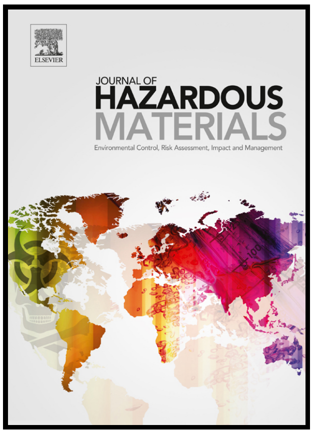

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# Constructing functional metal-organic frameworks by ligand design for environmental applications

Qian Sun [a,b], Lei Qin [a,b,*], Cui Lai [a,b,*], Shiyu Liu [a,b], Wenjing Chen [a,b], Fuhang Xu [a,b], Dengsheng Ma [a,b], Yixia Li [a,b], Shixian Qian [a,b], Zhexin Chen [a,b], Wenfang Chen [a,b], Haoyang Ye [a,b]

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## Abstract

Metal-organic frameworks (MOFs) with unique physical and chemical properties are composed of metal ions/clusters and organic ligands, including high porosity, large specific surface area, tunable structure and functionality, which have been widely used in chemical sensing, environmental remediation, and other fields. Organic ligands have a significant impact on the performance of MOFs. Selecting appropriate types, quantities and properties of ligands can well improve the overall performance of MOFs, which is one of the critical issues in the synthesis of MOFs. This article provides a comprehensive review of ligand design strategies for functional MOFs from the number of different types of organic ligands. Single-, dual- and multi-ligand design strategies are systematically presented. The latest advances of these functional MOFs in environmental applications, including pollutant sensing, pollutant separation, and pollutant degradation are further expounded. Furthermore, an outlook section of providing some insights on the future research problems and prospects of functional MOFs is highlighted with the purpose of conquering current restrictions by exploring more innovative approaches.

**Keywords:**

Metal-organic frameworks; Ligand design; Pollutant sensing; Pollutant separation; Pollutant degradation

## Environmental implication

A large number of toxic and harmful pollutants have been discharged into the environment. Some purification materials have high costs, low efficiency, and may generate secondary pollution. Metal-organic frameworks (MOFs) have many unique physicochemical properties and are one of the green and efficient materials for environmental pollution treatment. This study investigates three ligand design strategies for MOFs, as well as the challenges for subsequent research. Moreover, recent advances of functional MOFs by ligand design in environmental applications are presented, and the effects of ligand design on the performance of functional MOFs are explored from the mechanism perspective.

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## 1. Introduction

Metal-organic frameworks (MOFs) are network-like periodic framework structures assembled by coordination self-assembly of metal ions/clusters and organic ligands (Liu, S. et al., 2020b). It was until the discovery of the first generation of MOFs by Scott J. Pollack *et al.* in 1989 that real scientific research on MOFs began (Pollack et al., 1989). In 1995, Omar M. Yaghi *et al*. connected bipyridine with Cu(I) to form a diamond-like open network with planar trigonometric geometry, which ushered in the spring of rapid development of MOFs (Yaghi and Li, 1995). In recent years, rationally constructing MOFs with superior properties has become more and more popular, and various typical MOFs with well-defined topologies have been reported for potential applications (Pei et al., 2021; Shan et al., 2021).

MOFs usually possess large specific surface area and porosity, tunable structure and function, easy synthesis, recyclability, and other significant physicochemical properties (Ke et al., 2017; Kirchon et al., 2018; Meek et al., 2011; Qin, N. et al., 2022). According to these characteristics, MOFs are used in different fields, such as catalysis, gas storage and separation, energy conversion and storage, contaminant remediation, proton conduction, and chemical sensors (Indra et al., 2018; Ke et al., 2018; Meteku et al., 2020; Qin et al., 2021). It could be seen from the trend of MOF publications number each year that it gradually becomes a hot topic in the research field (Fig. 1). Through literature survey, it can be found that most studies focused on metal centers rather than ligands. The research on ligands mainly focused on synthesizing MOFs by using single- or mixed-ligand design strategies and applying them to the environment. In addition, the quantity of articles on the keywords “metal-organic frameworks + ligand design” is rising year by year. Fig. 1 illustrates the percentage of functional MOFs by ligand design in the environmental application, and it is also evident that they are gradually becoming the focus of environmental research. Meanwhile, some development time nodes related to ligands of MOFs were also summarized (Fig. 2).

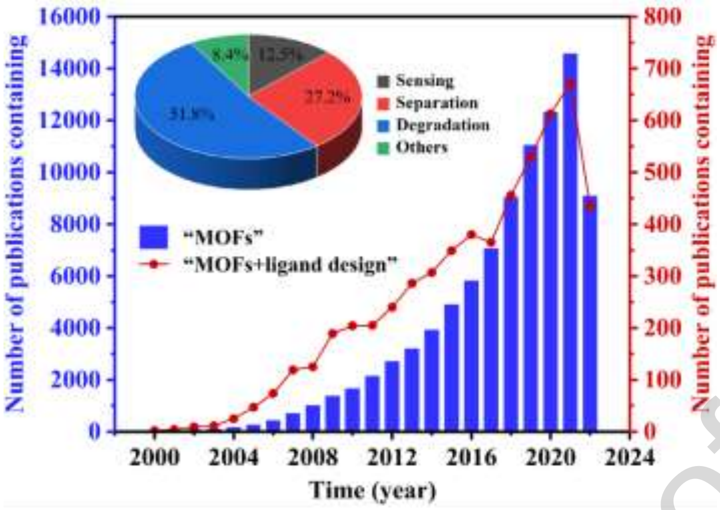


Fig. 1 Changes in the number of papers related to the keywords "Metal-organic frameworks" and "Metal-organic frameworks + ligand design" between 2000 and 2022 (July 26). The insert shows the per centum of existing scientific reports on the environmental applications of ligand design MOFs from 2000 to 2022 (July 26).

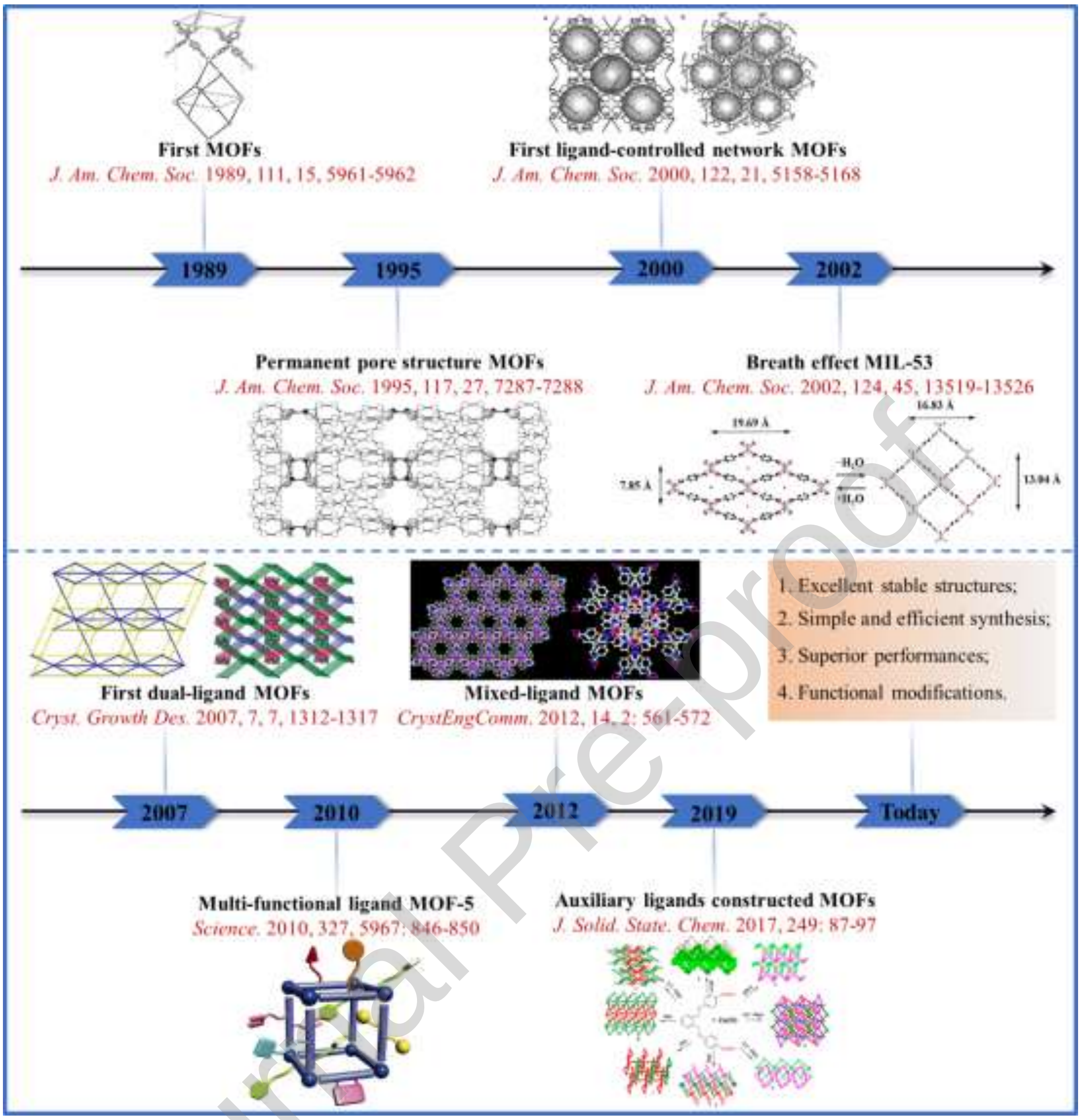


Fig. 2 Important research schedules of ligand-related MOFs from 1989 to the present.

The applications of MOFs are developing rapidly. For the past decades, many outstanding publications on designing the ligand length, multiple functional groups positional isomerism and geometry of functional MOFs and their applications have been published (Hu, Z. et al., 2021; Kim et al., 2021b; Kirchon et al., 2018; Pullen and Clever, 2018). Thereinto, reviews about ligand design of functional MOFs have been reported particularly frequently. For instance, Morsali and co-workers summarized the effects of different functional group types on ligands on the structure, host-guest chemistry, and applications of MOFs (Ali Akbar Razavi and Morsali, 2019). Morsali *et al*. also contributed a review on multicarboxylate ligands ($n_{COOH}$≥3) in MOF systems and their applications (Ghasempour et al., 2021). Simultaneously, Hong *et al*. deeply revealed the positional regioisomerism of multiple functional groups in organic ligands of MOFs from structures and functions (Kim et al., 2021a). Subsequently, Maji *et al*. gave insights into the use of mixed ligands to construct multifunctional MOFs of different dimensions, focusing on the geometry and different functional applications of flexible MOFs (Bhattacharyya and Maji, 2022). Although ligands in MOFs have been briefly mentioned in these reviews, more reviews tend to describe the application of MOFs or combine the application of MOFs with certain technologies, not to systematic and detailed analysis of the relationship between organic ligand design and the performance of MOFs during the MOFs synthesis. In fact, the number and type of different organic ligands have a great influence on the performance of MOFs. Deliberate ligand design was used to modulate the overall performance of MOFs for directing better environmental applications of MOFs.

On the one hand, the topological structure of MOFs is mainly determined by the geometry and connectivity of ligands, and their stability also relies on the combination kind of metal and ligand (Zhou and Kitagawa, 2014). On the other hand, many factors can interfere with the design and structure of MOFs, such as metal centers, suitable ligands, temperature, solvents, and counter ions (Lemaire et al., 2017; Stock and Biswas, 2012). Among these influencing factors, the most critical factors are ligands and metal ions (Du et al., 2017). In addition, by adjusting the shape, length, proportion, and functional groups of ligands, the size, topology, and inner surface properties of MOF can be modified to meet specific practical application requirements (Lu et al., 2014). The structure-activity relationship between different ligands and metal centers is different. Compared to single-ligand MOFs, the combination of mixed ligands MOFs may produce some coordination synergistic effects. Therefore, it is fact that a new review on ligands design for MOFs is essential for their rapid development.

Herein, this review systematically introduced three ligand designs of functional MOFs based on the number of different ligands used in the synthesis of MOFs, including single-, dual-, and multi-ligand designs. Compared with existing reviews, this review provides a more detailed and complete introduction to the impact of the number of different types of ligands on the functional properties of MOFs, making this aspect more comprehensive and specific. Furthermore, the topic of ligand number design of functional MOFs has not been mentioned in the published review. The performance of MOFs can be tuned by ligand design to guide them for better environmental applications. On this basis, examples of ligand design in MOFs with their guided environmental applications are summarized. Among them, the typical applications of functional MOFs for environmental pollutant sensing and removal in recent years are comprehensively displayed, and to elaborate the mechanisms from the perspective of ligands used in MOFs synthesis. Finally, the challenges and problems of functional MOFs by ligand design in future research are also pointed out. Through this review, we hope that readers realize the important effect of ligands in

MOFs and pay attention to this attractive area of advanced materials research to further advance the development of ligand design for functional MOFs.

## 2. Ligand design of functional metal-organic frameworks

With the continuous expansion of the coordination chemistry field, many polymers with novel structures and unique properties have emerged, and the types and numbers of MOFs are also increasing. The overall framework stability mainly depends on the robustness of coordination bonds among metal ions or clusters and ligands (Lv, X.L. et al., 2019). In addition, in order to better prevent the aggregation of isolated metal, the ligands can be regulated to change the distance of nearby metal atoms, promoting the formation of individual metal atoms and improving the overall framework stability of MOFs (Chen, S. et al., 2021). Therefore, it is very important to select appropriate ligands to closely combine with discrete metal atoms to modulate the overall properties while preparing effective organic-inorganic hybrid materials. MOFs with different morphologies, sizes, selected functions, and specific pore size distributions can be synthesized by regulating the types of functional groups on ligands and the types of metal salts. Most importantly, ligands largely determine the structural and physical properties of MOFs (Elahi et al., 2021). Ligand design for MOFs is beneficial for adjusting the structures and properties of MOFs. Therefore, this chapter will introduce three functional modification methods from the number of ligands in MOFs and the number of functional groups in ligands, which will lay the foundation stone for subsequent application introductions. The schematic illustration of the fabrication of functional MOFs by ligand is shown in Fig. 3.

