



## Review

# Design and sensing applications of metal–organic framework composites



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## ARTICLE INFO

## Keywords:

Biomedical imaging  
Biomolecular detection  
Electrochemistry  
Fluorescent detection  
Functionalization  
Metal–organic framework  
Polymer  
Porous material  
Sensing  
Signal transduction

## ABSTRACT

As crystalline molecular materials, metal–organic frameworks (MOFs) have unique chemical and physical properties, such as ultrahigh porosity, tunable structure, and high thermal and chemical stability. These characteristics make MOFs suitable for use in gas storage, separation, catalysis, biomedical imaging and sensing. Precise chemical modifications can especially endow MOFs with specific functions and offer the possibility of designing a new generation of sensing devices. This article focuses on the design of functional MOFs and signal-transduction strategy, including optical, electrochemical, mechanical, and photoelectrochemical schemes, for analytical applications in detection of solvent molecules, metal ions, DNA, proteins, and other important biomolecules.

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## 1. Introduction

As crystalline molecular materials, metal–organic frameworks (MOFs) are formed by association of metal centers or clusters and organic linkers, and offer unique chemical properties with an unprecedentedly large and permanent inner porosity. Moreover, these MOF structures are extremely versatile through the design of the architecture and functionalization of the framework [1–3]. Designed MOFs have shown promising applications in catalysis,

separation, gas storage, biomedical imaging, and drug delivery. Recently, several investigators have begun exploring the potential of MOFs as chemical sensors. The exceptional tunability of MOF structures and properties should constitute an important advantage over other conventional chemo-sensory materials. Therefore, MOF-based sensors have significant potential for developing powerful analytical techniques for the determination of biomolecules in clinical, environmental, and industrial applications.

To achieve specific molecular recognition, the MOFs need additional functionalities. Three different strategies have been identified to modify MOFs easily and endow them with specific functions:

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- the first method is to modify specific organic ligands or dope metal ions in the frame of the MOFs (e.g., lanthanide metal ions are employed as dopants to construct luminescent MOFs for optical sensing) [4];
- the second strategy is post-synthesis modification (PSM), in which the organic linkers with functional groups can be used for subsequent chemical grafting; Kurmoo et al. designed a trifunctional (carboxylate, imidazolite, and hydroxyethyl groups) tag for preparing a single-crystal MOF, and, after dehydration, two consecutive PSMs of elimination and bromination were realized for improving the gas uptake of the MOF [5]; and,
- the third approach is to entrap functional molecules and nanoparticles (NPs) within the framework, whose composites possess multifunctionalities for molecular recognition and signal transduction.

In principle, any changes of MOF properties depending on the guest could be measured as a sensing signal. On the basis of signal transduction, MOF-based sensors are categorized into four types: optical, electrochemical, mechanical, and photoelectrochemical.

It is not surprising that a large number of MOFs have been found to be photoluminescent because the linkers in most MOFs contain aromatic sub-units with luminescent emission. Interestingly, a chiral porous MOF system has been successfully devised for enantioselective fluorescence sensing of chiral amino alcohols with an enantiomeric quenching ratio of 3.12 due to steric confinement of the MOF cavity [6]. Although electrochemical methods have rarely been explored for MOFs due to the insulating properties of the majority of MOFs, the development of conductive MOFs is currently under way by hybridizing with nanomaterials based on carbon and metals [7].

MOF-based mechanical sensors, including surface-acoustic wave (SAW), quartz-crystal microbalance (QCM), and microcantilever devices, are appealing for their advantages of miniaturization and multiplexing. Most recently, a photoelectrochemical strategy was also introduced for the construction of MOF-based sensing devices.

This review highlights the recent advances in MOFs as chemical sensors and biosensors. We briefly examine the design and the functionalization of MOFs with many molecules through dopant modification, post-synthesis methods (PSMs), and entrapping functional NPs (Fig. 1). By incorporating appropriate signal-transduction capabilities, a series of MOF-based sensors, including optical, electrochemical, mechanical, and photoelectrochemical schemes, are summarized for their analytical applications in the selective detection of solvent molecules, metal ion, DNA, protein, and other biologically important targets.

