

Recent Progress in Synthesis, Mechanism and Applications of Zinc-Based Metal-Organic Frameworks for Fluorescent Sensing

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As more and more pollutants threaten human health, it is necessary and essential to develop sensitive, accurate and rapid methods and sensory materials to detect harmful substance. Metal-organic frameworks (MOFs) are inorganic-organic hybrids assembled from inorganic metal ions or clusters and suitable organic ligands. Zinc-based MOFs (Zn-MOFs) have emerged as one of the most promising sensory material of MOFs for practical applications, and attracted significant attention due to structural diversity and incomparable stability properties. However, there are few reviews on systemic summary of synthesis design, mechanism and application of Zn-MOFs. In this review, we summarize the synthesis design methods, structure types and luminescence mechanism of Zn-MOFs sensor recognition in the past ten years and their applications in metal cations, anions, organic compounds and other analytes. Finally, we present a short conclusion, and look forward to the future development direction of Zn-MOFs.

Keywords

Metal-Organic Frameworks, Pollutants, Sensory Materials, Mechanism, Application

1. Introduction

With the development of social economy, the problem of environmental and food pollution has become the center of attention, posing an increasing threat to

human health [1]. The main pollutants are heavy metals [2], anions [3], organic compound [4], antibiotics [5], pesticide residues [6]. They enter and accumulate in the human body through the food chain, causing acute, subacute or chronic harm due to their potential biological toxicity [7] [8] [9]. Therefore, the simple, sensitive, accurate and rapid methods of identifying and detecting potential pollutants have important practical significance for pollution control.

Commonly used techniques for the trace detection of contaminants, including high-performance liquid chromatography (HPLC) [10], atomic absorption spectrophotometry (AAS) [11], inductively coupled plasma atomic emission spectrometry (ICP-AES) [12] and inductively coupled plasma mass spectrometry (ICP-MS) [13], are sensitive and accurate. However, they are severely limited by expensive instruments, high maintenance costs, long detection time, complex sample pretreatment and large amount of detection sample [14].

Metal-organic frameworks (MOFs) are inorganic-organic hybrids assembled from inorganic metal ions or clusters and suitable organic ligands [15]. Due to the unusual structure diversity, exciting porosity, flexibility and tunable surface area [16] [17], MOFs have been widely used in various fields, such as chemosensors, gas separation and storage, electrochemical detection and drug transport [18]. In recent years, a great number of MOFs materials have been designed as fluorescent chemosensors to detect organic low molecular compound, pesticide residue, anion and metal ions [19]. However, MOFs generally face some problems such as unclear detection mechanism, poor water stability and low sensitivity [20]. With structural diversity, incomparable stability, Zn-MOFs are considered to be one of the most promising sensory material of MOFs for practical applications [21] [22].

In recent years, some recent reviews have also concerned MOFs and their sensing application [23]. However, these reviews mainly focus on lanthanide, zirconium elements, few reviews focus on zinc-based metal-organic framework materials. Therefore, this review focuses on the synthesis method, structure type, classification type and luminescence mechanism of fluorescent Zn-MOFs discovered over the past ten years. Further, the applications of fluorescence sensing in metal cations, inorganic anions, nitro aromatic compounds, anti-biological and other molecules are summarized systematically. Finally, the current challenges for Zn-MOFs in this research field are also outlined, and we also proposed some perspectives to address some existing research challenges.

2. Synthesis Strategy of Zn-MOFs

The synthesis of MOFs is formed by self-assembly of metal ions and organic ligand molecules through coordination bonds, and strong coordination bonds provide the basis for structural stability and high crystallinity. Multiple synthesis methods and specific experimental conditions have resulted in MOFs with different morphologies, crystal structures, and pore sizes, further affecting their functional applications. The efficiency of synthesis is related to metal ion, ligand, coordination environment, geometrical structure, surface hydrophobicity, steric hindrance, etc. The functionalization of fluorescent MOFs can be realized by *in-situ* synthesis and post-synthetic modification (PSM).