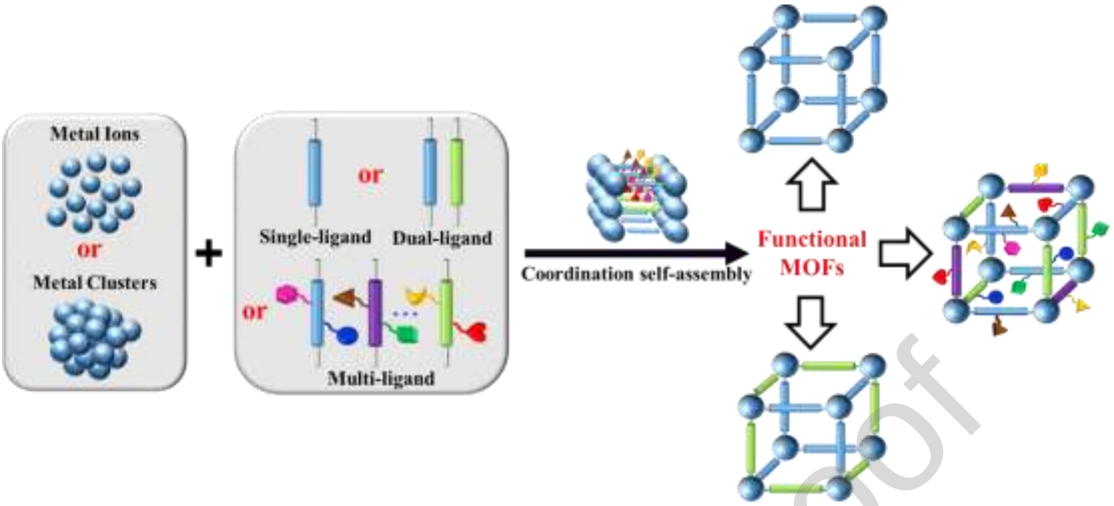


Fig. 3 The schematic illustration of the fabrication of functional MOFs by ligand design.

### 2.1 Single-ligand design

In the synthesis of MOFs, the commonly used ligands are mainly carboxylic acids, sulfonic acid, phosphonic acid, N-Heterocyclic, and porphyrin. The coordination mode of single ligands and metal centers is different, which ultimately results in different functional properties and topological structures of MOFs. In general, using only the same ligand during MOF synthesis is called the single-ligand design. For some single ligands, Almeida Paz *et al.* have reviewed the relationship between the properties of ligands and the structure or performance of MOFs (Almeida Paz et al., 2012). Types of porphyrin building blocks with different connectivity and their applications have also been introduced by Feng *et al.* (Feng et al., 2020). Therefore, this section mainly introduced the effects of carboxylic acid ligands and sulfonic acid ligands in MOFs synthesis.

### 2.1.1 Carboxylic acid ligand

Carboxylic acid ligands have a wide range of research and application in coordination chemistry due to their functional properties. Carboxylic acids as ligand materials mainly have the following advantages (Huang et al., 2020; Ma, P. et al., 2019), (1) Carboxylic acids types are diverse. (2) The coordination bonds formed with metal centers are strong, and coordination modes are diverse. (3) Many MOFs with large pore sizes and various structures can be synthesized. Carboxylic acid ligands enable self-assembly with metal ions or cluster centers through coordination bonds to form one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) MOFs (Lu et al., 2012). Moreover, attractive MOF structures are constructed by taking advantage of the fact that flexible carboxylic acid ligands may distort or deform with metal centers during assembly (Wang et al., 2013). For example, Serre and co-workers synthesized a 3D chromium carboxylate MIL-53 with terephthalic acid ligands (Serre et al., 2002). The flexible carboxylic acid ligands allow for great flexibility in the structure of MOFs. When the temperature changed, the MIL-53 framework was stimulated to contract or expand, and the process changed in size by more than 5 Å.

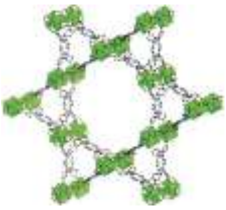
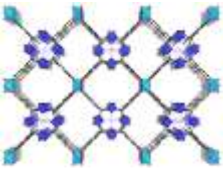
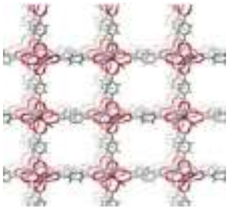
### 2.1.2 Sulfonic acid ligand

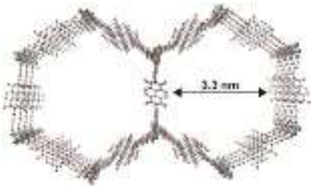
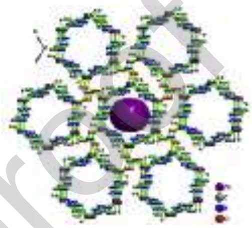
Sulfonate has a less coordinated tendency to metal centers, stricter synthetic conditions, and more hydrophobic characteristics (Wang, Y.-T. et al., 2020). Thus, they have been less studied in MOFs coordination chemistry. However, sulfonic acid ligands have multiple potential coordination sites on oxygen atoms and are easy to deprotonate and form hydrogen bonds with hydrogen donors, which makes coordination modes with metal ions more flexible, and beneficial to form MOFs with novel structures and high dimensions (Li, Jiyuan et al., 2017). Sulfonic acid-based MOFs have a high surface area, good thermal stability, high polarity, and hydrophilic porosity. Therefore, sulfonic acid-based MOFs possess better proton/$Li^+$ conductivity and $CO_2$ affinity and hold great potential applications (Zhang and Fei, 2019). For example, Liu *et al*. have summarized the research progress of proton-conductive sulfonate MOFs (Liu et al., 2021). Zhang *et al*. synthesized a non-interpenetrating sulfonic acid-based MOF with defective primitive-cubic topology, and the structure exhibited high stability (Zhang, G. et al., 2018). Moreover, its void space was the highest among MOFs containing sulfonic acid ligands (PLATON calculated at 42.5%). The addition of -$SO_3H$ significantly improved the gas storage capacity and adsorption of isovolumetric heat capacity of MOFs. Sulfonic acid-based MOFs also had good catalytic activity. A study by Fumin Zhang *et al*. reported efficient dual-functional sulfonic acid-based MOFs with high catalytic properties for 100% conversion of vanillin (Zhang et al., 2015). Excellent catalytic performance remained after many continuous cycles, and the influence on the degradation efficiency of target pollutants can be ignored.

### 2.1.3 Other ligands

Besides carboxylic acid ligands and sulfonic acid ligands, other single ligands with various features have also been used for functional MOFs synthesis. The properties of MOFs constructed by different ligands are also different. For example, pyridine-based ligands are very weakly linked, thus always constructing unstable MOFs. Imidazole/pyridine ligands have higher pKa and alkalinity, but the MOFs framework constructed by pyridyl ligands is slightly more stable. Nitrogenous ligands can decorate and enhance the performance of MOFs (Du et al., 2019a; Zhang, J.-P. et al., 2012). It is evident that MOFs with various topological structures can be synthesized by using different single-ligand. Table 1 summarizes some different MOF structures formed by different single-ligand.

**Table 1** Different MOF structures formed by different single-ligand.

| **MOFs** | **Ligand** | **Topology** | **Structure** | **Ref.** |
|---|---|---|---|---|
| MOF-535 | $C_{48}H_{30}N_4O_8$ | ftw-type |  | (Morris et al., 2012) |
| MOF-545 | $C_{42}H_{24}O_8$ | csq-type |  | (Morris et al., 2012) |
| HKUST-1 | 4,4′,4″,4‴-(porphyrin-5,10,15,20-tetrayl)tetrabenzoate | 3D MOF |  | (Kornienko et al., 2015) |
| IRMOF-1 | 1,4-benzenedicarboxylate | cubic crystalline |  | (Tsivion and Head-Gordon, 2017) |

| | | | | |
|---|---|---|---|---|
| Ni-NDISA | N,N′-bis(3-carboxy-4-hydroxyphenyl)-1,4,5,8-naphthalenetetradicarboximide | cubic hexagon |  | (Wentz and Campbell, 2018) |
| Zn(II)-tetrazole frameworks | 5-methyl-1H-tetrazole | tpd-type |  | (Li, Jing et al., 2017) |
| | 5-methyl-1H-tetrazole | 3D MOFs |  | (Li, Jing et al., 2017) |

### 2.2 Dual-ligand design

Although single-ligand MOFs have good performance in gas adsorption, sensing, and so on, their functional characteristics, topology tunability, and stability have many shortcomings. By contrast, simultaneously selecting two different ligands for MOFs synthesis provides better adjustability to construct multivariate MOFs for versatile applications. For instance, Jin and co-workers reported a dual-ligand Fe-based MOF (D-Fe-MOFs) (Jin, X. et al., 2021). The D-Fe-MOFs had a high specific surface area and pore capacity than single-ligand Fe-based MOFs. In dual-ligand design, the choice of each ligand is very important, different ligand combinations have significant effects on the functional properties of MOFs.

#### 2.2.1 Topology regulation

The topology of MOFs largely depends on the configuration of ligands (Lyu et al., 2019). Dual-ligands design has a great influence on the topology of MOFs, and using different dual ligands will produce different topological structures during MOFs synthesis. For clarity, some representative topological network structures from previous studies were shown in Fig. 4a (Kirchon et al., 2018). In a review of Qin's group, four types of dual-ligand MOFs with different structures were introduced (Fig. 4b) (Qin et al., 2017). These four structural types of dual-ligand MOFs had different applications in different fields. Another well-known example was that Gomez-Gualdron and co-workers used a dual-ligand strategy to synthesize three MOFs with different topologies, stabilities, and gas uptake properties, whose topologies were csp, scu, and ftw, respectively (Gomez-Gualdron et al., 2014).

Moreover, the introduction of different second ligands can also guide the adjustment of MOFs chain structure dimensions from 1D to 2D and 3D, and increase the porosity of MOFs structure (Zuo et al., 2018). For example, based on tetrabromoterephthalic acid and different nitrogenous ligands, Liu *et al*. constructed four chain structures with different dimensions and 3D structures formed by hydrogen bonding (Jiao et al., 2019). The synergy between different ligands and metals is different and eventually leads to the formation of MOF structures with different symmetries. Gong *et al*. successfully synthesized two 3D Co(II) MOFs with different topological symmetry by inducing two different auxiliary ligands to react with the primary ligand, respectively (Fig. 4c) (Gong et al., 2018). The primary ligand cooperated with metal atoms to form 3D main frameworks, and the auxiliary ligand to fill 3D cavities. At present, the introduction of functional dual-ligand into MOFs to create more complex and efficient materials is still being explored. This technology will further enrich the functional properties and coordination modes of MOFs.

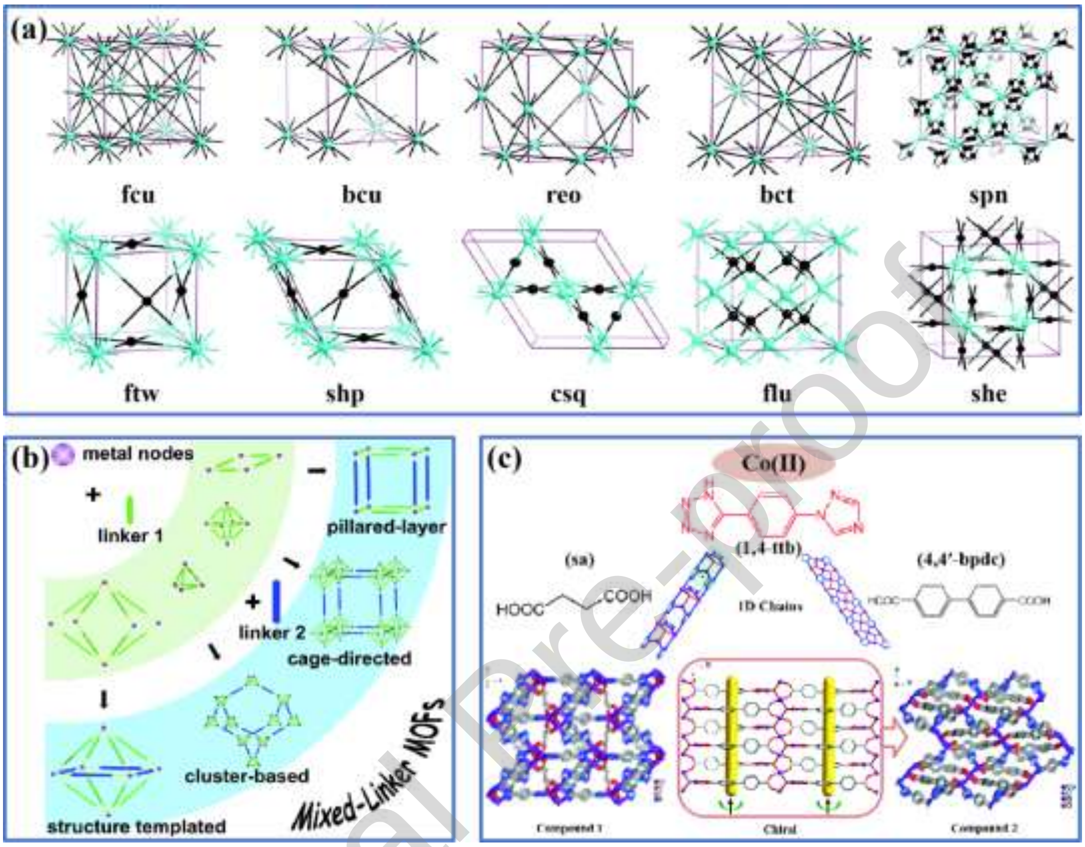


Fig. 4 (a) Representative network topologies in many reported MOFs. The topological symbols have been summarized in previous reviews. For example, fcu indicates a face-centered cubic net; scu and ftw refer to (4,8)- and (4,12)-connected network; reo originated from the packing of $ReO_3$ lattice. Adopted from Ref. (Kirchon et al., 2018). Copyright 2018, with permission of Royal Society of Chemistry. (b) Four types of dual-ligand MOFs: pillared-layer, cage-directed, cluster-based, and structure templated. Adopted from Ref. (Qin et al., 2017). Copyright 2017, with permission of Royal Society of Chemistry. (c) Schematic diagram of the achiral and chiral 3D Co(II) MOFs synthesis. Adopted from Ref. (Gong et al., 2018). Copyright 2018, with permission of Royal Society of Chemistry.

