exhibited a robust linear correlation with the concentration of Al^{3+} over a broad concentration range. Based on this, they developed a fluorescence sensor with high selectivity and high sensitivity to Al^{3+}, with a detection limit of 0.93 μmol/L [87].

Despite numerous reports on the identification of metal ions that have significant implications for human health using COFs, there is a dearth of studies examining the intricate pathways and mechanisms governing the interaction between these ions and COFs, including the coordination mechanism, binding mode, and electron transfer process. This shortfall makes it challenging to fully leverage the flexible design of functional groups, structural skeletons, pore size, and other advantages of COFs. Consequently, there exists tremendous potential for the development of superior COFs detectors.

3.2. Precious metal elements detection

Gold is a highly valuable and scarce precious metal that requires significant energy investment for its mining and extraction. The use of alternative methods to the highly toxic cyanide heap leaching process has been explored. However, there is a lack of COFs with specific affinity and sensitive response to gold for the selective detection and separation of gold from ultra-low concentration aqueous solutions. Zhou *et al.* have addressed this issue by designing a thioether functionalized COF (Fig. S5a in Supporting information). TTB-COF was synthesized through reversible imine condensation reaction of 2,5-bis(2-ethylthioethoxy)terephthaloyl hydrazine (BETH) and 1,3,5-triformylbenzene (TFB), with thioether side arms. The incorporation of Au^{+} binding sites in the cavity of TTB-COF confers the ability to selectively detect and recover low concentration Au^{+}. TTB-COF exhibits selective, qualitative and quantitative recognition of Au^{+} through significant luminescence quenching, which is superior to other low concentration metal ions [88].

Silver is a commonly used precious metal in various industrial sectors, but it poses a significant threat to human health and the environment due to its high toxicity and bioaccumulation. The discharge of silver-containing wastewater into the environment can cause severe water pollution, necessitating the timely detection and effective treatment of these harmful metal ions to control and purify environmental pollution. Studies have shown

that thiophene derivatives have extraordinary binding ability to silver ions [89]. Zhang's team developed a COF material called TAPA-BTDC based on dithiophene by designing the skeleton and pore environment, using tris(4-aminophenyl)amine as the connector and 2,2′-dithiophene-5,5′-dicarbaldehyde as the connector. They investigated the interaction between the host and guest and discovered that the charge transfer caused by the π complexation between silver ions and double thiophene-S chelating sites altered the π-π layered structure, enabling TAPA-BTDC to selectively detect silver ions by fluorescence enhancement (Fig. S5b in Supporting information). These dithiophene-S also provide numerous chelating sites for TAPA-BTDC to effectively remove Ag^{+} [31].

Palladium is a precious metal that has been found to cause skin irritation, cytotoxicity, allergy, and other forms of toxicity. Its ability to bind to DNA, RNA, amino acids, and proteins can interfere with normal cellular processes [90]. Therefore, it is important to effectively monitor and remove Pd^{2+} to protect the environment and human health. To address this issue, Yue's research group has synthesized a sp^2 carbon conjugated covalent organic framework (PY-SE-COF) containing a selenium diazole structure (Fig. S5c in Supporting information), which can be used for detecting and removing Pd^{2+} ions. PY-SE-COF exhibits high selectivity for Pd^{2+}, strong fluorescence, and good chemical stability in a wide pH range due to its olefin bond formed by Knoevenagel reaction [91].

The above COFs possess favorable fluorescence characteristics and recognition capabilities that present a promising design concept for the detection of precious metals. Although only a few COFs have demonstrated effective detection capabilities, their adaptable design, stable structure, and expanded π-skeleton offer the potential for enhanced fluorescence luminescence and coordination space, rendering them highly suitable as sensing matrix materials for metal ion detection. The parameters of the COFs for detecting Zn^{2+}, Co^{2+}, Ni^{2+}, Al^{3+}, Au^{+}, Ag^{+} and Pd^{2+} are listed in Table S3 (Supporting information).