2.1. In-Situ Synthesis

2.1.1. Solvothermal Method

Many methods have been explored to synthesize MOFs, mainly including solvothermal method, microwave-assisted method, reflux method, ultrasonic method, mechanical method and electrochemical method. However, solvothermal method is most widely used procedures for the preparation of MOFs [24]. Li *et al.* choose benzotriazole-5-carboxylic acid, 5-amino-1H-tetrazole by virtue of the mixed-ligand approach obtained photoluminescence sensors as luminescence thermometries over tunable temperature range. Linear correlations are presented between the luminescence intensities and the low temperatures [25]. Wang *et al.* employed ZnCl₂ and 4,4'-(1H-1,2,4-triazole-1-yl) methylene-bis (benzonic acid) synthesis luminescent zinc (II) metal-organic framework. The MOFs exhibits highly selective and sensitive luminescence sensing for $Cr_2O_7^{2-1}$ ions in aqueous solutions with high quenching efficiency $K_{sv} = 1.22 \times 10^4$ L-mol⁻¹ and low detection limit (0.023 μ M (S/N = 3)) [26].

2.1.2. Others Synthesis Method

In addition to solvothermal method, diffusion method and microwave assisted method are also commonly used to synthesize MOFs. Wang *et al.* choose TEMPO-oxidized cellulose nanofibrils and $Zn(NO_3)_2 \cdot 6H_2O$ into distilled water, and stirred by a magnetic stirrer at 800 r/min to form a uniform suspension, and then add disodium terephthalate into the above solution obtained Zn-BDC@TOCNF [27]. Compared with solvothermal method, microwave assisted method can greatly reduce the reaction time to improve efficiency. The amount of time of this method containing of high porosity, high crystallinity, very large surface areas, and very small nano scale dimensions was included 20 times faster than other methods and enhanced the stability of the MOF structures [28]. For instance, Gencer *et al.* choose a friendly way to develop carbon dots with controllable emission properties by incorporating zinc (II) ions into carbon dots through simple microwave-assisted synthesis [29].

2.2. Post-Synthetic Modification

Post-synthetic modification (PSM) refers to taking pre-synthesized Zn-MOFs as precursors and further processing them to obtain new materials with desired features or better performance. Cao *et al.* encapsulate the upconversion nanoparticles (UCNPs) into the metal-organic frameworks (ZIF-8) and incorporating molecularly imprinted polymer (MIP) by post-modification and use them for the detection of octopamine, the detailed preparation process is shown in **Figure 1**. The method with the detection limit of 0.081 mg·L⁻¹ would yield double functions of specific recognition and quantitative detection for octopamine without

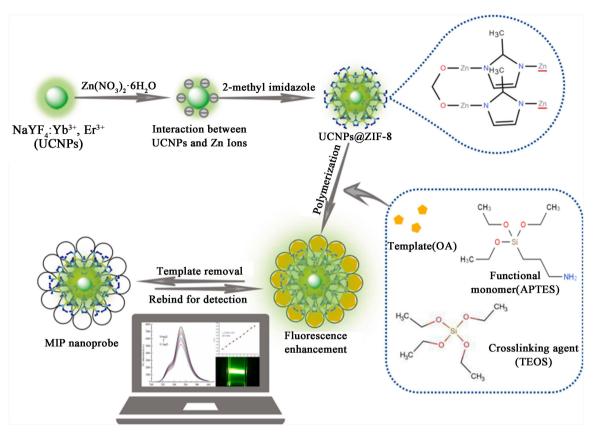


Figure 1. The detailed preparation process of UCNPs@ZIF-8@MIP [30].

sophisticated preprocessing [30]. Li *et al.* choose imidazole-2-formaldehyde, zinc nitrate hexahydrate and sodium formate in a Teflon-lined stainless steel autoclave at 120°C for 24 h, ZIF-90 crystals were gained after being filtered and washed with methanol for several times. Then, the fluorescent MOFs (ZIF-90-BA) by post-functionally modifying ZIF-90 with the Schiff base group. This probe was successfully used for OCl⁻ turn-on fluorescence sensing. It exhibited high selectivity over other potentially interfering species, and it showed high sensitivity (detection limit: 6.25 μ M) and fast response (15 s) [31].