### 2.2.2 Coordination mode

The combinatorial of double ligands not only creates many topologies but also makes MOFs have more diverse coordination modes. For instance, combining V-shaped polycarboxylates and flexible imidazole auxiliary ligand usually leads to MOFs with diverse coordination forms (Hu et al., 2015). Wang *et al*. investigated luminescence sensors of eight Zn-MOFs composed of V-shaped long di-carboxylic acid and auxiliary N-donor ligand and Zn(II) metal center connection (Fig. 5a) (Wang et al., 2017). Due to the role of dual ligands, the Zn-MOFs family showed different embroiled forms and conformational coordination modes (Fig. 5b). As a multi-response luminescence sensor, the Zn-MOFs family also had different detection capabilities for different ions, organic solvents, and nitro-explosives. The coordination units in MOFs also vary with the coordination modes between the dual ligands and the metals. For example, Tang and co-workers have synthesized three novel zeolite-like MOFs with diverse coordination modes by using dual-ligand (Tang et al., 2017). The coordination units of the three compounds contain different amounts of $Zn^{2+}$ to coordinate with different ligands, which had different stability and $CO_2$ absorption capacity (Fig. 5c). More importantly, the coordination environment of metal centers in MOFs generally changes with the introduction of auxiliary ligand, therefore resulting in different coordination forms (Gu et al., 2018). Wang *et al*. constructed three novel zinc porphyrin MOFs by introducing auxiliary nitrogen-containing ligands (Wang et al., 2019). The coordination synergistic effect between ligands resulted in these three MOFs exhibiting different coordination modes, which further led to the high porosity and anionic framework characteristics of MOFs structure. Therefore, the three MOFs had different selective adsorption properties for cationic organic dyes.

During the synthesis of MOFs, diverse coordination modes can make the interaction force between the ligands and metal nodes different, resulting in structural knock-on effects and some surprising properties. Therefore, the dual-ligand design brings some necessary properties to the framework while enriching the functional structures and coordination modes of MOFs.

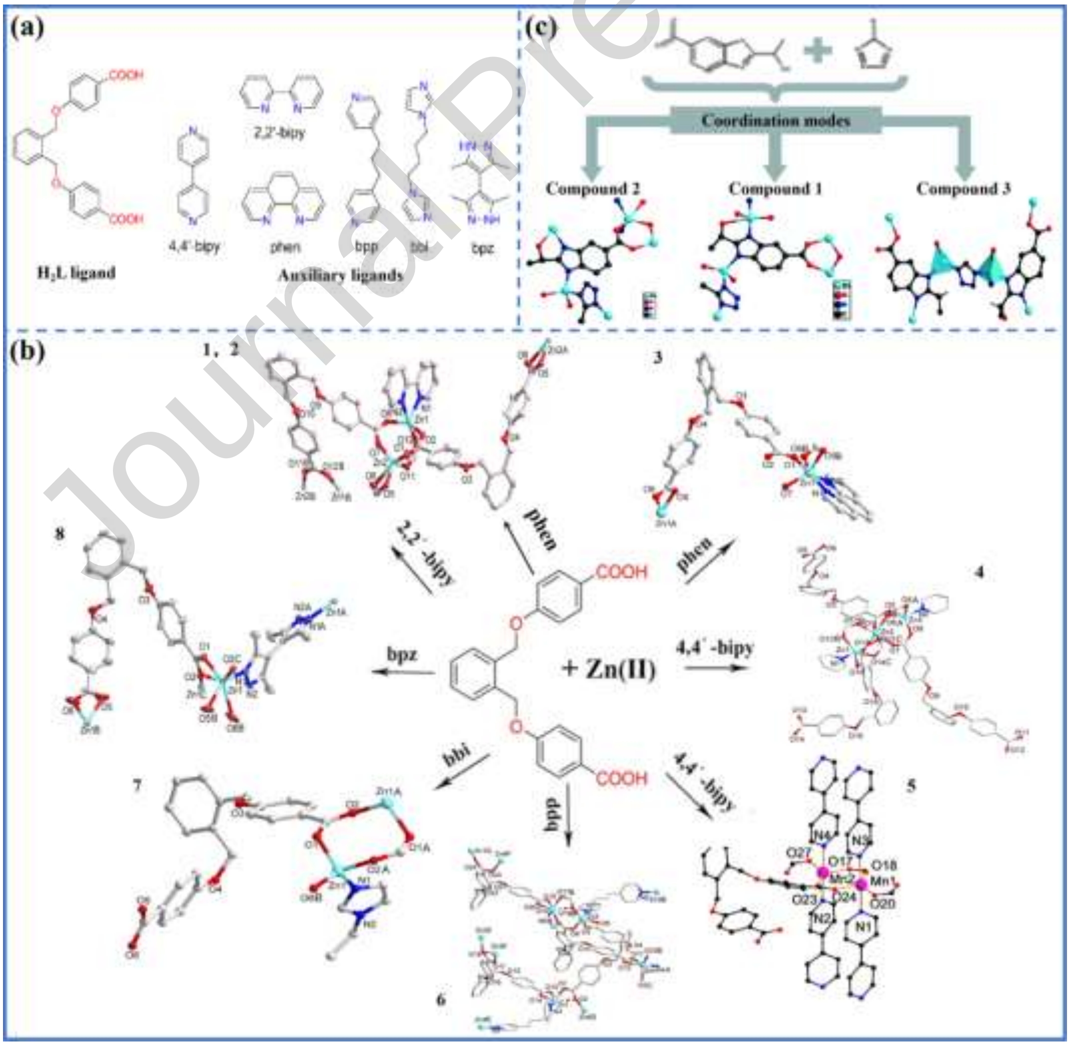


Fig. 5 (a) $H_2L$ ligand and auxiliary ligands. (b) Coordination modes of eight Zn(II) coordination polymers. Adopted from Ref. (Wang et al., 2017). Copyright 2017, with permission of Elsevier. (c) Three novel zeolite-like MOFs with diverse coordination modes. Adopted from Ref. (Tang et al., 2017). Copyright 2017, with permission of Royal Society of Chemistry.

### 2.2.3 Framework flexibility

The introduction of dual ligands with different properties can enable MOFs to obtain some functional effects that original single-ligand MOFs do not have. The flexible framework of MOFs is the main manifestation of this design result. Generally, flexible frameworks can respond to external stimuli through characteristic changes, such as swelling, breathing, polymorphic phase transitions, and cooperative gate opening processes (Dutta et al., 2021). Unlike rigid MOFs, MOFs with flexible frameworks do not need to adjust the pore size precisely and achieve higher gas capacity by enlarging the absorption difference between charge and discharge pressure (Zhang, J.-P. et al., 2018). Most importantly, the flexible framework of dual-ligand design could be precisely controlled the deformation of MOFs, fine-tune pore surface, thus enhancing surface area and overall framework stability (Chen et al., 2016). Henke and co-workers used a dual-ligand strategy to synthesize pillared-layered $[M_2L_2P]_n$ MOFs, in which one of the ligands was replaced by a flexible group to form a flexible ligand (Henke et al., 2012). When N,N-dimethylformamide (DMF) guest molecule was removed from compounds, the framework shrunk and gradually transferred from the large pore to the narrow pore, and porosity became 85% of the original MOFs. This pore size change was reversible.

In summary, the dual-ligand design strategy plays a significant role in functionalized MOFs. Using dual ligands, on the one hand, take into account the structural strain and coordination mode in the polymer to maximize the metal ratio of each ligand, resulting in topological structures with diverse and dynamic stability. On the other hand, making MOFs have a flexible framework, the expansion and contraction of pore channels further adjust the pore structure of MOFs, thus promoting the deformation of the framework and obtaining a larger specific surface area. The dual-ligand design induced more novel properties based on improving the properties of original MOFs, realizing multiple recycling of MOFs, and showing greater practical application value and prospects.

### 2.3 Multi-ligand design

In recent years, MOFs with multiple ligands combined in one framework have aroused great interest as efficient porous carbon materials. For multi-ligand design strategies, in most cases, ligands comprising diverse functional groups are introduced into MOFs to achieve the combination of multiple functional groups within the same framework, to meet diverse application demands. The multi-ligand strategy opens up new design avenues for a broader range of MOF applications.

The synergistic effect of functional groups on different ligands in the framework of MOFs may lead to a “1+1>2” result on the functional properties of MOFs.

Functional groups combined in the same material may make performance beyond a single functional group and creates greater utilization value. The introduction of different functional groups (sulfides, amino groups, substituted alkyls, carboxylic acid derivatives, etc.) has been systematically reported in previous studies (Kim et al., 2021b). These functional groups have different combinations, allowing MOFs to display fascinating structures and properties, such as controllable structural flexibility, high detection capability of contaminants, fluorescence enhancement effects, and superproton conductivity. Moreover, by connecting other ligands with the same length and geometry on the main chain of a given ordered MOF structure, the substituents and functional groups of MOFs present a disordered distribution, making them more heterogeneous and complex (Viciano-Chumillas et al., 2022). This provides the possibility of introducing multiple functions within the same frameworks for MOFs. In the synthesis process of MOFs, ligands with different functional groups were placed in the same crystal position, which can control the overall pore shape and chemical composition of the framework through the synergistic effects between ligands and metals (Qin et al., 2017).

In some previous studies, MOFs composed of multi-functional ligands have been reported. Deng *et al*. (Deng et al., 2010) perfectly demonstrated 18 typical multivariate MOFs-5 composed of ligands decorated with different functional groups combinatorial arrangements (Fig. 6a). The schematic diagram of MTV-MOF-5 structure is shown in Fig. 6b. Benefiting from this multi-ligand design, the adsorption capacity of MOFs with multi-functional group ligands for $H_2$ was higher than the single-ligand MOFs, and the selective separation effect for $CO_2$ and CO was four times better than the single-ligand MOFs. These results indicated that MOFs with mixed functional group ligands have better performance to some extent. In addition, the properties of multiple ligands combine as they combine as well, and these complementary or contradictory properties can give a single MOF with mixed ligands functional characteristics (Hirai et al., 2011). In another job, Kong *et al.* further explored the above work. They found that the multi-ligand MOFs of the EHI with three functional groups combined the properties of containing functional groups, and the lattice presented an alternating (Alt) model (Fig. 6c-d) (Kong et al., 2013). Among them, MOF-5 containing E-type ligands lacked selectivity, and the volume of MOF-5 containing I-type ligands was large to clog pores. The combination of functional groups alternately assigned to each other compensates for their shortcomings and creates adsorption materials with high selective adsorption sites and sufficient gap space. In their study, the same was true for other MOFs with different combinations of functional groups.

