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Optical chemosensors based on metal organic frameworks for selective detection of hazardous pollutants: A review

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ABSTRACT

The development of an appropriate selective chemical sensor for the detection and quantification of environmentally hazardous substances, such as heavy metals, has seen a substantial demand in scientific interest. Because optical changes occur when luminous metal-organic frameworks (LMOFs) interact with the analyte of interest, they have recently received a lot of attention as effective chemosensors. Metal-organic frameworks (MOFs), also known as porous coordination polymers (PCPs), are the crystalline compounds with the biggest pores. They are made up of metal ions linked to organic ligands. Because of the collective behavior of the functional units, controlled integration of MOFs and functional materials results in the fabrication of new multifunctional composites that outperform those of the separate components. Their design flexibility, as well as tunable and homogeneous pore sizes, make them appealing materials for a wide range of applications. Various methodologies, including the hydro/solvothermal technique, microwave, electrochemical, and mechanochemical processes, have been used to create a range of unique structures. The methodologies employed in the design of MOFs are critical in terms of the targeted application. Some of the promising applications of the MOFs are catalysis, energy storage, adsorption, drug-delivery systems, membrane separation, non-linear optics, gas storage and sensing towards various target components, including small molecules, solvents, pesticides, explosives, and biological markers. This review gives an overview of metal-organic frameworks, nomenclature, structure, synthesis methods, types of luminescent MOFs, the common sensing mechanisms, and application in sensing hazardous pollutants.

1. Introduction

Water sources are contaminated by organic pollutants and heavy metals released by industries like leather, food, cosmetics, plastic, textile, painting, and paper. Some metals are essential to life and growth. Others can be harmful to the living organisms, including plants, animals, and humans. Transition metal ions, including Fe^{2+}, Fe^{3+}, Cu^{+}, Cu^{2+}, Co2+, Cr(V), Cr(VII), Hg^{2+}, Ni^{2+}, and Pb^{2+}, have a negative impact on health because they generate oxidative species that damage DNA and generally harm the kidneys, reproductive organs, and central nervous system in addition to causing cancer. Additionally, divalent metal ions are common contaminants in drinking water and can lead to chronic illness even at very low levels[1]. Metal-organic frameworks (MOFs) are hybrid nanomaterials with extended porous network, formed by connecting inorganic metal ions and organic linkers[2].

MOFs outperform traditional porous materials such as zeolite, mesoporous silica, carbon, metal oxide, and polymer because they are often amorphous porous solids with irregular pores and poorly defined structures, making them unsuitable for use in many applications[3]. On the other hand, MOFs are receiving significant attention as one of the most fascinating materials in industrial and academic fields due to their multiple advantages such as large porosity and huge adsorption capacity, high surface area up which can reach to thousands of square meters per gram of sample, ease of tunability, sensitivity, selective binding to certain analytes, environmental sustainability, easily modified, good thermal stability[4]. These parameters allow for a variety of features and applications, such as liquid and gas separation, biomedicine, luminescence sensing, gas storage, drug delivery and catalysis, water treatment[2],[5].

Voltammetry, atomic absorption spectroscopy, inductively coupled plasma (ICP) mass spectroscopy, chromatography, and other analytical methods have all been employed to identify various species owing to their ability to detect metal ions accurately in very small concentrations (ppb level). These procedures, however, are complicated and difficult to apply due to their high cost

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and using large sample quantities (5 ml or more)[1]. Therefore, the development of inexpensive, quick, and selective detection methods is essential. These requirements are provided by luminescent MOFs (LMOFs), which, thanks to their selective "turn on" and "turn off" mechanisms, can easily detect a variety of analytes that are harmful to the environment, including heavy metals, nitro-aromatics, volatile organic carbons. In this way, MOF-based sensors are suitable for the commercial use[6].

1.1 Chemical structure and synthesis of MOFs

1.1.1 Nomenclature of metal-organic framework

The name "metal-organic frameworks" (MOFs) varies. The abbreviation MOF is commonly used, followed by a number to identify the nature of the substance. For example, MOF-74 is used for $Zn_2C_8H_4O_6$, MOF-101 is used for Cu_2 (m-benzene dicarboxylate-Br)$_2$(H_2O), and MOF-253 is used for Al(OH) (2,2-bipyridine-5,5-dicarboxylate).