3. Types of Zinc-Based Metal Organic Frameworks (MOFs)

Fluorescence sensing is the chemical reaction between the fluorescence sensor and the target analyte that causes the change of fluorescence signal, and the detection of the target analyte is realized by collecting the change of fluorescence signal. According to the change of fluorescence signal, Zn-MOF sensors can be divided into fluorescence turn-on, fluorescence turn-off and ratiometric fluorescence sensors.

3.1. Fluorescence Turn-on Zn-MOF Sensors

By introducing the analyte, the fluorescence intensity of the original Zn-MOF with weak or no fluorescence is significantly enhanced, which called turn-on Zn-MOF sensors. Farahani *et al.* design a fluorescent Zn-MOF (TMU-16) as

chemical sensing agents to detect Cd (II) ions and dichloromethane. The TMU-16 displays superb luminescence emission, and intensity significantly enhanced. This work demonstrates that luminescent MOFs may be rationally designed to serve as practical multi-responsive sensors for the detection of metal ions and small molecules [32]. Kaur *et al.* develop a 2-D Zn (II) based metal-organic frameworks (MOF) formulated as $[Zn(apca)_2]_n$ (Hapca =

3-aminopyrazine-2-carboxylic acid). The selectivity of the as-synthesized MOFs was studied for detecting phenolic structural analogs such as phenol,

2,6-dichlorophenol (2,6-DCP), 2,4-dichlorophenol (2,4-DCP), *et al.* The results observed that 2,6-DCP significantly enhance the fluorescence emission of the Zn-MOF, while other have induced negligible change in fluorescence response. It could be revealed that Zn-MOF are equipped with excellent recognition ability for almost exclusively 2,6-DCP [33]. The effects of different chlorophenols on the emission spectra are shown in **Figure 2**.

3.2. Fluorescence Turn-off Zn-MOF Sensors

Fluorescence turn-off is the interaction between fluorescent material molecules and solvent molecules or other solute molecules, resulting in fluorescence quenching. Zhang *et al.* has been synthesize a new fluorescent metal-organic framework (MOF), named $[Zn_2(TBAPy)(H_2O)(DMF)]\cdot 4DMF\cdot 2H_2O$ (JOU-34) (TBAPy = 1,3,6,8-tetrakis (p-benzoic acid) pyrene). Due to the introduction of pyrene groups, JOU-34 shows strong fluorescent emission cantered at about 470 nm, and a good fluorescence sensing performance toward nitroaromatic compounds, especially nitrobenzene (NB). In the presence of nitrobenzene, the quenching efficiency can reach 89%. The results indicate that JOU-34 can be

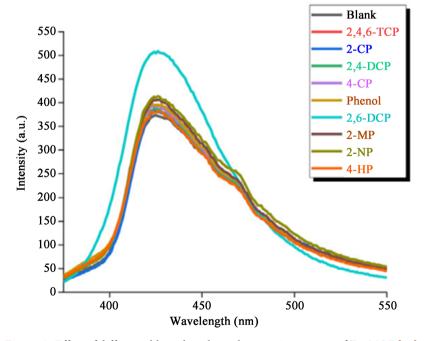


Figure 2. Effect of different chlorophenols on the emission spectra of Zn-MOF [33].

applied as a functional material for nitroaromatics detection [34]. Tehrani *et al.* introduce a new porous metal-organic framework (TMU-21). The fluorescence propertie of TMU-21 was preliminarily evaluated by immersing the activated MOF in three aromatic solvents, *i.e.*, benzene, toluene, and nitrobenzene. TMU-21 exhibits almost complete fluorescence quenching when they are immersed in nitrobenzene, with a quenching efficiency of >98% [35].