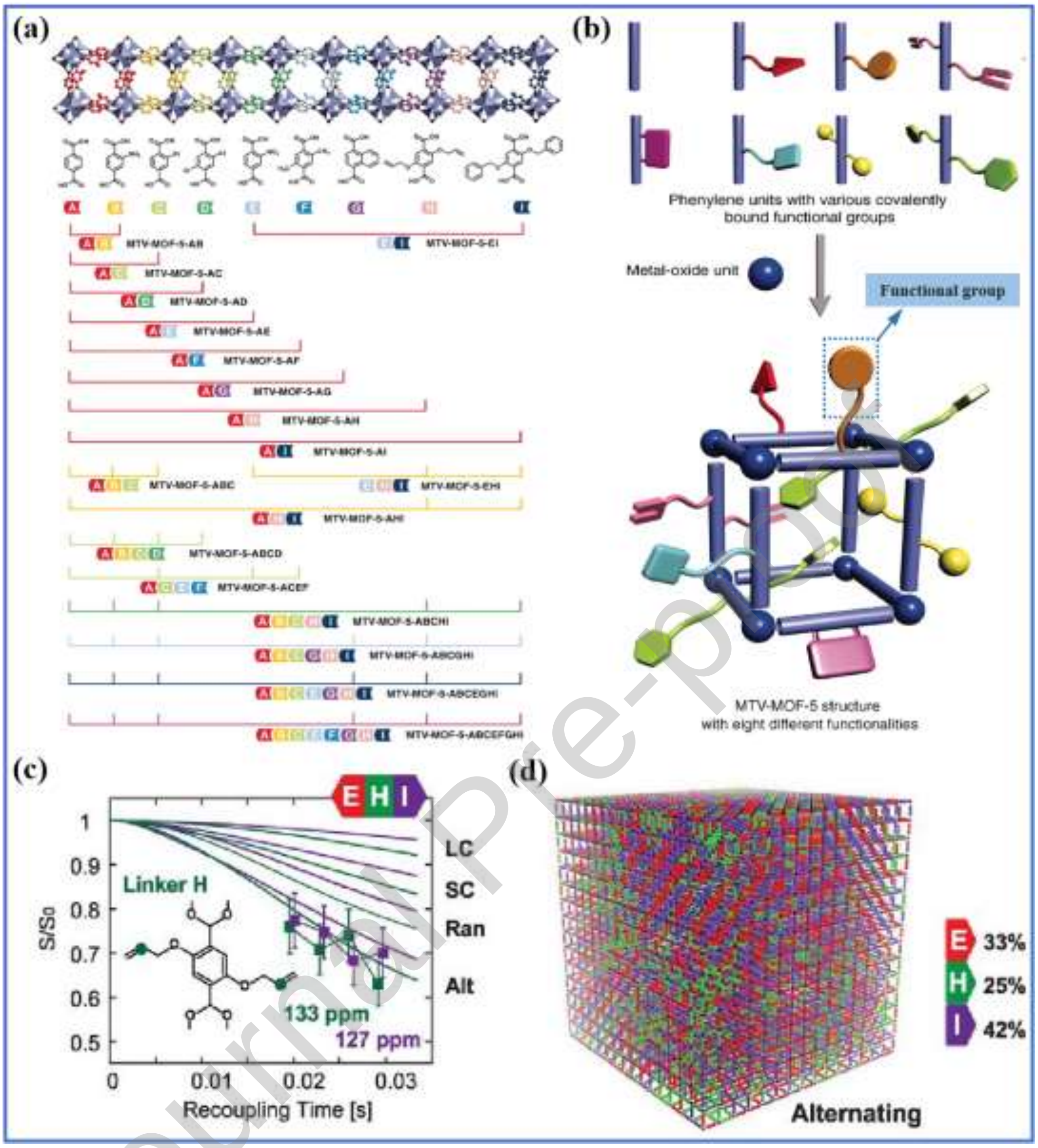


Fig. 6 (a) 18 different functional group combinations. (b) Schematic representation of MTV-MOF-5 structure. Different shapes represent different functional groups on the ligand. Adopted from Ref. (Deng et al., 2010). Copyright 2010, with permission of American Association for the Advancement of Science. (c) Molecular dynamics simulations of MTV-MOF-EHI. (d) Alternate distribution spatial structure of MTV-MOF-EHI. Adopted from Ref. (Kong et al., 2013). Copyright 2013, with permission of American Association for the Advancement of Science.

Multi-functional group ligands for the effect of MOFs properties may not be a simple linear combination, they can be used as codes to enhance particular properties or create new properties. Therefore, multi-functional MOFs with excellent properties, such as designable topology, tunable porosity and functionality, and variable surface environment can be obtained in a single material. However, compared with the study of single-ligand MOFs, there are fewer studies on mixed ligands MOFs. Table 3 and Table 4 of the later statistics also reflect this research phenomenon to a certain extent, so the data investigated are relatively small. Most mixed-ligand MOFs are synthesized by a one-step method, such operations lack control over the final structure, limiting the significance of the existence of mixed ligands. How to efficiently synthesize multi-functional MOFs with desired structures is a bigger challenge. In addition, it is necessary to reasonably select appropriate ligands to combine with metals, to avoid some obvious hydrophobicity, mutual insolubility, and instability, and to synthesize mixed ligands MOFs in a rapid way on large scale.

In brief, the three ligand design strategies are important means for regulating the structure and function of MOFs. Some single-ligand design strategies have many advantages of diverse types, strong coordination bonds, and flexibility, but the synthesized MOFs have poor stability and few active sites (Ding et al., 2019). Based on commonly used ligands, other ligands are introduced by using dual-ligand or multi-ligand design, and ligands with different properties are combined into MOFs. Thus, the coordination structures can be changed to achieve a graded porous structure, which can provide abundant mass transfer channels, affect the electron transfer rate and the mode of transfer (Khalil et al., 2021). In addition, the competitive coordination between different organic ligands can expose more defects and provide abundant active sites for better stability and tunability of MOFs (Dhakshinamoorthy et al., 2020; Ghasempour et al., 2021). Compared with single-ligand MOFs, mixed ligands MOFs can be further developed in terms of improving the catalytic performance and sensitivity of MOFs due to their advantages, such as multiple combination types and abundant coordination modes. However, the synthesis of mixed ligands MOFs is a major problem. In many cases, a one-pot synthesis is used, which reduces the modifiability of their structures. Improper synthesis and conditions may lead to the structural collapse and worse stability of mixed-ligand MOFs than single-ligand MOFs. Therefore, different ligand designs have different positive and negative effects on their functional applications, and the reasonable choice of ligand design methods adds to the development of MOFs.

Furthermore, the engineering strategy for synthesizing functional MOFs is the same as ligand design strategy. Many reviews have summarized the engineering strategies for MOFs synthesis (Ma et al., 2022; Qiu et al., 2021; Raza et al., 2021). Among them, solvothermal/hydrothermal synthesis, microwave-assisted chemistry, electrochemical synthesis, sonochemical method, and mechanochemistry are commonly used methods (Zhang et al., 2022). Table 2 summarized the common engineering strategies for ligand design of functional MOFs, and highlighted the advantages and disadvantages of each technique. Multiple synthesis methods have resulted in MOFs with different morphologies, crystal structures, and pore sizes, further affecting their functional applications (Ding et al., 2022).

**Table 2** Summaries of some common engineering strategies for the synthesis of functional MOFs.

| **Engineering strategies** | **Characteristics** | **Reaction time** | **Major modulator parameters** | **Advantages** | **Disadvantages** |
|---|---|---|---|---|---|
| Solvo/hydrothermal Method | The reactions take place in closed vessels under autogenous pressure above the boiling point of the solvent. | Hours to days | Temperature, autogenous pressure, solvent, additives (template or SDA), solution pH, and reaction time | Uniform size; Good crystallinity; Large specific surface area; Tunable topology and morphology. | Low yield (<50%); Hazardous reagents; High reaction temperature; Long reaction time, not conducive to mass production. |
| Microwave-assisted chemistry | Rapid and uniform heating of liquid medium, owing to molecular rotations induced by coupling of an electric field and the permanent dipole moment of molecules. | Minutes to hours | Microwave irradiation power, solvent, additives, solution pH and polarity, and reaction time | Shorter synthesis periods; Smaller crystal sizes; Higher product purity; Greater energy efficiency. | Low yield; Hazardous reagents; High reaction temperature. |

| | | | | | |
|---|---|---|---|---|---|
| Electrochemical synthesis | Uses the principle of electrolysis to turn the metal anode into metal ions to assemble MOFs with an electrolyte solution containing organic ligands. | Minutes to hours | Electrolyte solution, pH, electrochemical deposition cycles, and voltage-current density | Fast synthesis and low reaction temperature; No residual anions in final products; High Faraday efficiencies and high utilization of the organic linkers; Permitting formation of layers. | Hazardous reagents; High equipment and maintenance cost. |
| Sonochemical method | Synthesis relies on cavitation, a process of bubble formation, growth, and collapse in liquid caused by ultrasound wave that can give rise to extremely high local temperatures (~5000 K) and pressures (~1000 bar). | Minutes to hours | Ultrasonic (ULS) frequency, reactants concentrations, and reaction time | Short synthesis time; Simple operations; Low costs; High energy efficiency. | Low product yields, Hazardous reagents; Unsuitable for industrial production. |

| | | | | | |
|---|---|---|---|---|---|
| Mechanochemistry | Mechanical forces bring about the mechanical breakage of intramolecular bonds, resulting in chemical reactions in mechanochemical synthesis. | Hours | Time and applied mechanical force speed, and solvent used (as an additive) | Simple; Eco-friendly; High yields; Green method; Clean-energy; Economic process. | Low purity; The particle size of the final product is hard to control and often very small. |

Adapted from (Ding et al., 2022; Younis et al., 2021; Zhang et al., 2022).

## 3. Environmental applications of functional metal-organic frameworks

Large quantities of harmful and poisonous pollutants have been discharged into the environment with the fast development of society (Lai et al., 2018; Liu, S. et al., 2020a; Ye et al., 2022). The materials used in some environmental purification technologies have high costs and low efficiency and may generate secondary pollution (Qin, L. et al., 2022a; Sharma and Feng, 2019). Therefore, it is urgent to find efficient and low-cost green treatment methods. Functional MOFs with good performances can meet these requirements to some extent. Metal ions leaching and structural collapse are relatively common problems in environmental applications of MOFs. In addition, the structural stability and functional properties of MOFs also depend mainly on the synergistic interaction between metal nodes and organic ligands (Lv, X.L. et al., 2019). In ligand design strategy, appropriate types, quantities and properties of ligands can be selected to closely combine with metal atoms according to the needs of environmental applications. Then, MOFs with different morphologies, sizes and functional properties can be synthesized to make their environmental applications more reasonable and effective, such as better degradation performance, more sensitive and efficient sensing performance, higher adsorption capacity and better stability. This chapter will comprehensively introduce the recent progress of functional MOFs by ligand design in environmental applications, including pollutants sensing, separation, and degradation. More importantly, the influence of ligand design on MOFs performance is deeply explored from the mechanism perspective.

### 3.1 Pollutant sensing

In recent years, MOFs have flourished in pollutant sensing with their characteristics of simplicity, fast response, high sensitivity, good selectivity, and multiple emission centers (Lustig et al., 2017; Wu et al., 2020). MOFs are important sensing materials, where the ratio of metal ions to ligands has a considerable effect on the sensitivity and other properties of the sensor. In the environmental pollutant sensing application, ligands usually have some electron-rich functional groups, which makes MOFs have certain luminescence properties (Liu et al., 2019). Most importantly, MOFs as fluorescent probes to detect environmental contaminants can compensate for the vulnerability to inactivation and complex preparation of biological probes (Chen et al., 2022). In addition, most of the sensor applications are mainly focused on fluorescence detection, the colorimetric, electrochemical and other detection methods are relatively few. Based on the above, this chapter mainly introduces the application of MOFs in fluorescence sensing, including metal ions, non-metal ions, organic pollutants, and other environmental pollutants detection. Table 3 summarized the limit of detection (LOD) and linear range of functional MOFs by ligand design for fluorescence sensing of organic or inorganic pollutants.

**Table 3** The LOD and linear range of functional MOFs by ligand design for fluorescence sensing of organic or inorganic pollutants.

| MOFs | Ligand | Design type | Detection method | Target | Linear range | LOD | Response time | Reusability | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| Tb/Eu-bop | 5-boronoisophthalic acid | Single-ligand | Ratiometric fluorescence | $Hg^{2+}$ | 0.1 ~ 40 μM | 4.83 nM | - | - | (Wang et al., 2022) |
| BUT-39 | 4,4′,4″-(1H-benzo[d]imidazole-2,4,7-triyl)tribenzoic acid | Single-ligand | Fluorescence | $Cr_2O_7^{2-}$ | 10 ~ 500 μM | 1.5 μM | < 1 min | Stability excellent | (He et al., 2018) |
| CAU-10-OCOCH$_3$ | 5-acetoxyisophthalic acid | Single-ligand | Fluorescence | Perborate | - | 1.19 μM | 5 min | 0 cycles | (Nandi, S. et al., 2020) |
| Mg-APDA | 4,4′-(4-aminopyridine-3,5-diyl)dibenzoic acid | Single-ligand | Fluorescence | $Fe^{3+}$ | 0 ~ 12 | 152 | - | - | (Xu et al., |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | 0 μM | ppb | | | 2018) |
| | | | | Nitrofurazone | 2.5 ~ 35 μM | 108 ppb | - | 5 cycles | |
| | | | | Nitrofurantoin | 2.5 ~ 30 μM | 126 ppb | - | - | |
| | | | | 2,6-dichloro-4-nitroaniline | 2.5 ~ 42.5 μM | 150 ppb | - | 5 cycles | |
| CSMCRI-1 | Azobenzene-4,4’-dicarboxylic Acid, and meso-α,β-di(4-pyridyl) glycol | Dual-ligand | Fluorescence | $Fe^{3+}$ | 0 ~ 2.5 mM | 1.29 μM | - | 5 successive cycles | (Goswami et al., 2019) |
| MOPs I | 4-pyridinecarboxaldehyde, and diphenyl-2-pyridylphosphine | Dual-ligand | Fluorescence | 4-nitrophenol | - | 0.142 μM | - | - | (Gholivand et al., 2020) |
| Cd-L MOFs. | 4’-(4′-pyridyl)-2,2’:6′,2″-terpyridine, and 3,5-bis-(3-carboxy-benzyloxy)-benzoic acid | Dual-ligand | Fluorescence | Methylene blue | 30 ~ 100 ppm | 30 ppm | 1 min | At least 5 times | (Lv et al., 2022) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| MOF-Calix | 5-nitro-1,3-benzenedicarboxylic acid, and 25,26,27,28-tetra-[(4-pyridylmethyl)oxy]calix[4]arene | Dual-ligand | Fluorescence | Glyphosate | 2.5 ~ 45 μM | 2.25 μM | 1 min | 5 parallel measurements | (Yu et al., 2020) |
| | | | | Trinitrophenol | 0 ~ 160 μM | 0.04 μM | - | | |
| Zn3-ttb-bdc | 1-(triazo-1-ly)-4-(tetrazol-5-ylmethyl)benzene, and 1,4-benzenedicarboxylic acid | Dual-ligand | Fluorescence | $Fe^{3+}$ | 0 ~ 100 μM | 0.13 μM | 2 min | In aqueous solutions for 7 days | (Gai et al., 2021) |
| | | | | $Cr_2O_7^{2-}$ | 0 ~ 100 μM | 0.10 μM | - | | |

### 3.1.1 Metal cations

According to previous studies, the mechanism of MOFs-based sensors for metal cations detection usually has the following aspects (Du et al., 2018): (1) Framework collapse; (2) Ion exchange; (3) Competitive adsorption of energy at emission wavelength between the host framework and analyte; (4) Interaction between MOFs and metal atom.