3.3. Harmful metal elements detection

3.3.1. Hg^{2+} detection

In the aqueous environment, mercury usually exists in the atomic (Hg), water-soluble (Hg^{2+}) and complex (HgS) forms [92]. Currently, numerous studies have been conducted to develop effective methods for detecting and removing Hg^{2+}. Thiol and thioether functionalized covalent organic frameworks (COFs) have been found to possess specific coordination binding abilities to Hg^{2+}. Therefore, COFs such as TAPB-BMTTPA [93] and COF-S-SH [94] have been developed to adsorb mercury with high selectivity and excellent Hg^{2+} removal performance, but they cannot meet the needs of rapid on-site detection. Ding *et al.* have designed and applied a thioether-functionalized hydrazone-linked COF (COF-LZU8) for the selective sensing and effective removal of toxic Hg^{2+}. COF-LZU8 exhibits a strong fluorescence luminescence in both its solid and solvent forms, likely due to its longer thioether side chain preventing the aggregation-caused quenching (ACQ) that could occur during 2D layer stacking. This burst may be a result of the electron transfer that occurs when Hg^{2+} binds to the sulfur atoms of the side chain, leading to the excitation and transfer of electrons from the conjugated backbone to the unoccupied orbital of Hg^{2+} (Fig. S6a in Supporting information). This is the first time that a fluorescent COF has been used for the detection and removal of metal ions [95]. However, the strong affinity between mercury and sulfur makes the regeneration of these COFs very difficult. Cui *et al.* have reported a novel highly luminescent nitrogen-based TFPPy-CHYD COF by integrating pyrene-based structural blocks with flexible carbon hydrazide (CHYD) connectors (Fig. S6b in Supporting information). Unlike previous COFs that use sulfur-based ligands, the nitrogen-based ligands in TFPPy-CHYD possess good reversibility and higher selectivity. This greatly enhances their luminescence ability and allows them to be used as mercury-specific reversible binding receptors for simultaneous detection and adsorption of mercury [96].

Current research has primarily focused on the design of nitrogen-rich and thioether groups' affinity with Hg^{2+} in fluorescent COFs. However, the coordination patterns between these groups have not been thoroughly explored, and improving the selectivity, sensitivity, and stability of these COFs remains a significant challenge. For the specific recognition and recovery of Hg^{2+}, to address this challenge, Yu's group developed aryl and hydroxyl-functionalized AH-COFs as specific receptor sites for Hg^{2+}, which formed unique mercury-containing products with five-membered rings through specific mercury-promoted reactions. AH-COFs can be easily recycled after adsorption in the presence of $NaBH_4$, expanding the design and application of Hg^{2+} specific recognition anchors [97]. Sulfur- and nitrogen-rich COFs for the detection of Hg^{2+} have been developed and reported successively, such as TPE-S-COF [98], Tp-TSC [99], BATHz-Bt [100]. Moreover, COFs can form complexes with carbon dots, MOFs, carbon nanotubes and other nanomaterials by encapsulation, *in-situ* growth or hydrogen bonding due to their good pore size channels, stable coordination modes and adjustable topology. Qin's group reported a new composite material, TpPa-1COF@CDs, synthesized by reverse emulsion polymerization using carbon dots as fluorescence sensing elements and TpPa-1-COF as a supporting skeleton. Nitrogen-rich carbon dots prepared from 2,4,6-triaminopyrimidine exhibit high sensitivity and selectivity to Hg^{2+}, but it is challenging to remove harmful Hg^{2+} from water using a single carbon dot, let alone recycle and separate it. The formation of TpPa-1COF@CDs through the encapsulation of carbon dots by COF not only improves the stability of carbon dots but also enables recyclability after adsorption. More importantly, it can detect and remove Hg^{2+} in actual water samples, making it highly valuable for practical applications [101].

3.3.2. Pb^{2+}, Cd^{2+}, As^{3+} detection

With the mass production of industries, a large amount of waste gas substances containing metallic elements such as lead, cadmium, mercury and arsenic are produced, which can easily be released into the environment to pollute our water and soil if not properly treated. These toxins can cause serious health problems such as kidney, stomach, liver, and brain toxicity once they enter the body [102]. They are commonly found in water bodies in ionic form and have become one of the most prevalent and harmful environmental pollutants [103]. The use of fluorescent COFs for detecting Hg^{2+} is crucial for protecting and remediating environmental pollution. However, the application of COFs for fluorescence sensing of Pb^{2+}, Cd^{2+} and As^{3+} needs further exploration. Currently, only Zhang's group has successfully synthesized a carbazole-grafted COF backbone (COF-CB) through a Schiff base and post-grafting reaction. This COF-CB can be used as a "turn-on-type" fluorescent COF sensor with high selectivity and good interference resistance for identifying and detecting Pb^{2+} with a detection limit as low as 1.48 μmol/L [104]. For the detection of Cd^{2+}, the literature is also particularly scarce. Jin *et al.* synthesized two hydroxyl-functionalized porphyrin COFs (2,3-DhaTph and 2,5-DhaTph), which exhibited fluorescence response to Cd^{2+} through the chemical coordination of abundant phenolic hydroxyl groups and porphyrins with Cd^{2+}, achieving the dual functions of specific optical recognition and efficient adsorption of Cd^{2+} (Fig. S7a in Supporting information). Under the excitation at 468 nm in pure DMF solvent, 2,3-DhaTph without Cd^{2+} absorption gave two strong fluorescence peaks at 538 and 680 nm, respectively. After the adsorption of Cd^{2+}, both peaks exhibited enhanced fluorescence with a slight redshift (Fig. S7b in Supporting information). Different from 2,3-DhaTph, 2,5-DhaTph emitted