3.3. Ratiometric Fluorescence Zn-MOF Sensors

Ratiometric fluorescence is to collect fluorescence intensity at two or more different emission wavelengths at the same time, and use the ratio of fluorescence intensity as the output signal to establish an internal standard to detect the target analyte. This method can eliminate the interference of environmental factors such as probe concentration and instrument efficiency, so as to achieve more sensitive and reliable detection of target analytes. Yang et al. constructed a metal-organic framework (MOF) with the dual emitting system (CDs@ZIF-8) by hydrothermal method. CDs@ZIF-8 with dual-emitting centers can be utilized for detecting copper ions as a ratio fluorescence sensor. The fluorescence sensor shows excellent sensitivity, selectivity and strong environmental suitability for sensing Cu2+ ion, and the limit of detection (LOD) for Cu2+ ion is 11.712 µM [36]. Wang et al. propose a method for embedding highly luminescent doped QDs into a MOF (ZnS:Eu@ZIF-8) to be applied to the fluorescence detection of pollution hazards. When the TNP solution was added, the luminescence intensity of ZnS:Eu@ZIF-8 underwent a significant sudden extinction. The double-ratio fluorescence sensor was observed to be highly selective for the detection of TNP [37].

4. Structure Design Types of Functional Zn-MOF

Functional organic ligands and structurally stable MOF materials are of great significance for the realization of highly selective detection and practical application [38]. According to the composition of structure, fluorescence sensors can be divided into MOFs and MOFs-based composites. Due to the advantages of good porosity, multi-function, diverse structure and controllable chemical composition, MOFs and MOFs-based composites have been widely used in various fields [39].

4.1. MOFs

MOFs with high porosity, large surface area, controllable morphology, variable structure and the synergistic effect of metal-organic ligand, are gradually applied in fluorescence sensing. Shao *et al.* constructed two new title MOFs, $[Zn(BTA)_2]_n$ (LMOF-1) and $[Zn_3(BTA)_2(5-tbuip)_2]_n$ (LMOF-2) (BTA = 1H-benzotriazole,5-tbuip = 5-tert-butylisophthalic acid), as multiresponsive fluorescence sensors for Fe(III) and Cr(VI) ($CrO_4^{2-}/Cr_2O_7^{2-}$ ions) detection. LMOF-1 and 2 show good stability in many solvents and strong blue luminescence and may be useful to the development of fluorescent materials [40]. Hu *et al.* designed a new MOF formulated as $[Zn_2(trz)_2(btdb)] \cdot 4DMF$ (trz = 1,2,4-triazole, H₂btdb =

4,4'-(benzo[c][1,2,5]thiadiazole-4,7-diyl) dibenzoic acid). The fluorescence sensor shows excellent sensitivity and selectivity sensing Fe³⁺ ion in both aqueous and non-aqueous solution through quenching mechanism, given a detection limit of 3.1 and 17.0 μ M in methanol and H₂O solution, respectively [41]. Kajal *et al.* synthesized highly stable zinc-based luminescent metal-organic framework (LMOF) via solvothermal method. Synthesized MOF samples show excellent recyclability in fluorescence quenching for the various nitro-analytes (2,4-DNP, 2-Nitrotoulene, 4-Nitrophenol, and Nitrobenzene) even after the fourth cycle, and the results can generalize the explosive sensor technology and sensing various nitro-based pollutants [42].

4.2. MOFs-Based Composites

MOFs-based composites have a high specific surface area and an adjustable pore structure and are rich in unsaturated metal active sites and multifunctional groups [43]. The remarkable properties of MOF-based composites have provided new ideas for the development of novel and efficient strategies as well as for the detection trace analyte. Baghayeri et al. designed a magnetic MOF-based composite by a simple solvothermal method. A good selectivity for As(III) detection by the proposed the MOF-based composite. And this sensor was employed for the As (III) monitoring in environmental water samples, and the accuracy of obtained results were confirmed by inductively coupled plasma-optical emission spectrometer (ICP-OES) system [44]. Yang et al. constructed a metal-organic framework with dual emitting system (CDs@ZIF-8) by hydrothermal method. The CDs@ZIF-8 fluorescence sensor shows excellent sensitivity, selectivity and strong environmental suitability for sensing Cu²⁺ ion with the limit of detection (LOD) [36]. Zheng et al. use a natural amino acid derivative as the luminescent moiety to result in a lamellar coordination polymer, and further embed luminescent dye molecules in the crystal matrix to result in a luminescent dye@MOF sensor. The composite sensor exhibits excellent sensitivity for decoding different VOCs with clearly differentiable fluorescence emission [45].