IRMOF (isoreticular metal-organic framework) is sometimes used to refer to MOF materials that share the same symmetry. For instance, IRMOF-1 for $Zn_4O(BDC)_3$, where BDC= (1,4-benzodicarboxylate) and IRMOF-16 for Zn_4O nodes with p-terphenyl-4,4′-dicarboxylate struts between the nodes. Several MOFs are categorized based on the research institutions and places where they were discovered, including LIC (Leiden Institute of Chemistry), HKUST (Hong Kong University of Science and Technology), MIL (Materials of Institut Lavoisier), and UiO (Universitetet I Oslo). Another important family of MOFs that share the zeolite topology is called ZIFs (zeolite imidazole frameworks), in which tetrahedral composed of nitrogen atoms surround metal ions and are attached by imidazole rings. Zeolite imidazole is the prefix used to name this family, and it is followed by a specific number. In addition to the classification of some research groups that produced some MOFs, such as CPL (coordination polymer with pillared layer structure), F-MOF-1 (fluorinated metal-organic framework), and MOP-1 (metal–organic polyhedral)[7].

1.1.2 Structural aspects

MOFs are a type of self-assembling polymerized porous inorganic-organic hybrid materials. They consist of metal clusters bonded coordinately to organic ligands. Metal nodes are inorganic secondary building units (SBU) that serve as the "joints" in MOF formations. Inorganic secondary units consist of polyhedral or a tiny cluster. While the organic linkers or organic SBU, act as "supporter" in MOF structures[8]. Organic linkers (Ligands) are typically composed of di, tri, or tetra-dentate atoms like N or O donor atoms. Among the most utilized ligands are carboxylates, pyridyl and cyano groups, crown ethers, phosphonates, and polyamines (especially those derived from imidazole, oxalic acid, and benzene). The properties of MOF materials are influenced by the choice of the starting materials used for their production. MOFs can be made with a variety of metal centers and organic ligands, giving them the flexibility to have their physical and chemical properties changed. Different porosity structures of MOF are produced by changing the linkage length of the organic linkers without changing the metal ions and employing the same ligands and using different metal ions. Furthermore, it has been demonstrated that the way of linkages between the raw elements have a significant effect on the characteristics of MOFs[9, 10] (Table 1).

1.1.3 Synthesis routs

There are numerous suitable synthetic techniques for synthesizing MOFs. Without a doubt, The reactive mixture that is selected (metal source, organic ligand, and solvent) has a considerable impact on the structure and characteristics of the MOF. However, the synthetic procedures and numerous other variables including solvent, temperature, reaction time, pressure, and pH have an impact on MOF's structure, morphology, particle size and yield. Depending on the required structures and features, a variety of synthetic methods, such as conventional solution, diffusion synthesis, solvothermal, microwave, sono-chemical, electrochemical, iono-thermal and mechanochemical can be used to produce MOFs[72,73] (Figure 1).

Conventional solution method:

This procedure requires the precise proportional mixing and stirring of a metal source, organic ligands, and other basic materials in a specific solvent for a defined duration of time at a specific temperature (Figure 2). The synthesis takes below the boiling point of the solvent by using open flasks at atmospheric pressure. To obtain pure MOF crystals, the reaction product is then collected through filtration and subjected to further solvent evaporation. To achieve the highest yield of the desired MOF, pH must also be adjusted. Using this technique, a ceramic-based MOF was synthesized such as ZIF-8 (Ye et al., 2018). Optical ceramics are dense and have a millimetre dimension that transmits 84 percent of visible light. Also MOF-5, MOF-74, MOF-177 have been produced by this method[74].

Advantages of this method

- This method produces MOFs with high chemical and thermal stability.
- The synthesis process is carried out at room temperature.
- A short time scale is needed for MOFs crystallinity.
- Need no advanced equipment[75].

Disadvantages of this method

- When using kinetically more inert ions, specific systems need an increase in reaction temperature to attain the desired crystallinity and reaction rates[71].