**Lead ion ($Pb^{2+}$)**

In $Pb^{2+}$ detection, the functional groups on ligands can be combined with $Pb^{2+}$, resulting in fluorescence quenching or enhancement of the originally fluorescent

MOFs. MOFs functionalized with functional groups have been well applied to detecting $Pb^{2+}$ in fluorescence sensors. For example, amino-functionalized dual-ligand MOFs could efficiently and selectively detect trace amounts of $Pb^{2+}$ with a LOD of $5.0\times10^{-7}$ M (Wang, Z.J. et al., 2018). The weak interaction between N atoms on the amino group and $Pb^{2+}$ led to the increase of fluorescence intensity. Sulfonic-functionalized MOFs could detect $Pb^{2+}$ at ppm or sub-ppm levels in water within milliseconds with a LOD of 25.2 ppm. The $-SO_3H$ had strong attractive coordination effects on $Pb^{2+}$ to realize the detection (Nazari et al., 2021). The selective detection of $Pb^{2+}$ by carboxyl-functionalized 3D quadrilateral MOFs had high sensitivity and good reusability, with a LOD of 0.8 μM (Hou et al., 2019), because the weak interactions between uncoordinated -COOH functional group and metal resulted in fluorescence quenching.

### Copper ion ($Cu^{2+}$)

MOFs are applied as a highly responsive fluorescent probe with fast and specific detection performance for $Cu^{2+}$. In 2010, a luminescent MOF with micropores was used for $Cu^{2+}$ detection in aqueous solutions (Xiao et al., 2010). The binding of $Cu^{2+}$ to Lewis basic carboxylateoxygen sites on ligands reduced the energy transfer efficiency and resulted in a decrease in fluorescence intensity. Subsequently, Li and co-workers investigated a porphyrin-type MOF (MOF-525) luminescence sensor for $Cu^{2+}$ detection with a response time as low as 40 s and a LOD of 67 nM (Li, L. et al., 2017). In addition, MOF-525 showed better selectivity for $Cu^{2+}$ because the affinity of porphyrin core to $Cu^{2+}$ was stronger than other cations. Later, Zhou’s team adopted a dual-ligand strategy to synthesize 3D MOFs with bbf-type topology and used it for selective detection of $Cu^{2+}$ through utilizing the strong host-guest interaction between MOF and $Cu^{2+}$ to cause fluorescence quenching (Zhou et al., 2018). As a result, a good linear range of $10^{-4}$ M to $10^{-3}$ M and a LOD of $10^{-4}$ M were obtained.

**Other metal ions**

The widespread use of other metal cations, such as $Fe^{3+}$, $Ag^{+}$, and $Ni^{+}$ can lead to many diseases, so their detection is also important (Kamal et al., 2023). Ni-BDC MOF with 3D rhombohedral microcrystal structures has also been used for fluorescence detection of $Fe^{3+}$ (Kaur et al., 2023). This sensor had high selectivity and sensitivity, with a good linear detection range of 0~1.4 nM and a LOD of 0.159 nM. The Ni-BDC MOF sensor also had good stability. After up to 5 cycles, the detection performance of $Fe^{3+}$ did not change much. Besides, the test results of real samples were satisfactory. The quenching mechanism was mainly attributed to the competitive energy absorption of MOFs with $Fe^{3+}$. Additionally, a dual-emission fluorescence probe (EuUCH) was designed by introducing organic ligands and metal ions with different luminescent components into MOFs (Xia et al., 2022). The EuUCH could selectively detect $Fe^{3+}$ in different response modes, which had high detection sensitivity, low detection limit, good anti-interference performance, and fast response. What’s more, the sensor enables simultaneous detection of $Fe^{3+}$ and $Al^{3+}$ in complex swine wastewater. Furtherly, MOFs synthesized by dual-ligand were also used to detect $Fe^{3+}$ with a LOD of 1.55 ppm (Rubin and Reynolds, 2019). After exploring mechanism, it was found that the interaction of $Fe^{3+}$ with the free amine and/or carboxylate of ligand caused fluorescence quenching. For $Ag^+$ detection, Zhang *et al*. reported a fluorescence functionalized MOFs-based fluorescent sensor for detecting $Ag^+$ selectively, with a good linear range of 0.07~0.75 ppm and a LOD of at or below 0.1 ppm (Zhang, L. et al., 2012). The selective detection was attributed to the interaction between thiourea groups on the ligand and $Ag^+$. Xia and his partners developed a new type of ratiometric fluorescent sensor by using a one-pot method (FA-CDs@Eu-MOFs) (Zhang, Y. et al., 2021). The developed FA-CDs@Eu-MOFs-based RF probe was ultrasensitive and selective for the detection of $Ag^+$ with a broad range of 0.3~100 nM and an ultralow LOD of 80 pM. The detection of $Ag^+$ was due to that the C=N group on the ligands and $Ag^+$ specific coordination led to fluorescence quenching.

### 3.1.2 Inorganic anions

Some anions, like halogen ions, $ClO^-$, $CN^-$, $SO_4^{2-}$, $S^{2-}$, and $NO_3^-$, widely exist in the natural environment (Qin et al., 2018). However, the detection of inorganic anions by functional MOFs based on ligand design mainly focuses on $F^-$ and $ClO^-$. Therefore, the recent research progress on these two anions is highlighted in this section.

**Fluoride ions ($F^-$)**

As a kind of multi-functional nanomaterial, MOFs by ligand design are commonly used as signal generators in fluorescence sensors. In the presence of $F^-$, MOFs can be stimulated to generate optical signals, thus selectively detecting $F^-$ according to the changes in fluorescence signals. The fluorescence sensing response modes of functionalized MOFs nanomaterials to $F^-$ mainly include fluorescence turn-off, fluorescence turn-on, and ratiometric response (Guo et al., 2017).

Wan and co-workers reported a 3D porous single-ligand Tb-based MOF with good thermal and chemical stability (Wan et al., 2017). It could be used as a fluorescent sensor for selecting and fast quantifying $F^-$ detection between aqueous solutions containing a variety of interfering ions. The interaction of $F^-$ with different functional groups on the MOFs' surface might generate some necessary electron acceptors, which could capture the excited electrons of MOFs and lead to fluorescence turn-off (Ahmadijokani et al., 2021). In another work, amino-functionalized octahedral MOFs ($NH_2$-UiO-66) similarly achieved fluorescence turn-on detection of $F^-$ in aqueous solutions, and had excellent stability with strongly acidic and alkaline conditions, allowing the detection capability of 1.0 $g{\cdot}L^{-1}$ and the LOD of 0.229 $mg{\cdot}L^{-1}$ (Zhu et al., 2019). The mechanism of fluorescence enhancement could be attributed to the formation of hydrogen bonds between free amino groups in $NH_2$-UiO-66 and $F^-$, resulting in the transfer of electrons from ligands to Zr-oxo clusters.

**Hypochlorite ions ($ClO^-$)**

As a strong oxidizer and disinfectant, $ClO^-$ is widely used in food industries and daily life (Shangguan et al., 2019). Therefore, developing sensitive and selective detection methods is of great significance for $ClO^-$ detection (Guo et al., 2019). In this respect, Zeng and co-workers prepared highly stable octahedral MOFs by mixed ligands strategy [2-aminoterephthalic acid ($H_2BDC$-$NH_2$), 2,6-pyridine dicarboxylic acid ($H_2PDA$)] for selective and efficiency (response time 15 s) fluorescence detection of $ClO^-$ (Fig. 7a) (Zeng et al., 2020). The linear range was 0.1~60 μM, and the LOD was 0.10 μM. Results showed that the blue emission was enhanced and the red emission was unchanged in presence of $ClO^-$ (Fig. 7b). The good performance was attributed to the rigidity of $H_2BDC\text{-}NH_2$ ligand, where hydrogen bonds formed between H of $-NH_2$ and O of $ClO^-$, thereby reducing the structural relaxation of non-radiative attenuation, causing the fluorescence turn-on. In addition, amino-functionalized Cu-MOFs ($NH_2$-Cu-MOFs, $H_2BDC\text{-}NH_2$ as ligands) were also used for fluorescence quenching detection $ClO^-$. The LOD was lower than that of the above study, at 0.036 μM (Huo et al., 2020). The mechanism of fluorescence quenching was hydrogen bonding formation between the ligand of $H_2BDC\text{-}NH_2$ and $ClO^-$, and hydrogen bonding acted as the bridge to promote electron transfer between them.

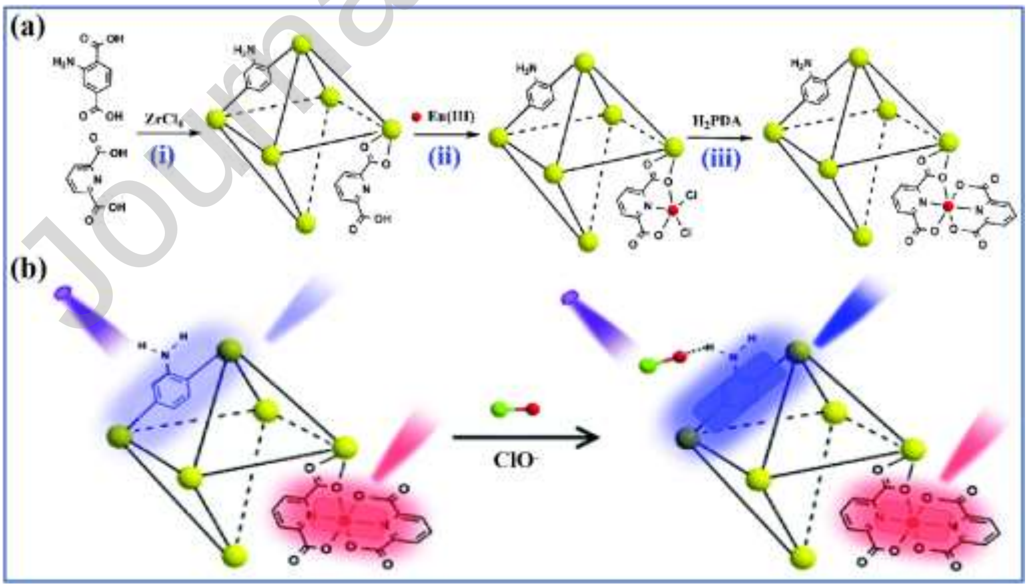


Fig. 7 (a) Synthesis process of PDA/Eu/PDA-UiO-66-$NH_2$. (b) The fluorescent sensing mechanism of PDA/Eu/PDA-UiO-66-$NH_2$. Adopted from Ref. (Zeng et al., 2020). Copyright 2020, with permission of Royal Society of Chemistry.

### 3.1.3 Organic pollutant

Many organic pollutants exist in the environment, and it is relatively difficult to detect them (Liu et al., 2022). Nowadays, many luminescent MOFs have been used to detect organic pollutants, especially explosives. In this chapter, the detection of trinitrophenol (TNP), pesticides, and antibiotics were mainly introduced. The sensing mechanism of organic pollutants mainly involves the following three aspects (Fig. 8) (Yang, G.L. et al., 2021): (1) Photoinduced electron transfer (PET); (2) Intramolecular charge transfer (ICT); (3) Förster energy transfer (FRET).

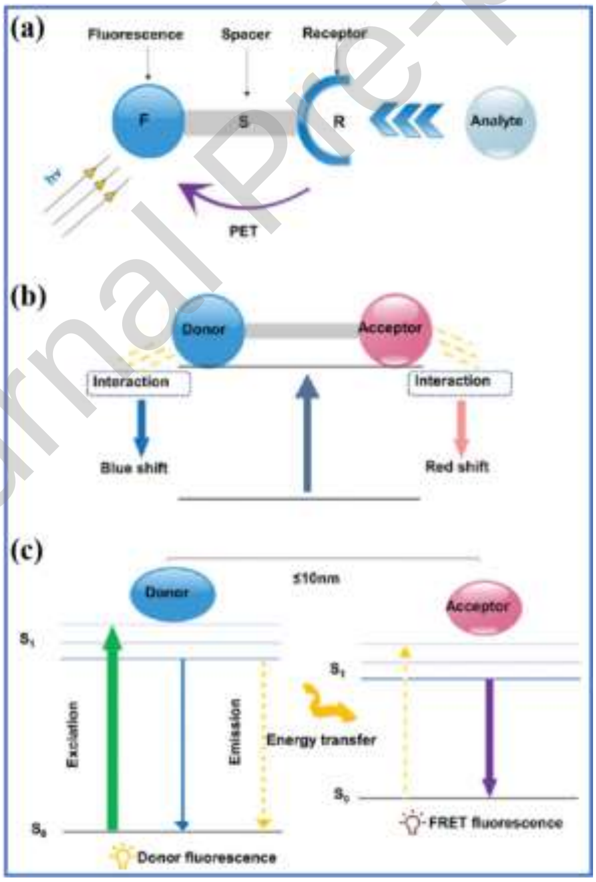


Fig. 8 The sensing mechanism of organic pollutants: (a) PET mechanism. (b) ICT mechanism. (c) FRET mechanism. Adopted from Ref. (Yang, G.L. et al., 2021). Copyright 2021, with permission of Wiley-VCH.