5. Detection Mechanism of Fluorescence Sensor Based on MOFs

According to the change of fluorescence signal, the sensing mechanism can be divided into photoinduced electron transfer, fluorescence resonance energy transfer, aggregation-induced luminescence and inner filter effect.

5.1. Photoinduced Electron Transfer (PET)

Photoinduced electron transfer is the phenomenon of intramolecular or intermolecular transfer of electrons induced by light. In PET fluorescent molecular probes, there is a photoinduced electron transfer between fluorophore and acceptor unit, which has a very strong quenching effect on fluorescence. Therefore, before binding to the guest, the probe molecule does not emit fluorescence, or fluorescence is very weak. Once the receptor is bound to the guest, the photoinduced electron transfer is inhibited or even completely blocked, and the fluorophore will emit fluorescence. Pan et al. prepared a novel three-dimensional zinc-based metal-organic framework (Zn-MOF) as a fluorescent sensor for detection of nitrobenzene. The synthesized Zn-MOF exhibited fluorescence quenching for nitrobenzene (NB). The theoretical computation was employed to investigate quenching mechanism of Zn-MOF toward NB. The result of quenching mechanism might be ascribed to the electron transfer from the electron donor Zn-MOF to NB adsorbed on the Zn-MOF [46]. The research group of Xie. synthesized a new zinc metal-organic framework (Zn-MOF) for detection of nitrobenzene and Fe (III). The Zn-MOF displays remarkable fluorescent quenching effect toward nitrobenzene (NB) and Fe3+ ion due to the electron transfer quenching mechanism (PET) [47]. Fan et al. constructed a hydrolytically stable amino-functionalized Zinc (II) metal-organic framework detecting Cr (VI) anions and nitroimidazole/nitrofuran antibiotics exhibiting fluorescence quenching response. The result show photo-induced electron transfer (PET) of course plays an important role during the quenching process [48].

5.2. Fluorescence Resonance Energy Transfer (FRET)

Fluorescence resonance energy transfer (FRET) is a short-range non-radiative energy transfer process. When fluorescence resonance energy transfer occurs, the excited donor transfers energy to the adjacent ground state receptor by non-radiative means, and made the receptor excited. The fluorescence intensity of the donor is weakened, but the fluorescence intensity of the receptor is enhanced [49]. Liu et al. reported a Water-Stable Zinc (II)-Organic framework using zinc nitrate salt and benzotriazole-5-carboxylic acid (H2btca) ligand. It can be applied as a "turn-off" fluorescence probe to detect Fe³⁺ and Cr⁶⁺ ions in an aqueous solution with selectivity and sensitivity. They suggested that resonance energy transfer (RET) may affect the quenching process of Fe^{3+} , CrO_4^{2-} and $Cr_2O_7^{2-}$ [50], and this was consistent with previous reports [51] [52]. Sheng et al. designed a zinc-based fluorescent organic framework based on a polyfunctional groups ligand [1-{2-(2-pyridyl)-benzo [d] imidazole}-2-(5-hydroxyisophthalic acid) ethane] (H₂L). The Zn-MOFs has good recyclability and can be regenerated multiple times for detecting TNP or Fe³⁺. The study result shown that the resonance energy transfer between Zn-MOFs and Fe³⁺ or TNP during luminescence sensing, resulting in fluorescence quenching [53].