strong fluorescence at 650 nm, which was decreased by Cd^{2+} resulted in the emergence of a weak fluorescence peak at 500 nm and the obvious redshift of the wavelength to 680 nm (Fig. S7c in Supporting information). The fluorescence intensity at the short-wavelength (538 nm for 2,3-DhaTph and 500 nm for 2,5-DhaTph) is mainly influenced by the electron ring flow on the whole conjugated backbone, while the fluorescence emission peak at the longer wavelength is related to the porphyrin monomer. Cd^{2+} interacts with 2,5-DhaTph by forming two six-membered rings, which are constructed through the coordination of Cd^{2+} with a hydroxyl oxygen atom on 2,5-Dha and a nitrogen atom on the imine bond. In addition, bulk materials (PS@COFs) were prepared by *in-situ* growth of 2,3-DhaTph or 2,5-DhaTph on the pore wall of dopamine-treated heat-resistant polyurethane sponge. PS@COFs have interconnected large pore channels and thin COF layers uniformly distributed on the pore walls, resulting in faster adsorption kinetics and shorter adsorption equilibrium time compared to COFs (Figs. S7d–g). PS@COFs have potential in practical applications, as they can remove more than 99% of Cd^{2+} from water samples with good reusability [105]. Arsenate (As^{3+}) and arsenate (As^{5+}) are the two most common forms of arsenic. As^{3+} is known to be 50–100 times more toxic than As^{5+} and other forms. Yin's group developed a weakly fluorescent Dpy-TFPBCOF with PET effect by condensing 5,5′-diamino-2,2′-bipyridine (Dpy) and 1,3,5-tris(3′-formylphenyl)benzene (TFPB). When As^{3+} was introduced, the hindered PET process was turned off, and the fluorescence was turned on in the form of a distinct color change. This allowed for an ultra-low detection limit (8.86 nmol/L) for As^{3+}. This switched-on fluorescent probe showed clear visualization, good sensitivity, and real-time response [106].

3.3.3. UO_2^{2+} detection

Uranium, a radioactive and highly toxic element, is a crucial fuel for the advancement of nuclear energy. However, excessive exposure to uranium can cause irreversible harm to living organisms, including DNA damage [107]. The mining and smelting of uranium, improper reprocessing of spent fuel, and frequent nuclear accidents have led to the creation of vast amounts of uranium-containing waste, which poses significant health risks to both ecosystems and human populations once released into the environment [108]. To address this challenge, some novel nanomaterials enabling the detection and extraction of uranium, have been developed, such as composite hydrogels [109], porous organic polymers (POPs) [110], and MOFs [111]. MOFs possess advantageous properties such as adjustable topology, high crystallinity and ease of preparation, however they are not particularly stable due to the ligand bonding, particularly when exposed to acidic conditions [27]. POPs, whose chelating sites are usually buried by irregular small pores leading to degradation of adsorption properties, severely limit their utilization under environmentally relevant conditions [112]. Hydrogels, while excellent adsorbent materials, often require the combination of a responsive element for simultaneous detection and adsorption uranium, which can be difficult to ensure their stability [113]. As such, COFs with ordered pore sizes, high stability and high tunability has been of great interest for simultaneous detection and absorption of uranium [114,115].