Diffusion synthesis method

The diffusion method involves bringing the reacting species gradually into contact. There are three types of diffusion; the first type is the liquid phase diffusion (Figure 3). In this method the organic ligand and metal ions are dissolved in an incompatible solvent with varying densities. The crystal growth takes place at the interface of the two solvents when the dissolved species meet each other. The second type is gel diffusion. This approach depends on mixing the metal ion in the solution with a gel substance that has been dispersed with the organic linkers for a predetermined amount of time, the gel diffusion method produces MOF crystals in the gel phase. This technique can produce single crystals suited for x-ray diffraction investigation by slowing down the diffusion process and preventing the material's bulk precipitation. The third type is gas phase diffusion method (Figure 4), the solvent utilized in this approach is a solution of volatile organic ligands. MOFs are formed when the metal ions in the solution and the organic linkers mix sufficiently to produce a reaction.UiO-66 was created by this method through the addition of $ZrCl_4$, H_2BDC, H_2O, and acetic acid to a conical flask containing N,N′-dimethylformamide. The mixtures were stirred until they formed a clear solution.[74,76].

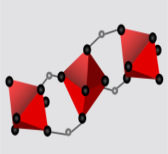
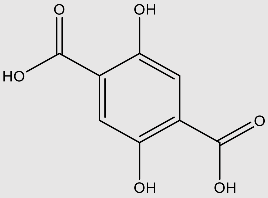
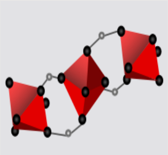
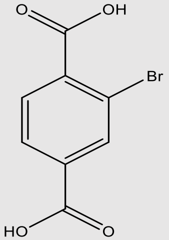
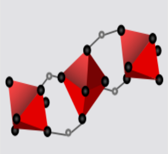
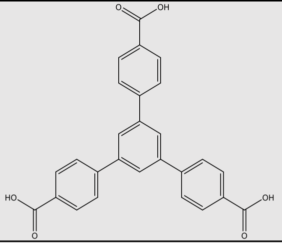
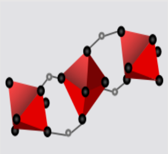
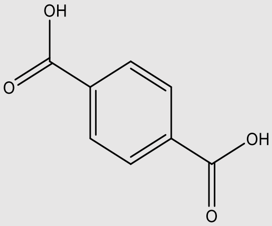
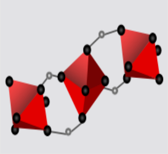
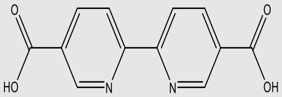
Advantages of this method

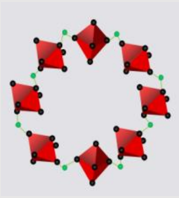
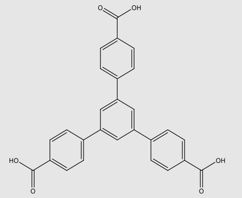
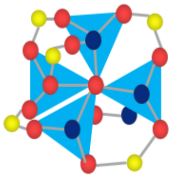
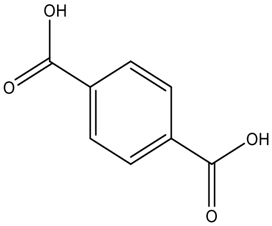
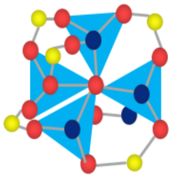
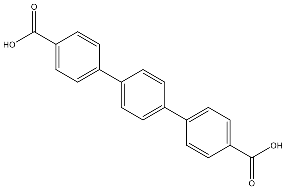
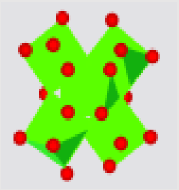
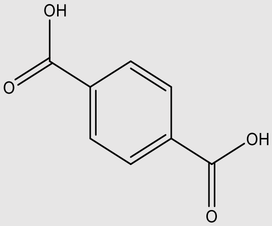
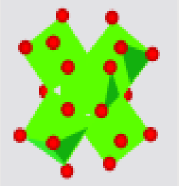
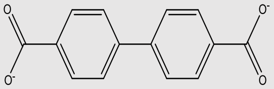
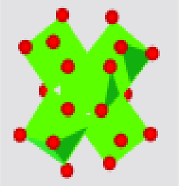
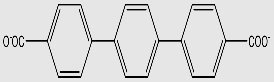
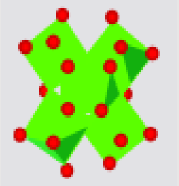
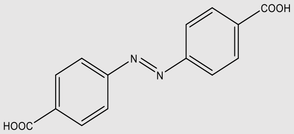
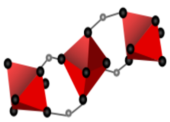
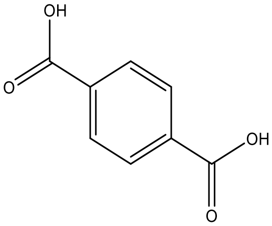
- MOFs are synthesized under mild reaction conditions[77].