5.3. Aggregation-Induced Emission (AIE)

The phenomenon of aggregation-induced luminescence is that for some fluorescent molecules, and they do not emit light or emit weak fluorescence in the solution state, but emit strong fluorescence in the aggregated state [54]. The research group of Pang. constructed a molecular amines fluorescence sensor Zn-TCPE sensing of amines. In an aqueous solution, Zn-TCPE fluorescence is quenched by water molecule coordination. After the introduction of amino groups, competitive coordination substitution and electrostatic interactions with amino groups inhibit the movement of the AIE-active organic ligand, leading to the re-enhancement of fluorescence. The result show that Zn-TCPE enables the highly sensitive and selective detection of potentially harmful amines with low detection limits of 18.7 - 68.5 nM [55]. Ameen *et al.* synthesize a ultra-small and higly fluorescent zinc-based MOFs (FMOF-5) to detect tetracycline (TC). The tetracycline (TC) selectively tuned the blue emission of FMOF-5 to greenish-yellow emission (520 nm) with dramatic enhancement through aggregation induced emission (AIE). The prepared FMOF-5-based probe showed high stability and reusability [56]. Li *et al.* designed a MOF material, which can perform as a fluorescence "off-on" probe for highly sensitive detection of Al³⁺ in aqueous media. They study shown that hydroxyl group can selectively chelate Al³⁺, which is directly related to the dissociation of nonfluorescent MOF and consequent activation of the AIE process [57].

5.4. The Inner Filter Effect (IFE)

The inner filter effect of fluorescence is a phenomenon in which the excitation light or emitted light is absorbed by the fluorescence or other light-absorbing substances when the concentration of the fluorescence is large or coexists with other light-absorbing substances. In fluorescence analysis, the inner filter effect can lead to the deviation of the linear relationship between fluorescence intensity and concentration, and even cause the distortion of spectral shape. Zhang et al. developed a novel fluorescence sensor with high sensitivity and selectivity based on nitrogen-doped carbon dots embedded in zinc-based metal-organic frameworks. The fluorescence of the MOFs was effectively quenched in the presence of tetracycline due to the inner filter effect (IFE) [58]. Zhang et al. choose Zinc nitrate and 1,2,4-triazole as raw materials to synthesis a novel metal organic framework material (Zn-MOF). The experimental results show that the fluorescence intensity of Zn-MOF decreases significantly after the addition of Fe³⁺, and other metal ions have no significant change, indicating that Fe³⁺ has a certain effect on fluorescence quenching of Zn-MOF. According to the UV-visible absorption spectrum experiment, Fe³⁺ can absorb the excited state energy of Zn-MOF and make it return to the ground state, thus reducing the energy transfer from ligand to Zn²⁺, resulting in fluorescence quenching [59]. Wang et al. constructed a metal-organic framework (MOF) with fluorescent properties using imidazole derivative 4,4'-bis (2-methyl-1H-imidazol-1-yl)-1,1'-biphenyl (4,4'-BMIB), 2,5-dimethoxyterephthalic acid (H₂DTA) and Zn (II) ion. The fluorescence of the MOF is quenched after adding Fe³⁺. Due to competitive absorption between metal ions and MOF [60].

6. Sensing Applications of Zn-MOFs

Due to fascinating and unique characteristics, Zn-MOF based sensors have been

applied in sensing of analytes in environment, food and other fields. In this section, we have summarized the luminescence Zn-MOF based sensor for detecting various analytes, including metal cations, anions, organic compounds and other analytes.

6.1. Sensing of Metal Cations

With the rapid development of industry, the problem of metal ion pollution has raised global concern. Metal ions enter and accumulate in the human body via the food chain, lead to many diseases threatening human health. Therefore, it is essential to develop effective, rapid detection methods for metal ions [61]. As shown in the **Figure 3**, Zhang *et al.* designed a chiral luminescent Zinc (II)-MOF $[Zn(BPDPE)_2(dca)_2]_n$ (BPDPE = 4,4'-bis(pyridy) diphenyl ether, H₂dca = Dextro-camphoric acid). The experiments revealed that Zn-MOF has highly selective and sensitive fluorescence sensing performances for detecting Fe³⁺ ion through luminescence quenching [62].