**TNP**

MOF luminescent sensor based on ligand design has been well studied in detecting TNP. For example, Hu and co-workers investigated a carboxyl-functionalized USTC-7-based chemical sensor for selective and sensitive detection of TNP by fluorescence quenching, with a good linear range of 0 ~ 0.012 mM and a LOD of $2.78\times10^{-4}$ mM (Hu et al., 2016). The quenching mechanism might be a combined process of electron transfer, energy transfer, and electrostatic interaction between TNP and N of ligand. In another work, Rachuri *et al*. reported two luminescent dual-ligand 3D MOFs synthesized from angular dicarboxylates and n-donor-containing flexible imidazole ligands for specific and sensitive fluorescence detection of TNP with a LOD of 35 ppb (Rachuri et al., 2018). PET and RET between the mixed ligands MOFs and the target analyte led to fluorescence quenching. In 2021, the LOD of TNP was further reduced. Hu *et al*. used $-CF_3$ functional groups to modify the pores of MOFs to synthesize functional MOFs with good stability, and the LOD of TNP detection reached 2.07 ppb (Hu, M.L. et al., 2021). The hydrogen bonding between $-CF_3$ (C-F) bonds and TNP (H-O) bonds induced π-electrons transfer, leading to strong quenching of PL emission, thus the sensor had higher detection sensitivity for TNP.

**Pesticides**

MOFs constructed by mixed ligands strategy have more easily adjustable porosity, which can increase the probability of host-guest interactions and improve the detection limit and sensitivity of pesticides (Tang et al., 2019). Tao *et al*. synthesized a novel columnar-layer MOF with a three-layer interpenetrating structure for sensitive and quantitative detection of dichloro-nitroaniline pesticides through a dual-ligand strategy, with a good linear range from 0.94 ppm to 16.92 ppm with a LOD of 0.13 ppm (Tao et al., 2017). Electron transfer, electrostatic interactions, and energy transfer easily occurred between nitroaromatic and ligands, leading to the reduction and even quenching of luminescence intensity. Chen *et al.* achieved selective and sensitive detection of paraquat by introducing two triangular ligands to construct a double-permeable stability 3D MOF, with a LOD of $9.73\times10^{-6}$ mol·L$^{-1}$ (Chen et al., 2019). Further mechanism exploration found the electrostatic interaction and energy transfer between ligand and paraquat. Similarly, the electrostatic transfer from electron-rich ligands to electron-deficient pesticides resulted in fluorescence quenching and increased the sensitivity of pesticide detection (Liu, J. et al., 2020).

**Antibiotics**

The massive discharge of antibiotics poses a huge threat to the ecosystem (Lai et al., 2021; Qin, L. et al., 2022b). Now the detection of antibiotics has achieved a better research results. Yu *et al.* used a multi-functional group strategy to synthesize 3D-structured MOFs (RhB@Tb-dcpcpt) (Yu, M. et al., 2019). RhB@Tb-dcpcpt could be sensitively and selectively detecting nitrofurans (LOD of 0.502 μM (99 ppb)) and quinolones antibiotics (LOD of 0.448 μM (107 ppb)). Among them, the detection of nitrofurans and quinolones was achieved through the luminescence quenching and the luminescence color change process, respectively. The mechanism of sensing involved PET and internal filtering effects. Bi and co-workers synthesized a micro-MOFs composite membrane with regular geometry using a multi-ligand strategy to selectively detect tetracycline antibiotics (oxytetracycline hydrochloride, doxycycline, tetracycline, etc.), with a linear range of 20~1000 ng·mL$^{-1}$ and a LOD of 20 ng·mL$^{-1}$ (Bi et al., 2022). At the same time, due to the large aperture and hydrophobic effect of the benzene ring, the adsorption capacity of the film was also good.

### 3.1.4 Mixtures

It is commonly known that there is always not only one kind of pollutant in actual water samples, and the existence of a variety of pollutants can affect the accuracy of one sensor. Therefore, it is necessary to develop dual-functional or even multi-functional sensors to solve this problem. MOF sensors constructed by using ligands design bring this bright flare.

**Bi-metal**

In recent years, great results have been achieved in detecting bi-metal, especially Fe$^{3+}$ and Cu$^{2+}$. As shown in Fig. 9a, a synthesis of three structurally diverse and stable porous chromium-based Cd-MOFs(I-III) by using flexible polycarboxylate ligands and auxiliary ligands of different sizes has been reported (Du et al., 2019b). Cd-MOFs(II) had high sensitivities and selectivities for the Cu$^{2+}$ and Fe$^{3+}$ detection, with LODs of 4.987×10$^{-5}$ and 8.939×10$^{-6}$ M, respectively. Detection results showed that the luminescent intensities of Cu$^{2+}$ and Fe$^{3+}$ decreased from 3000 a.u. to 263 a.u. and 3000 a.u. to 134 a.u. at 318 nm (λex=264 nm), respectively. For Cu$^{2+}$, weak interaction between Cu$^{2+}$ and non-coordinated carboxyl O atoms, energy transfer, and d-d transition induced luminescent quenching. For $Fe^{3+}$, the coexistence of energy transfer and weak O-Fe coordination binding affinity in the framework led to fluorescence quenching. In another work, a 2-fold interpenetrating bcu-type 3D porous luminescent MOF was successfully constructed by introducing auxiliary ligands (Li et al., 2021). It had good sensitivity, selectivity, and short response time for detecting trace $Fe^{3+}$ and $Cu^{2+}$ in DMF, with the LODs of $Fe^{3+}$ and $Cu^{2+}$ being 1.45 and 1.66 μM, respectively. Most importantly, $Fe^{3+}$ and $Cu^{2+}$ could be distinguished according to the difference in luminescent titration concentration and response time.

### Multi-metal

It is valuable to mention that multi-metal sensing has also been well developed. For instance, Wang and co-workers used amino-modified MOFs (MIL-101-$NH_2$) as a general sensing platform. Low LODs (0.0018, 0.0016, and 0.0052 mM, respectively) and wide linear range (0.01~0.2, 0.01~10, and 0.01~1 mM, respectively) were achieved for $Fe^{3+}$, $Cu^{2+}$, and $Pb^{2+}$ detection (Lv, S.-W. et al., 2019). The detected substance could be confirmed according to the wavelength position of the peak ($Fe^{3+}$, $Cu^{2+}$, $Pb^{2+}$ at 450 nm, 430 nm, and 440 nm, respectively) (Fig. 9b). Furthermore, amino-modified ligands achieved greater fluorescence emission, eliminating the need to add additional luciferin. Ratiometric electrochemical sensing of carboxylic acid-functionalized $NH_2$-UiO-66 has also been reported for the simultaneous detection of $Cd^{2+}$, $Pb^{2+}$, and $Cu^{2+}$ (Wang, X. et al., 2020). Based on the unique structural features and good electrochemical properties of the MOFs, realizing the simultaneous detection of $Cd^{2+}$, $Pb^{2+}$, and $Cu^{2+}$ with LOD of 8.5 nM, 0.6 nM, and 0.8 nM, respectively. The detection results were evaluated according to the potential and peak current of $Cd^{2+}$, $Pb^{2+}$, and $Cu^{2+}$ (Fig. 9c). The method was practical, simple, sensitive, and reliable, and had broad application prospects in environmental multi-metal detection.

**Hydrogen sulfide ($H_2S$) and metal ions**

$H_2S$ detection is often carried out together with some metal ions. Nandi's team synthesized a stable MOFs fluorescent sensor (CAU-10-V-H) using a mixed ligands strategy (Nandi, Soutick et al., 2020). The sensor exhibited a highly selective shutdown response to $H_2S$ and $Pd^{2+}$ over a broad pH range (2~12), with good sensitivity (the LOD of 1.65 μM and 110 nM, respectively). The quenching time and quenching rate of $H_2S$ and $Pd^{2+}$ were different. When $H_2S$ existed in solution, the fluorescence intensity of CAU-10-V-H reached 80% quenching at moment; If $Pb^{2+}$ existed, the fluorescence intensity quenched 70% within 5 minutes and quenched 90% after 30 minutes. Significantly, Yang *et al*. developed the first dual-functional MOFs sensor with uniform nanoscale polyhedron morphology through a dual-ligand strategy and tandem process, which exhibited high selectivity and sensitivity to $H_2S$ and $Cu^{2+}$ detection (Yang, X.L. et al., 2021). Among them, the linear turn-on detection for $H_2S$ had a linear range of 0.08~0.42 μM and a low LOD of 3.3 nM. Interestingly, The addition of $H_2S$ as a second turn-off sensor exhibited selective fluorescence quenching for $Cu^{2+}$ in the linear range of 0~0.22 μM with a LOD of 2.6 nM (Fig. 9d). Density functional theory (DFT) calculations showed the energy transfer paths between different functional groups in UiO-66-$NH_2$ after various treatments. For the $H_2S$

sensing process, π-π* transition induced fluorescence recovery, while the addition of $Cu^{2+}$ changed the destination of charge transfer, causing the d-d transition to consume non-radiative energy and induce fluorescence quenching.

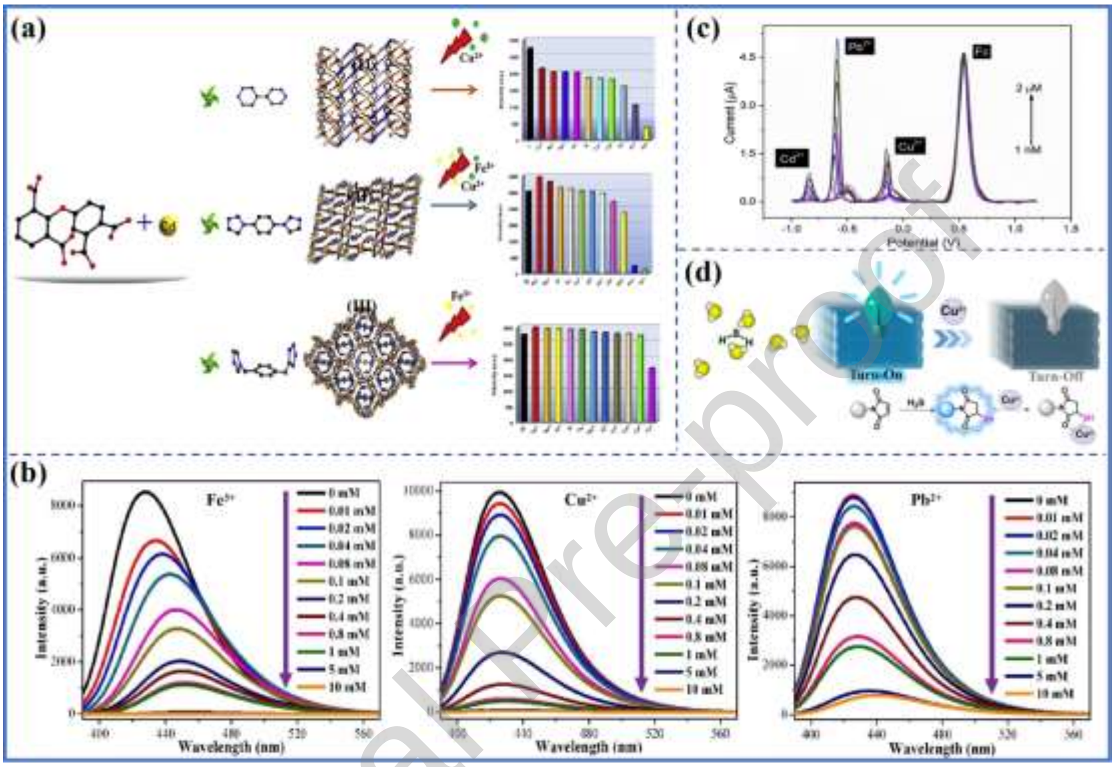


Fig. 9 (a) Synthesis steps of three dual-function MOFs luminescence sensors and fluorescence detection intensity of different metal ions. Adopted from Ref. (Du et al., 2019b). Copyright 2019, with permission of Elsevier. (b) Fluorescence intensity and peak location of $Fe^{3+}$, $Cu^{2+}$, and $Pb^{2+}$ at different concentrations. Adopted from Ref. (Lv, S.-W. et al., 2019). Copyright 2019, with permission of Elsevier. (c) DPASV current signals of $Cd^{2+}$, $Pb^{2+}$, and $Cu^{2+}$. Adopted from Ref. (Wang, X. et al., 2020). Copyright 2020, with permission of Elsevier. (d) Schematic diagram of UiO-66-MA fluorescent turn-on and turn-off sensing. Adopted from Ref. (Yang, X.L. et al., 2021). Copyright 2021, with permission of Elsevier.

### Other intermixtures

MOF sensors based on ligand design can also be used for the co-detection of organic pollutants and metal ions. Du *et al.* constructed 3D hexagonal MOFs with excellent recovery by using auxiliary ligands for highly sensitive and selective detection of nitroaromatic explosives and $Fe^{3+}$ (Du et al., 2018). In this study, the reasons for their fluorescence quenching were specified as resonance energy transfer and electron transfer, and competitive adsorption, respectively. An amino-functionalized MOF fluorescent probe ($MOF\text{-}5\text{-}NH_2$) has even been reported for $Cu^{2+}$, $Pb^{2+}$, and pyrophosphate ($P_2O_7^{4-}$, PPi) detection, whose fluorescence emission was induced by ligands (An et al., 2021). The LOD was 0.057, 0.25, and 0.32 mu mol·$L^{-1}$ for $Cu^{2+}$, $Pb^{2+}$, and PPi, respectively. The coordination of $Cu^{2+}$ and $Pb^{2+}$ with the amino groups on the surface of $MOF\text{-}5\text{-}NH_2$ caused fluorescence quenching. The addition of PPi blocked the electron transfer process between the target and MOFs, resulting in fluorescence recovery. In the aqueous environment where phosphate ions ($PO_4^{3-}$) and metal ions coexist, MOFs with good thermal and water stability could also be constructed as fluorescent detection sensors for detecting these intermixtures by dual-ligand design, the quenching effect was not interfered with by other existing ions (Wang, Q.-S. et al., 2018). Therefore, mixed ligands design strategies can be used to design and assemble multifunctional luminescent sensors based on MOFs.