The amidoxime group is widely recognized for its ability to specifically coordinate with uranium, making it a valuable component in various uranyl adsorbents such as hydrogels [116], nanofiber materials [117,118], MOFs [119], and COFs. The reported COFs modified with amidoxime groups have shown very good results in the selective adsorption of uranyl ions such as COF-HHTF-AO [120], TPB-BPTA-COF-AO [121], and COF-TpDb-AO [89]. However, there are limited reports on the detection of UO_2^{2+} using COFs, making further investigation into UO_2^{2+} detection adsorption regimes crucial for environmental protection. Professor Qiu's group has made significant contributions to the detection and extraction of radionuclides by developing fluorescent COFs, including TFPT-BTAN-AO [122], COF-PDAN-AO [123] and TAPM-DHBD [124]. These highly stable and strong crystalline fluorescent COFs with amidoxime groups have been successfully utilized in the rapid and sensitive detection and extraction of UO_2^{2+}. TFPT-BTAN-AO is synthesized using the triazine-containing monomer TFPT and the acetonitrile-rich monomer BTAN through the Knoevenagel reaction. It exhibits favorable luminescence yield, outstanding chemical and thermal stability, and a substantial quantity of amidoxime groups on its pore wall to precisely detect UO_2^{2+}, resulting in an ultra-sensitive reaction time of 2 s and a detection limit as low as 6.7 nmol/L. Moreover, it has a stable and open one-dimensional channel that can simultaneously extract uranyl ions with an adsorption capacity of 417 mg/g [122]. Building on these benefits, Li and Zhang *et al.* developed two sp^2-carbon COFs, COF TP-COF-AO [125] and COF-PDAN-AO [123], based on the same principle and similar cyanide-containing monomers, which also exhibit superior uranium detection and extraction capabilities.

In addition to the amidoxime group, Professor Qiu's group had integrated biphenyl diamine and pyrene-containing monomer (TFPPy) into the π-conjugated framework to synthesize a fluorescent covalent organic framework TFPPy-BDOH. Based on the excellent fluorescence characteristics of pyrene-containing monomers and the synergistic effect of hydroxyl and nitrogen atoms in the imine bond (Fig. S8a in Supporting information), TFPPy-BDOH not only has ultrafast fluorescence response, but also overcomes the serious interference problem caused by vanadium ions on amidoxime groups (Figs. 8b and c in Supporting information). Moreover, this work has explored its application value in actual wastewater. Experiments showed that it also has good quenching effect and good fluorescence recovery ability in simulated nuclear wastewater, which is expected to be used for the practical application of uranium removal from radioactive waste liquid [126]. It is important to note that while most current fluorescent COFs are 2D with a large π-conjugated plane, the potential of 3D COFs as sensing platforms for radionuclide detection or extraction is still in its infancy and requires further exploration. Therefore, their functions are still largely unexplored. Recently, Qiu's group reported a hydroxyl-functional 3D fluorescent COF (TAPM-DHBD) for simultaneous detection and extraction of uranium by integrating tetra(4-aminophenyl)methane (TAPM) with 3,3′-dihydroxy-[1,1′-biphenyl]-4,4′-dicarbaldehyde (DHBD). The synergistic effect of imine bonds and hydroxyl groups in the interconnected 3D microporous skeleton significantly enhanced the affinity of TAPM-DHBD for UO_2^{2+}, enabling highly selective detection and adsorption of UO_2^{2+} under harsh conditions with a very low detection limit (4.08 nmol/L). In addition, TAPM-DHBD enables actual samples spiked with 1 ppm UO_2^{2+}, such as river water, seawater and industrial wastewater, to decrease to less than 0.1 ppm [124]. By evaluating its utility in real water samples, the group well demonstrated that such 3D COFs with selective binding sites are an ideal strategy for rapid, sensitive and highly selective binding of UO_2^{2+} [127]. The parameters of the COFs for detecting Hg^{2+}, UO_2^{2+}, Pb^{2+}, Cd^{2+} and As^{3+} are listed in Table S4 (Supporting infoamation).

4. Conclusions

In this review, we summarize fluorescent COFs materials for metal ions detection, focusing on the interaction mechanism between COFs and metal ions, and revealing the great potential of COFs fluorescent sensors for environmental monitoring. Achieving real-time monitoring of metal ions requires accurate identification and quantification, which is always a crucial step, especially in complex environments. Nevertheless, COFs for metal ion fluorescence detection suffer from limited application conditions and low

selectivity. This is probably attributed to the fact that most COFs are composed of C, N and O as the main elements, which largely limits the types of functional groups that can be attached. Despite the COFs fluorescence sensor developed, the interaction mechanisms between the functional groups of COFs and metal ions remain obscure, and the effects of COFs topological structures on metal ions are still being explored. Consequently, further research into the recognition mechanisms between metal ions and related functional groups, such as O,N,O′-chelate sites with Fe^{3+}, amidoxime groups with $UO_2{}^{2+}$, and thioether groups with Hg^{2+}, is required to understand the interaction between COFs and metal ions at the microstructural level. We aspire to explore more excellent COFs fluorescent materials for real-time monitoring of metal ions with high sensitivity and specificity.

Declaration of competing interest

The authors declare that they have no financial and personal relationships with other people or organizations that can influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2023.109249.

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