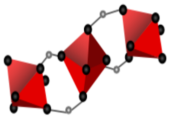
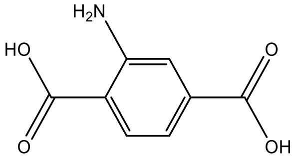
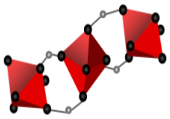
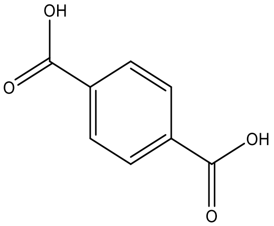
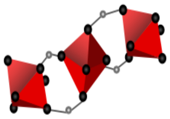
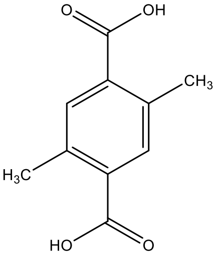
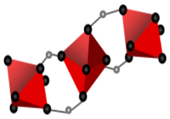
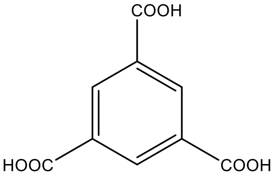
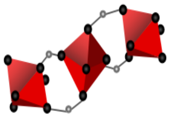
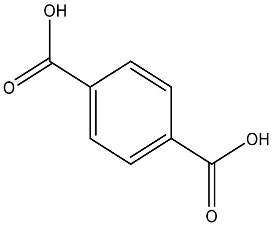
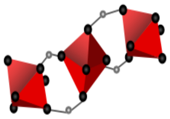
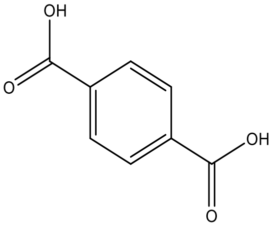
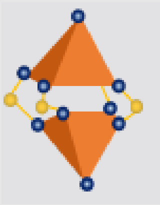
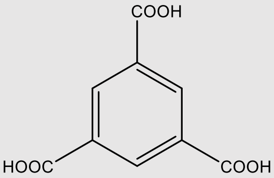
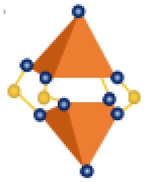
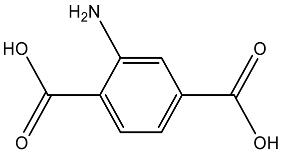
Disadvantages of this method

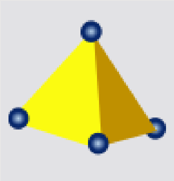
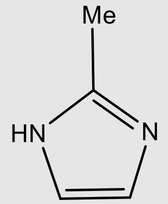
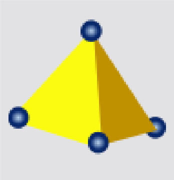
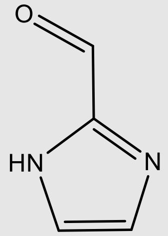
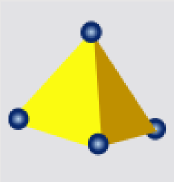
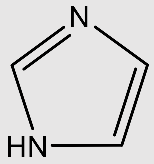
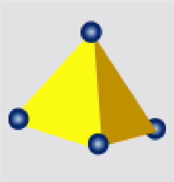
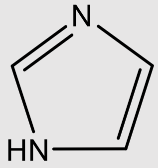
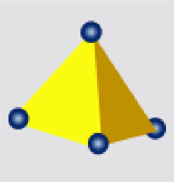
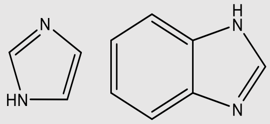
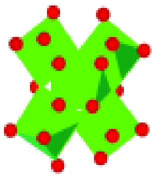
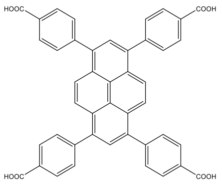
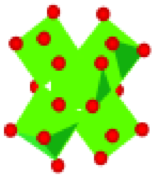
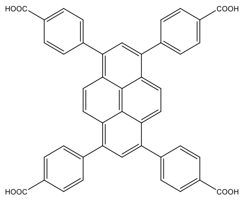
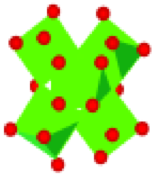
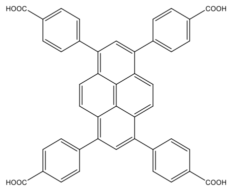
- Production of MOFs consumed too much reaction time (many weeks) [78]