Xiao *et al.* synthesized two new inorganic-organic hybrid zinc phosphate frameworks. The fluorescence titration experiment results shown that fluorescence intensity of Zn-MOF decreases significantly after the addition of Fe^{3+} , so the

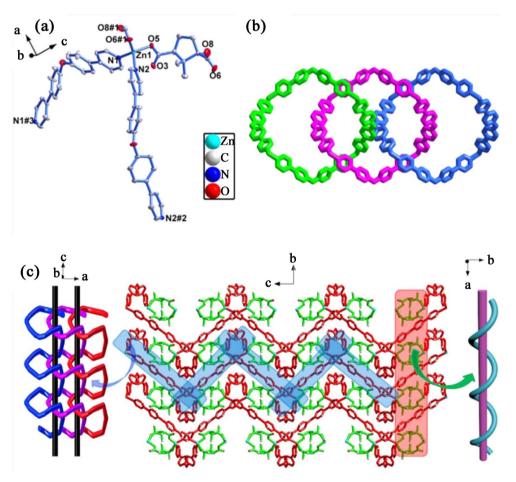


Figure 3. (a) Coordination environment of Zn(II) ions in MOF; (b) Two fold interlocked helical chains constructed by BPDPE and Zn^{2+} ; (c) Two kinds of spirals chains linked each other to form a three dimensional framework [62].

as-prepared two Zn-MOF can be used as fluorescence sensor for selective Fe^{3+} detection [63]. The research group of Wang. constructed a fluorescence metal-organic framework $[Zn_3(APT)_4]\cdot 2H_2O$ (Zn-APT) using $Zn(NO_3)_2\cdot 6H_2O$ and 2-amino-6-purinethiol (ATP). Zn-APT can emit strong luminescence, so it can be used as a fluorescent probe to detect Fe^{3+} ion effectively [64]. Cheng *et al.* synthesized a zinc metal-organic framework material (Zn-MOF) based on fluorenone carboxylate ligand. The experiment results shown that it is a fluorescent probe that can quickly recognize Al^{3+} and Fe^{3+} ions [65]. Hu *et al.* chose two similar ligands (bpta = 3,5-bis(4-pyridyl)-1,2,4-triazole, bpat =

3,5-bis(4-pyridyl)-4-amino-1,2,4-triazole) and synthesized two MOFs with similar structures, ${Zn_2(bpta)_2(hpta)(H_2O)_2 \cdot 6H_2O}n$,

 ${\rm Zn_2(bpat)_2(hpta)(H_2O)_4\cdot 4H_2O}_n$. The fluorescence sensing performance results reveal that they both show obvious fluorescence enhancement effect to high valence metal ions (Fe³⁺, Al³⁺, Cr³⁺, In³⁺ and Zr⁴⁺) [66].

6.2. Sensing of Anions

Anionic pollutants put forward negative impacts on the environment, so designing a potential fluorescent sensor for recognizing hazardous anions is necessary. Minmini et al. synthesized metal organic framework by the solvothermal process of 2-(4-carboxyphenyl)-1,3-dioxoisoindoline-5-carboxylic acid with Zn(OAc)₂·2H₂O. The luminescent studies indicates that the obtained Zn-MOF could be an efficient material for selectively sensing CrO₄²⁻, and the fluorescence measurement illustrate that chromate anion has the quenching effect upon trapped into the porous framework [67]. Bi et al. reported a novel metal-organic framework based on the coordination of acylhydrazide ligand and Zn²⁺. Compared with other anions, only $Cr_2O_7^{2-}$ virtually entirely quenched the emission of Zn-MOF, with a quenching percentage of over 92 percent. Therefore, the MOF should be a promising luminescent sensor for the detection of $Cr_2O_7^{2-}$ [68]. Cao et al. designed a unique three-dimensional Zn-MOF framework. The luminescence properties confirm that the emission behavior of the Zn (II) complex possesses excellent thermal and chemical stabilities. The fluorescence titration experiment shown that the MOF can be sensitive, efficient and fast in detecting MnO₄-resulting the fluorescence quenching [69]. Xie et al. constructed a Zn-based MOF using benzotriazole-5-carboxylic acid and pyridine as ligands. The luminescent results reveal that MOF can be a luminescent sensor for sensitively detecting PO₄³⁻ through luminescent enhancement effect [70]. Fu et al. reported a water stable zinc-base metal-organic framework SG7@FIR-53 (SG7 = 8-hydroxypyrene-1,3,6-trisulfonate). The composite SG7@FIR-53 exhibits a sensitive fluorescence quenching response against $Cr_2O_7^{2-}$ and MnO_4^- in aqueous solution [71].