As mentioned above, as a class of multifunctional materials with high porosity, luminescent MOFs are functionalized by specific functional groups to modify the pore structure, making them more sensitive to detecting pollutants to meet the demand for high sensing performance. If designed properly, organic ligands are also sensitive elements of sensors. That is when target analyte interacts with the luminescence system of MOFs, the structure or properties of target analyte will change, which causes a reaction of luminescence intensity or peak position, thereby resulting in luminescence detection. To explore the LOD, the system sensing phenomenon should be further quantified. In addition, selecting multi-ligand synthesis or adding appropriate functional groups during the synthesis of MOFs can increase the synergies between components of the MOFs framework, promote electron (or energy) transfer between different components, and improve the detection selectivity and sensitivity of MOFs-based sensors.

## 3.2 Pollutant separation

### 3.2.1 Adsorption separation

As a new technology, adsorption separation has been widely used in gas separation, material separation, water treatment, and other environmental fields. As mentioned earlier, functional MOFs by ligand design with extraordinary structural and surface properties can provide excellent performance for adsorption separation technology. In addition, MOFs have the characteristics of both macromolecules and coordination compounds, making them suitable for high-capacity adsorbents for pollutant separation (Dhaka et al., 2019). For example, the amino-functionalized constructed series of MOFs, including MIL-101-$NH_2$(Cr), MIL-53-$NH_2$(Al), UiO-66-$NH_2$(Zr), and MOF-5-$NH_2$(Zn) exhibited similar properties for adsorption removal of metal ions (Lv, S.-W. et al., 2019). Among them, the largest adsorption amounts of MIL-101-$NH_2$ reached 3.5, 0.9, and 1.1 $mM·g^{-1}$ for $Fe^{3+}$, $Cu^{2+}$, and $Pb^{2+}$, respectively. The selective adsorption of pollutants was mainly achieved through the interaction between MOFs and adsorbate, such as electrostatic interaction, hydrogen bonds, acid-base interaction, the influence of framework metal, hydrophobic interaction, and π-π stacking/interaction (Hasan and Jhung, 2015).

MOFs modified with different single-functional groups have been effectively used in the adsorption and separation of pollutants. For example, amino-functionalized MOFs are used for the adsorption removal of $F^-$. After the introduction of amino functional groups, the pore size of MOFs decreased and the specific surface area increased (Jeyaseelan et al., 2021a). Volume filling theory of mesopores, the additional volume of amine functional groups, and partially altered framework structure led to the above phenomena. In addition, there was an electrostatic attraction between the protonated amino group ($-NH_2 \rightarrow NH_3^+$) and $F^-$, which further increased the adsorption capacity of $F^-$ to reach 4.92 $mg·g^{-1}$ (Fig. 10a) (Jeyaseelan et al., 2021b). In another study, MIL-53(Fe) modified by different functional groups ($-NH_2$, $-NO_2$, and -Br) was reported by Yu and co-workers (Yu, J. et al., 2019). The introduction of functional groups changed the pore size and specific surface area of MOFs. Adsorption removal mechanism involved π-π interaction, hydrogen bonding, acid-base interaction between functional groups and tetracycline, and the breathing effect of functionalized MOFs. Consequently, the adsorption capacity of the functionalized MOFs for tetracycline was different and superior to that of original MIL-53(Fe), and the functionalized MOFs had better reusability.

MOFs modified by multi-functional groups have been well studied for dyes and radioactive $TcO_4^-$ adsorption removal. For example, sulfonic acid and carbonyl functional groups were introduced into ligands and synthesized unique hexagonal prismatic mesoporous MOFs (Hong et al., 2020). The electrostatic attraction and ion exchange interface interaction made the functionalized MOFs show fast and significant selective adsorption performance for methylene blue dye. Woo *et al.* performed melamine functional group modification on MOFs containing free amino groups (MIL101-Mela) (Woo and Jhung, 2021). Importantly, MIL101-Mela maintained the integrity of the original material during the modification process. There were hydrogen bonds between the $-NH_2$ functional groups of ligands and the $-NO_2$ or $-SO_3^-$ of dye, especially with a six-membered ring formed (Fig. 10b). MIL101-Mela had better stability and recycling properties. After 4 cycles, the adsorption removal quantity of martius yellow was 6.9 fold that of fresh active charcoal. In another study, a MOF (iMOF-2C) based on dual-functional group ligands was reported. The crystal shape of iMOF-2C was triangular pyramid, which had strong chemical stability, and could quickly select adsorption of non-radioactive perrhenate $ReO_4^-$ (radioactive $TcO_4^-$) (Dutta et al., 2020). The negatively charged imidazole ring and benzene ring on the ligand could attract positively charged $Ni^{2+}$ so that iMOF-2C had more recognition sites of oxo-anions for lower charge density $ReO_4^-$, thus improving the adsorption capacity of $ReO_4^-$ ($691\ mg \cdot g^{-1}$). Xue *et al.* prepared multi-functional groups ($-NH_2$ and $-OH$) modified Al-based MOFs (CAU-1)

(Zhong et al., 2021). The structure of CAU-1 had a large specific surface area (1636.3 $m^2 \cdot g^{-1}$), and micropore volume (0.51 $m^3 \cdot g^{-1}$). The electrostatic attraction of the protonated $-NH_2$ on MOF frameworks to $ReO_4^-$, and N-O chelation resulted in CAU-1 adsorption performance better than most porous materials previously reported (Fig. 10c).

In general, the modification of MOFs by functional groups can increase the interaction between MOFs and pollutants. It is a simple and effective measure to regulate and improve the adsorption capacity and intrinsic characteristics of MOFs for pollutant removal by introducing functional groups on ligands or using multiple ligands.

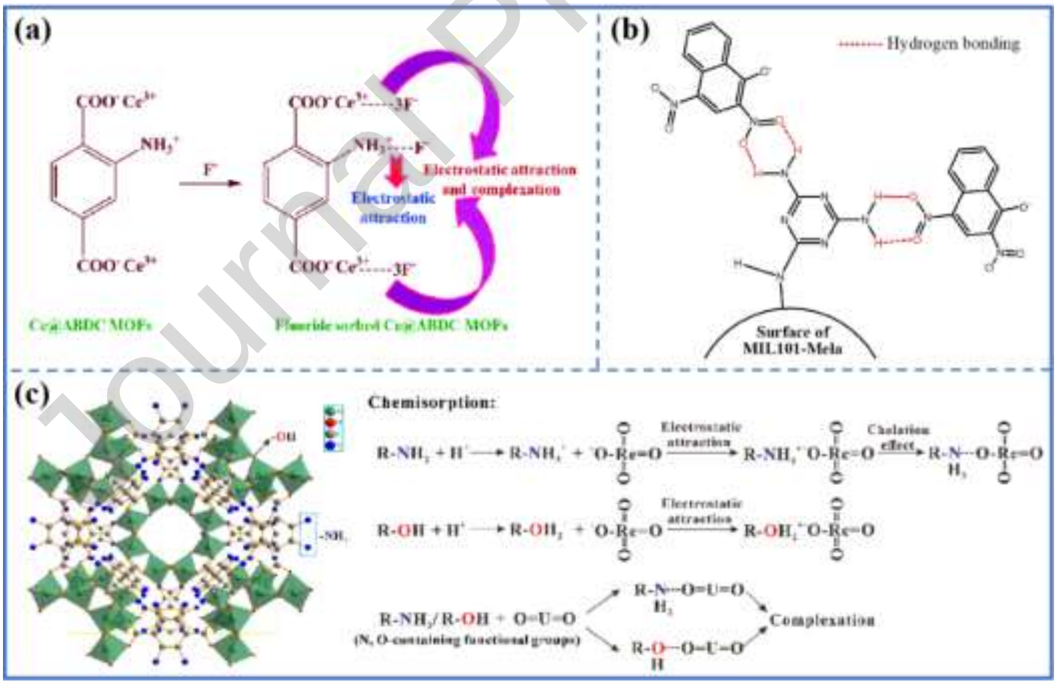


Fig. 10 (a) $F^-$ removal mechanism of Ce@ABDC MOFs. Adopted from Ref. (Jeyaseelan et al., 2021b). Copyright 2021, with permission of Royal Society of Chemistry. (b) Adsorption of martius yellow on MIL101-Mela via six-membered rings with hydrogen bonds. Adopted from Ref. (Woo and Jhung, 2021). Copyright

2021, with permission of Elsevier. (c) Adsorption mechanism of $ReO_4^-$ ions adsorbed on CAU-1. Adopted from Ref. (Zhong et al., 2021). Copyright 2021, with permission of Elsevier.

### 3.2.2 Membrane separation

In the past decades, membrane separation technology has been rapidly developed in solving environmental problems. Compared with traditional separation technology, the membrane separation industry has the advantages of a wide separation range, high efficiency, low secondary pollution, and high environmental safety (Tawalbeh et al., 2018). Membrane separation is mainly to selectively permeate or transport specific substances from impurities. Separation performance is affected by the membrane, separated substance, and their interaction. MOFs as emerging inorganic and organic hybrid crystals were installed on the carrier for *in situ* growth or 2D MOFs nanosheet self-assembly to form microporous framework membranes (Qiu et al., 2014). The membrane structure and chemical properties of MOFs largely determine separation performance, and the pore structure could be functionalized by various ligands. MOF microporous membrane has better advantages in structure and function, so it is one of the most widely studied membrane separation technologies at present (Dou et al., 2021).

Mixed ligands strategies are an effective approach for modifying the porosity structure of skeleton membranes (Qin et al., 2017). There are generally two ways to synthesize mixed ligands framework membranes: direct mixing or post-synthesis exchange (Dou et al., 2021). Ma *et al*. prepared zeolite imidazolate MOFs membranes (ZIF-7-$NH_2$) by direct mixing method (Ma, L. et al., 2019). The membrane surface morphology and cross-section showed uniform, defect-free, and continuous characteristics. The addition of second ligands (2-aminobenzimidazole) led to more structural defects in the ZIF-7-$NH_2$ membrane framework, which remarkably increased the pore size, permeability, selectivity, and adsorption capacity of the membrane, expanded the adjustable porosity range of gas separation, and accelerated the rate of gas molecules entering the framework cavity. Most interestingly, ZIF-7-$NH_2$ framework membrane had stronger flexibility and respiration performance, and its regular hexagonal pore structure after the framework shrinks was beneficial to improving gas uptake capacity and diffusion selectivity.

In another work, ZIF-8 membranes with breathing effects were prepared by post-synthesis exchange (exchange of 2-methylimidazole with 2-aminobenzimidazole) and reduced the membrane micropore size (Eum et al., 2019). Due to the existence of amine groups, the affinity of $CO_2$ was enhanced, and the selectivity of ZIF-8 membrane for mixed gas $CO_2/N_2$ and $CO_2/CH_4$ was promoted. The exchange of ligands restored the membrane properties. Membrane surface exchange of 2-methylimidazole with 2-imidazolaldehyde was also reported (James et al., 2020). In this study, the partial exchange of ligands narrowed the effective pore size of the ZIF-8 membrane, leading to a noticeable improvement in the selectivity of propylene/propane gas. In addition, during the exchange process, the crystallinity of the membrane tended to decrease and then increase with the diffusion rate of the imidazole-type ligand in the framework.

In summary, incorporating multiple-ligand with different coordination characteristics to the skeletal membrane can optimize the membrane structure, such as pore size contraction and distribution, porosity, framework hydrophobicity, flexibility, and coordination, thereby inducing new separation properties, and providing a better way for the synthesis of multifunctional MOFs microporous skeletal membranes.

### 3.3 Pollutant degradation

Catalytic degradation technology has the advantages of high efficiency, low cost, and less secondary pollution, it is a clean method to degrade organic pollutants (Xu et al., 2021). MOFs, as a promising type of hybrid materials, contain a variety of functional components with good pore structure and intracavity chemical environments (Gao et al., 2019). MOFs have less energy consumption and more efficiency than conventional catalysts, so they can be used to effectively degrade organic pollutants in the environment. For example, polyphosphine ligands Ag-MOF with abundant coordination sites was used for degradation removal of nitroaromatic, which was accompanied by the formation of ·OH in the reaction process. The catalytic efficiency did not decrease significantly after 5 cycles (Wu et al., 2015). Table 4 summarizes some typical examples of functional MOFs by ligand design for catalytic degradation of organic pollutants.