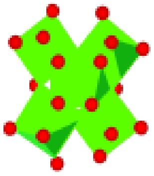
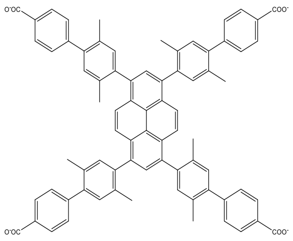
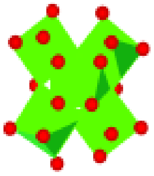
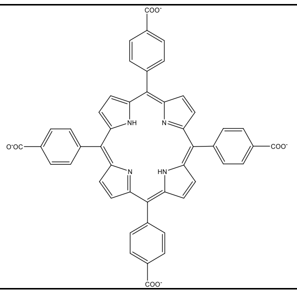
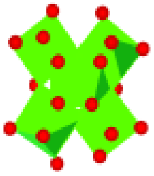
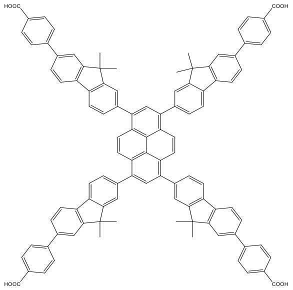
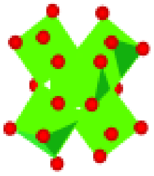
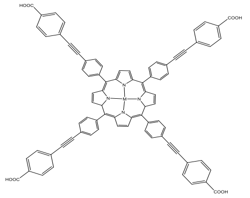
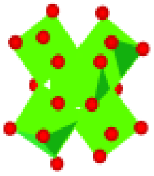
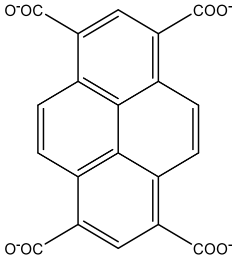
Table 1. Examples of some common MOFs names and their structure.

No.	Abbreviation	Abbreviation interpretation	Example	Metal	Inorganic Node	Organic Linker Name	Organic Linker Structure	Ref.
1	MOF	Metal-Organic Frameworks	MOF-74	Zn		(H4dhtp) 2,5-Dihydroxy-terephthalic acid		[12-15]
			MOF-101	Cu		(BDC-Br) 2-bromo-1,4-benzene-dicarboxylic acid		[16,17]
			MOF-177	Zn		(BTB) 4,4′,4″-benzene-1,3,5-triyl-tribenzoate		[18,19]
			MOF-235	Fe		(BDC) 1,4-benzene-dicarboxylic acid		[20,21]
			MOF-253	Al		(BPYDC) 2,2 -Bipyridine-5,5 -dicarboxylic acid		[22,23]

			MOF-520	Al		(BTB) 4,4′,4″-benzene-1,3,5-triyl-tribenzoate		[24]
2	IRMOF	Iso Reticular Metal-Organic Frameworks	IRMOF-1 (MOF-5)	Zn		(BDC) 1,4-benzenedicarboxylic acid		[25-27]
			IRMOF-16	Zn		(TPDC) p-Terphenyl-4,4″-dicarboxylic acid		[28,29]
3	UiO	Universitetet i Oslo	UiO-66	Zr		(BDC) 1,4-benzene-dicarboxylic acid		[30-32]
			UiO-67	Zr		(BPDC) biphenyl-4,4'-dicarboxylate		[30-33]
			UiO-68	Zr		(TPDC) 1':4',1-terphenyl-3,3'-dicarboxylate		[34-36]
			UiO-abdc	Zr		(abdc) 4,4′-azobenzene dicarboxylic acid		[37,38]
4	MIL	Materials of Institute Lavoisier	MIL-53	Al		(BDC) 1,4-benzenedicarboxylic acid		[39-41]