6.3. Sensing of Organic Compounds

Organic compounds, such as trinitrophenol, nitrobenzene,1,3-dinitrobenzene,

usually are hazardous and sometimes can be explosive [72]. Recognizing these organic compounds, especially nitroaromatic compounds, will have the important significance. Li et al. synthesized a novel dual functional composite (MOFL-TpBD) through solvothermal methods, with stable 2,4,6-Trinitrophenol (TNP) fluorescence detection performance. MOFL-TpBD was capable of fluorescent sensing of TNP, with a linear range from 0.01 to 1 mM and a limit of detection of 3.52 µM. The MOFL-TpBD provided a potential candidate material for the detection of heavy metal ions and explosives in environmental water samples [73]. Xian et al. designed a zinc metal-organic framework (MOF) by the solvothermal method. The sensing detection results show that it has obvious fluorescence quenching behavior towards nitrobenzene (NB) in the range of 0 - 250 ppm, and the fluorescence intensity decreases exponentially when the NB concentration increases. The MOF sample may be used as a potential NB probe in liquid environment [74]. Fang et al. synthesized a luminescent zinc metal-organic framework under solvothermal conditions by using atriazolate-carboxylate bifunctional ligand, 4-(1H-1,2,4-triazol-1-yl) benzoic acid (Htba). The systematic luminescence experiments reveal that the MOF can be potentially used as a fast-response fluorescence sensor for the sensitive detection of nitrobenzene through drastic fluorescence quenching [75]. Wang et al. designed a multi-functional metal-organic framework (MOF) under solvothermal condition. The fluorescence sensing results reveal that MOF has sensing performance, which can sense anilines selectively and reversibly through fluorescence enhancement or quenching effect [76]. The detail fluorescence sensing results are shown in Figure 4.

6.4. Sensing of Other Analytes

Based on nearly ten years of literature, studies have shown that zinc-based MOF sensors can be used for sensing temperature, water, *et al.* [77]. Cai *et al.* synthesized a biological MOF, Zn_3 (benzene-1,3,5-tricarboxyl)₂(adenine)(H₂O) (ZnBTCA) for

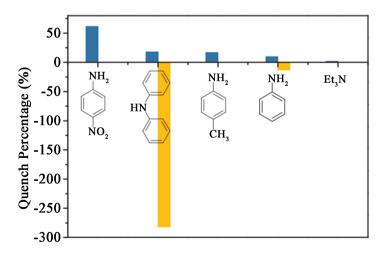


Figure 4. Percentage of fluorescence quenching or enhancement of MOF obtained for different analytes in ethanol solutions at room temperature [76].

monitoring temperature at the cellular level. The MOF exhibits highly efficient ratiometric temperature-sensing properties under physiological cellular conditions but also can be excited under visible light [78]. Zhang *et al.* constructed a new mixed-ligand metal-organic framework (MOF), ZnATZ-BTB, as a luminescent ratiometric thermometer by making use of the intrinsic dual emission at cryogenic temperatures. The novel MOF thermometer shows significantly higher sensitivity than the previously developed MOF ratiometric thermometers [79]. Bhattacharya *et al.* designed a 3D porous metal-organic framework (MOF) of Zn (II) ions. The MOF shows remarkable potential to detect traces of water in various organic solvents [80].

7. Conclusions and Prospects

Although Zn-MOFs have gained interest in sensing applications, there is still a need to explore more to improve their properties [81]. For instance, 1) more efforts should be made to improve the yield of the product. The high yield synthesis strategy can be employed to improve product quality and fluorescence sensing efficiency, and even scale up their industrial applications. 2) The introduction of functional materials with a variety of properties can endow the Zn-MOF with upgraded properties for sensing applications. 3) The water stabilities of Zn-MOF still need to be explored and enhanced by selecting specific ligands via structural calculation and theoretical simulation to understand the relationship between structure and performance. 4) The mechanical properties of Zn-MOFs also need to be systematically studied by theoretical calculation to broaden the practical applications. In conclusion, future research needs to overcome the above shortcomings and further explore new methods to expand more application fields of Zn-MOFs in the future.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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