## 2. Design and functionalization of MOFs

### 2.1. Design of MOFs

In general, MOFs are synthesized through the coordination of polydentate-bridging ligands with inorganic centers, which forms

well-defined, low-density networks. Based on the different molecular functionalities and architectures of various ligands and inorganic nodes, the MOFs demonstrate unique chemical and physical properties. Thus, design of specific ligands and doping metal ions in the frame became popular methods for functionalization of MOFs. Typically, Ir, Re, and Ru complexes with dicarboxylic acid functionalities have been incorporated catalytically into a highly stable, porous  $Zr_6O_4(OH)_4(\text{bpdc})_6$  (UiO-67, bpdc = *para*-biphenyldicarboxylic acid) framework using a mix-and-match synthesis strategy. These doped MOFs are highly effective catalysts for water oxidation,  $\text{CO}_2$  reduction, and organic transformations [8]. Doping small amounts of  $\text{Ru}^{\text{II}}$  into a ultramicroporous, fluorescent  $\text{Zn}^{\text{II}}$  coordination polymer produced phosphorescent materials with highly tunable oxygen-quenching efficiency, and were employed to construct a simple, color-changing, ratiometric oxygen sensor [9].

The expansion of organic linkers also provides the possibility of giving MOFs various functionalities. For example, a chiral anionic MOF has been rationally constructed by means of a predesigned size-extended hexatopic ligand, namely, 5,5'5''-(1,3,5-triazine-2,4,6-triyl)tris-(azanediyl)trisophthalate. The luminescence intensity of the designed MOF is significantly enhanced in toluene and benzene, while quenching effects are observed in acetone and ethanol, providing a potential application for luminescent probes [10].

A porous, iron-based MOF, MMPF-6, has been constructed by self-assembly of iron(III) *meso*-tetrakis(4-carboxyphenyl)porphyrin chloride with  $Zr_6O_8(\text{CO}_2)_8(\text{H}_2\text{O})_8$  generated *in situ* under solvothermal conditions. MMPF-6 shows interesting peroxidase activity, comparable to that of heme protein myoglobin [11].

Rosseinsky and co-workers successfully assembled the peptide-based colorless crystals of  $[\text{Zn}(\text{Gly-Thr})_2]\cdot\text{CH}_3\text{OH}$  via the reaction of zinc nitrate and Gly-Thr in a methanolic solution [12]. This peptide-based MOF exhibited selective adsorption of  $\text{CO}_2$  in preference to  $\text{CH}_4$ .

These research efforts open the door to the design of an advanced generation of biomimetic materials for bioanalysis applications.

### 2.2. Functionalization of MOFs by post-synthesis methods

Once the building blocks (ligands and inorganic nodes) for the framework construction are selected, additional functionalities can be imparted to the porous crystals by PSM via chemical reaction [13]. As shown in Fig. 2, when the reaction involves a covalent bond of the organic linker, it is termed a covalent PSM. The concept of post-synthesis deprotection (PSD) is that a protecting group is first introduced onto an organic linker. After the linker is incorporated into a MOF under standard solvothermal conditions, the protecting group is removed in a post-synthesis fashion to reveal the desired functionality.

Covalent PSM has proved to be a powerful, versatile method for introducing a broad range of chemical groups into MOFs. For example, amino, bromo, nitro, and naphthalene-functionalized UiO-66 MOFs have been synthesized through reticular chemistry to generate new, functionalized frameworks via PSM [14]. A

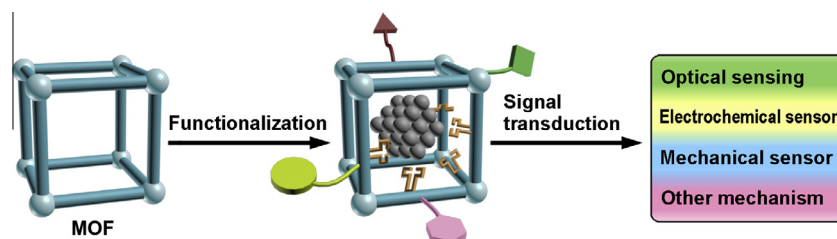


Fig. 1. Functionalization and signal transduction of metal-organic framework (MOF)-based composites for sensing applications.

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