			MIL-53(Al)-NH$_2$	Al		(BDC-NH$_2$) 2-amino-1,4-benzenedicarboxylic acid		[42,43]
			MIL-88B-Fe	Fe		(BDC) 1,4-benzenedicarboxylic acid		[44]
			MIL-88B-4CH$_3$	Fe		(BDC-Me$_2$) 2,5 dimethyl-1,4-benzenedicarboxylic acid		[45]
			MIL-100-Fe	Fe		(BTC) benzene-1,3,5-tricarboxylate		[46,47]
			MIL-101	Cr		(BDC) 1,4-benzenedicarboxylic acid		[48]
			MIL-140	Ce		(BDC) 1,4-benzenedicarboxylic acid		[30,49]
5	HKUST	Hong Kong University of Science and Technology	HKUST-1 (MOF-199)	Cu		(BTC) benzene-1,3,5-tricarboxylate		[50,51]
6	LIC	Leiden Institute of Chemistry	LIC-1	Gd		(BDC-NH$_2$) 2-amino-1,4-benzenedicarboxylic acid		[52]

7	ZIF	Zeolite Imidazolate Framework	ZIF-8	Zn		2-methyl imidazole		[53-55]
			ZIF-90	Zn		Imidazole-2-carbox-aldehyde		[56]
			ZIF-3	Zn		Imidazole		[57]
			ZIF-4	Zn		Imidazole		[58-60]
			ZIF-62	Zn		Imidazole		[61,62]
8	Nu	Northwestern University	NU-901	Bi		(TBAPY) 1,3,6,8-tetrakis(p-benzoato)-pyrene		[63]
			NU-1000	Zr		(TBAPY) 1,3,6,8-tetrakis(p-benzoato)-pyrene		[64,65]
			NU-1100	Zr		(TBAPY) 1,3,6,8-tetrakis(p-benzoato)-pyrene		[66]

			NU-1101	Zr		(Py-XP) 4' ,4''',4''''',4'''''''-(Pyrene-1,3,6,8-tetrayl)tetrakis(2' ,5' -dimethyl-[1,1' -biphenyl]-4-carboxylic acid)		[67,68]
			NU-1102	Zr		(TCPP) tetrakis (4-carboxyphenyl) porphyrin		[69]
			NU-1105	Zr		(Py-FP) 7,7' ,7'',7'''-(Pyrene-1,3,6,8-tetrayl)tetrakis(9,9-dimethyl-9H-fluorene-2-carboxylic acid)		[70]
			NU-1104	Zr		(Por-PTP)		[70]
			NU-1106	Zr		(PTCA) Pyrene-1,3,6,8-tetracarboxylic acid		[10]