**Table 4** Functional MOFs by ligand design for catalytic degradation of organic pollutants.

| **MOFs** | **Ligand** | **Design type** | **Synthesized method** | **Pollutants** | **Degradation efficiency** | **Degradation time** | **Reusability** | **Ref.** |
|---|---|---|---|---|---|---|---|---|
| 1-Gd | 1,3,5-tris(carboxymethoxy)benzene | Single-ligand | Solvothermal | Tetracycline | 82% | 130 min | 5 cycles | (Tan et al., 2021) |
| $[(Cd_4(L)_3(DMF)Cl_2)\cdot H_2O]_n$ | 1,1′-di(4-carbonylphenyl)-2,2′-biimidazoline | Single-ligand | Solvothermal | Methylene blue | 89.2 % | 100 min | - | (Wang, J. et al., 2020) |
| Mn(DMTDC)(DMF)a | 3,4-dimethylthieno[2,3-b]thiophene-2,5-dicarboxylic acid | Single-ligand | Solvothermal | Methylene blue | 90.8 % | 70 min | - | (Fang et al., 2018) |
| UiO-66-$NO_2$/$NH_2$ | 2-nitro-terephthalic acid, and 2-amino-terephthalic acid | Dual-ligand | Solvothermal | Rhodamine B | 95.5 % | 50 min | Superior to single-li | (Jin, J.-C. et |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | gand MOFs | al., 2021) |
| MTV-UiO-66-BE | $NH_2$-1,4-benzendicarboxylate, and Br-1,4-benzendicarboxylate | Dual-ligand | Acetic acid modulated procedure | Dimethyl 4-nitrophenylphosphate | 3 times more active than single-ligand | - | Higher than single ligand UiO-66 | (Kalaj et al., 2019) |
| PL-MOFs | Camphoric acid, and 2-(1-hydroxyethyl) benzimidazole | Dual-ligand | Solvothermal | Crystal violet | 96% | 10 min | 3 cycles | (Tang et al., 2018) |
| $[Ag_3(bib)_2]\cdot(H_3L)_2$ | 1,3-bis(3,5-dicarboxylphenoxy)benzene, and 1,4-bis(1-imidazoly)benzene | Dual-ligand | Solvothermal | Basic green | 83.31% | 100 min | 4 cycles | (Yin et al., 2021) |
| $Co(sbdc)(4,4'\text{-}bbibp)]_n$ | 4,4′-stilbenedicarboxylic, and 4,4′-bis(benzoimidazo-1-ly)biphenyl | Dual-ligand | Solvothermal | Methylene blue<br>Methylene violet | 94.7%<br>97.4% | 120 min | - | (Luo et al., 2017) |
| [Co(4,4′-Hcpmb)(1,3-bi | 4-(4-carboxylphenylmethylthio)benzo | Dual-liga | Solvothe | Methylene blue | 95% | 120 min | 5 cycl | (Fan |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| b)$]_n$ | ic acid, and 1,3-bis(1-imidazo-1-ly)benzoic acid | nd | rmal | | | | es | et al., 2019) |
| | | | | Methylene violet | 94.7 % | | - | |
| | | | | Rhodamine B | 94.1 % | | - | |
| 2.5CMCD @NU-1000 -TCPP(Pd) | β-cyclodextrin, benzoic acid, 1,3,6,8-Tetra(4-carboxylphenyl)pyrene, trifluoroacetic acid, and 4-morpholineethanesulfonic acid | Multi-ligand | Solvothermal | 4-chlorophenol | Nearly 100 % | 60 min | 5 cycles | (Zhang, W. et al., 2021) |

The open pores of functional MOFs could capture and enrich the target pollutants and their intermediates, prolong the residence time of substrates at the reactive site, thereby enhancing the degradation efficiency (Zhang et al., 2020). Guo *et al*. reported a porous amino-functionalized MOF [AQS-NH-MIL-101(Fe)] decorated with 2-anthraquinone sulfonate (AQS) (Fig. 11a) (Li, X. et al., 2017). The crystal morphology was unusual octahedral with abundant pore structures and specific surface area. AQS-NH-MIL-101(Fe) had good catalytic properties to degrade more than 97.7% bisphenol A (BPA) within 180 min, and the rate constant (k) was usually higher than the common catalyst. The modified AQS was a good electron-transfer mediator in this degradation reaction. Further exploring its catalytic mechanism found that some free radicals ($SO_4^{-\bullet}$, ·OH, and $O_2^{-\bullet}$) participated in the degradation reaction, of which $SO_4^{-\bullet}$ was the dominant (Fig. 11b).

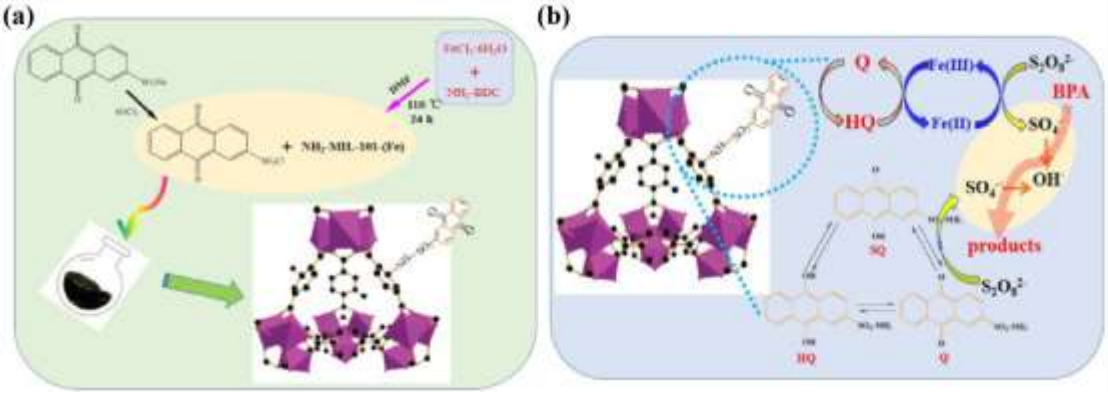


Fig. 11 (a) Modification process of $NH_2$-MIL-101(Fe). (b) Mechanism of catalytic oxidation of BPA by AQS-NH-MIL-101(Fe). Adopted from Ref. (Li, X. et al., 2017). Copyright 2017, with permission of Elsevier.

Further, functional MOFs have semiconductor properties and structural characteristics, so other micromaterials can be packaged into MOFs to form efficient and stable solar-driven photocatalysts (Usman et al., 2017). MOFs ($NH_2$-UiO-66) with a good visible light response, large specific surface area, and superior stability were also reported (Yao et al., 2018). The researchers prepared $TiO_2$@$NH_2$-UiO-66 nanocomposites by encapsulating tiny $TiO_2$, achieving strong degradation activity and good mineralization ability of styrene under visible light for the first time. The removal efficiency achieved was 90% in 80 min and finally reached almost full removal. The degradation mechanism had some similarities with the above examples, mainly because the rich nanopores of MOFs could quickly capture pollutants. The sensitivity of amino groups on the ligand to photocatalytic active sites could enhance light absorption and improve catalytic activity.

Therefore, the catalytic property of MOFs can be increased by introducing ligands with different specific properties into the same MOFs through ligand design, especially for some refractory dyes and drugs (Chen, X. et al., 2021; Jin, J.-C. et al., 2021; Yao et al., 2020). Mixed ligands MOFs catalysts have big specific surface areas. High porosity, and rich catalytic sites, can promote the attachment of more pollutants and improve degradation efficiency. Furthermore, most functional MOFs are obtained by hydrothermal synthesis, and high yields can be achieved by adjusting the ligand to metal ratio, providing a prerequisite for rapid mass production in the industry.

In addition, the application of anything is two-sided, and the same is true for MOFs. At present, the toxicity of MOFs during the application process has been reported in some literature. For example, The toxicity of MOF nanoparticles in vitro and in vivo and the influencing factors were reviewed in detail by Ettlinger and Salehipour *et al.* (Ettlinger et al., 2022; Salehipour et al., 2021). Yang's group reported the toxicity and mechanism of MOF-199 to pea seedling plants and nitrogen-fixing bacterium *Azotobacter vinelandii* in 2021 and 2022, respectively (Guan et al., 2021; Ouyang et al., 2022). The toxicity of MOFs during pollutant removal has also been reported (Kontogiannis et al., 2022; Kumar et al., 2019; Zhang, Q. et al., 2021). Many studies have found that certain concentrations of MOFs will release metal ions, which penetrate the cell membrane and enter the cytoplasm, thus arousing oxidative stress and differentially expressed genes that inhibit cell growth and/or lead to cell death. To sum up, the toxic effects of MOFs on plants, animals and human beings are mostly derived from the toxicity of intermediate products produced in the process of pollutant removal or bioaccumulative effects caused by metal ion leaching. Lower toxicity of intermediate products or more stable structure of MOFs during the reaction will greatly reduce the toxic effect of MOFs and minimize environmental hazards.

## 4. Conclusions and perspectives

So far, MOFs have wide applications and their synthesis is gradually shifting from single ligands to mixed ligands. The mixed ligands design is beneficial to improving the overall performance of functional MOFs, making them superior to single-ligand synthesized MOFs in catalysis, chemistry sensing, environmental remediation, and other applications. However, the structure and properties of MOFs with mixed ligands remain further discussed. Previous reviews have described the potential applications of MOFs in various aspects. Nevertheless, this review is unique in that it focuses on ligand design strategies of functional MOFs, including single-, dual-, and multi-ligand designs. Firstly, the synthesis process of MOFs designed by single-ligand is relatively simple, and the coordination methods of different single ligands and metal centers are different. However, there are still many deficiencies in functional properties, topology tunability, and stability of single-ligand MOFs. Secondly, many MOFs designed by dual-ligand can compensate for the deficiency of single ligands to some extent. The combination of two different ligands may produce a synergistic effect that makes the internal environment of the framework more coordinated. Therefore, dual-ligand design can synthesize functional MOFs with diverse topologies, and the strategy is mainly focused on ligands with different functional groups. The synergistic effect between functional groups may make the same MOFs combine the advantages of all functional groups to create multifunctional

MOFs with broader application prospects. Although the research of functional MOFs by ligand design is increasingly mature, as a new environment-friendly functional material, considering the actual situation, it still needs to overcome the following problems and challenges.

(I) MOFs have a high surface area and pore rate. It is easy to cause pore blockage and structure collapse during the pollutant treatment process. Organic ligands rich in functional groups can precisely control open pore structures of MOFs, maintain the material crystallinity and structural integrity, and provide more precise active sites for the capture and removal of target pollutants, to improve the above problems.

(II) Most multi-ligand MOFs have poor stability because of weak coordination bonds between ligands and metals. Therefore, ligands with larger bond energy can be selected to combine with metals to improve the overall rigidity and stability of the framework. Furthermore, the formation of isolated metal can be promoted by regulating different ligand ratios, providing stronger attachment sites for the target analyte, and improving material stability.

(III) During the mixed ligands MOFs synthesis, different ligands will have different synergistic effects on the metal center, resulting in a series of exciting properties, such as luminescence, magnetism, and high-efficiency selectivity. It is worth exploring how to use experiments and related theoretical calculations to determine the electronic structure, and active sites of materials, and further explain the mechanism of MOFs with excellent properties.

(IV) Functional MOFs by ligand design still have great limitations in environmental application, and the exploration of their mechanisms is relatively simple. How to utilize characterization techniques and theoretical calculations is crucial for further exploring the mechanisms of functional MOFs.

(V) Noteworthily, the ligand design strategy can be used to better tolerate the second ligand deletion phenomenon, increase the porosity, specific surface area and stability of MOFs for better development of superior breathing effects. For example, the breathing effect and large specific surface area of functional MOFs can be used to absorb and contact more pollutants, resulting in longer residence time, fuller contact, and more complete degradation of pollutants during removal.

(VI) In the field of environmental pollution control, the treatment of pollutants is not an easy task. The treatment process inevitably generates and/or is accompanied by other contaminations. Different synergies between multiple ligands and metal atoms may result in a performance multiplication of MOFs, thus creating multifunctional MOFs. Therefore, selecting suitable single or multiple ligands according to certain objectives may achieve twice the result with half the effort.

In conclusion, functional MOFs based on ligand design still have great limitations, and the structures and properties of mixed ligands MOFs need to be discussed. Future research needs to overcome the above shortcomings and further explore, laying a foundation for more practical environmental applications. At the same time, we firmly believe that this review will provide new opportunities for future research in developing multi-ligand MOFs with better performance.

## Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgments

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## Environmental implication

A large number of toxic and harmful pollutants have been discharged into the environment. Some purification materials have high costs, low efficiency, and may generate secondary pollution. Metal-organic frameworks (MOFs) have many unique physicochemical properties and are one of the green and efficient materials for environmental pollution treatment. This study investigates three ligand design strategies for MOFs, as well as the challenges for subsequent research. Moreover, recent advances of functional MOFs by ligand design in environmental applications are presented, and the effects of ligand design on the performance of functional MOFs are explored from the mechanism perspective.

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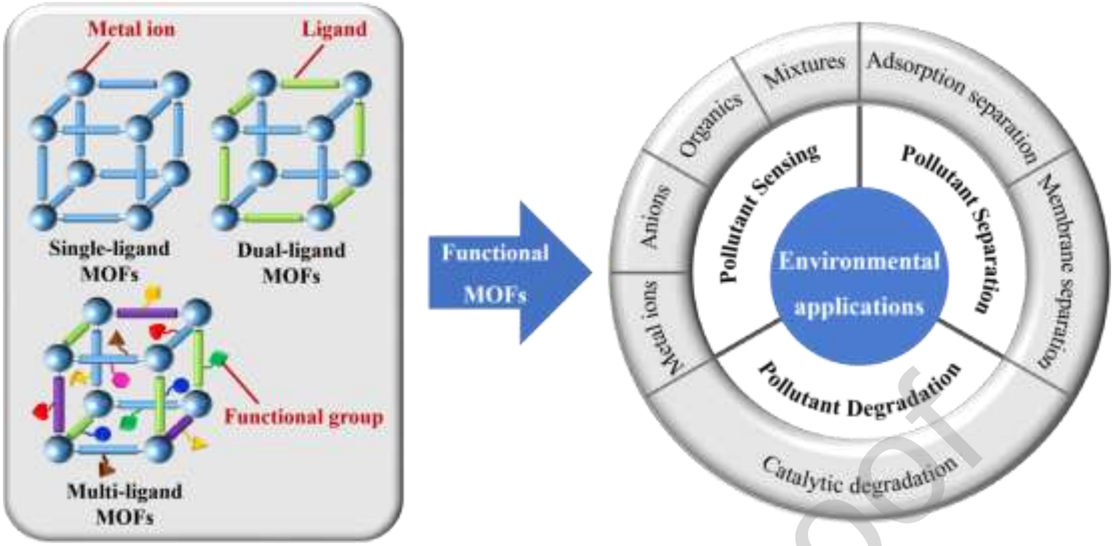
Graphical abstract



## Declaration of Interest Statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Highlights

- Three ligand design strategies for functional MOFs are systematically presented.
- The recent advances of functional MOFs in environmental applications are presented.
- The mechanisms of functional MOFs in environmental applications are discussed.
- Problems and challenges of functional MOFs by ligand design in future research are proposed.