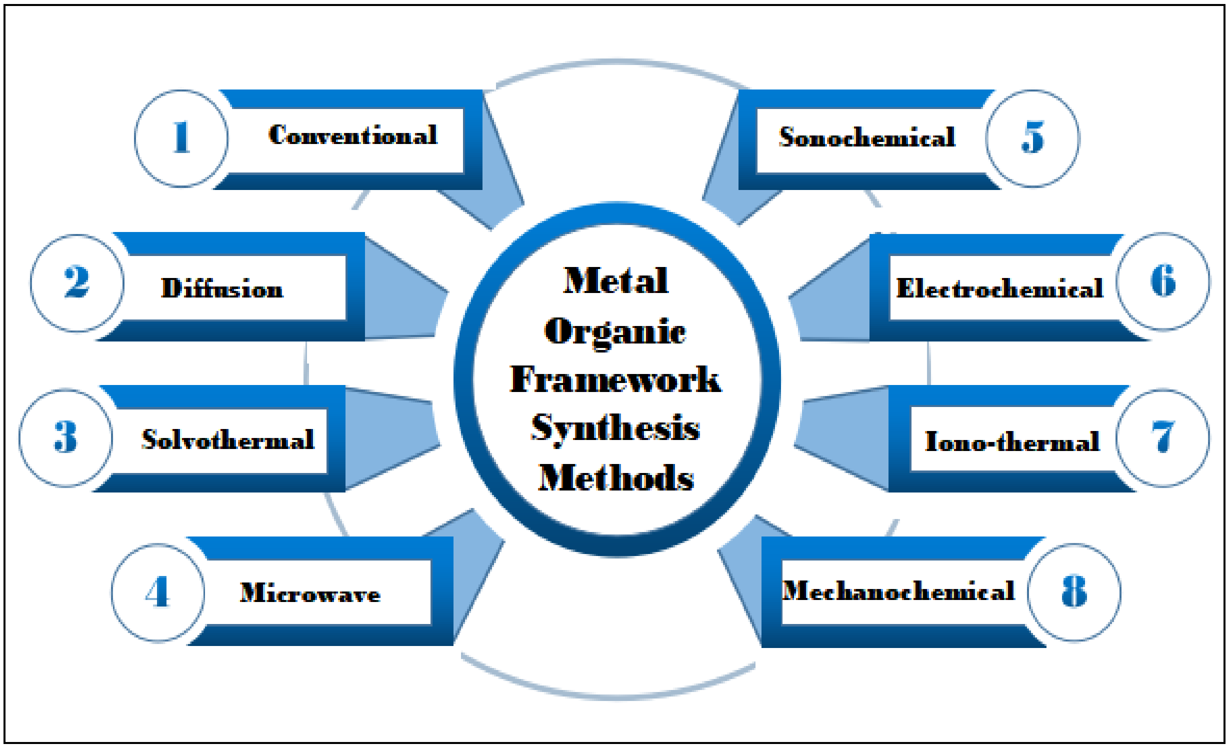


Figure 1. Different approaches of MOF synthesis, (1) Conventional solution method, (2) Diffusion method, (3) Solvothermal method, (4) Microwave method, (5) Sono-chemical synthesis method, (6) Electrochemical synthesis method, (7) Iono-thermal process method, (8) Mechanochemical method[71].

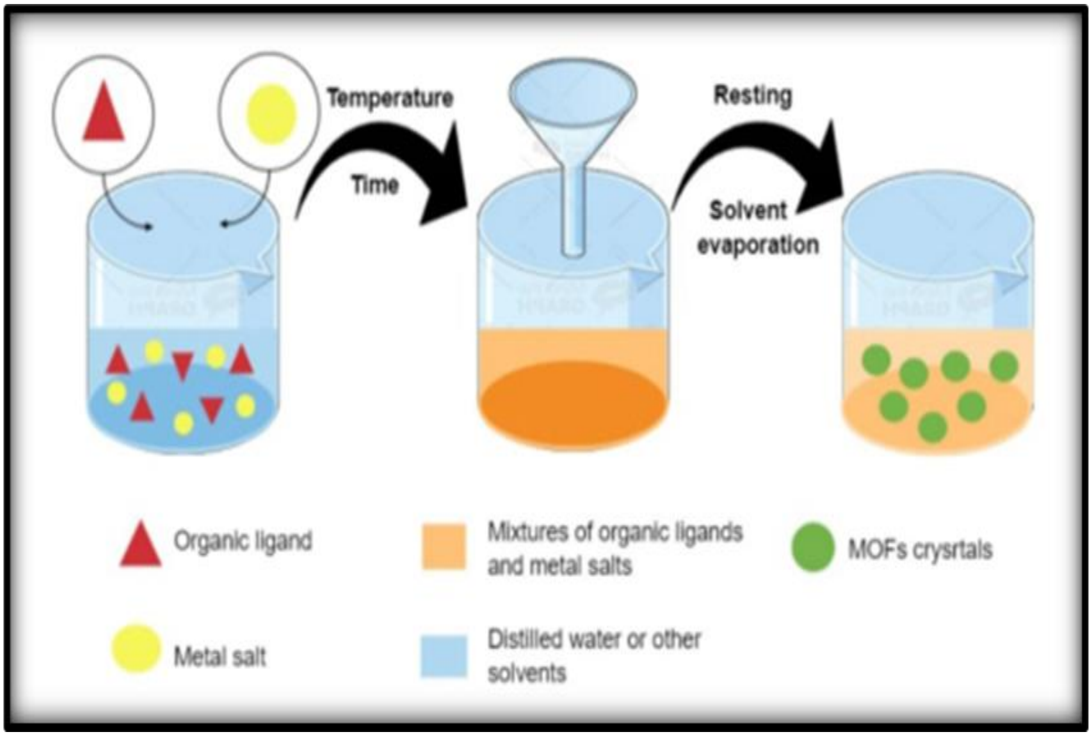


Figure 2. Diagrammatic representation of the conventional solution method to synthesize metal organic frameworks (MOFs)[74].

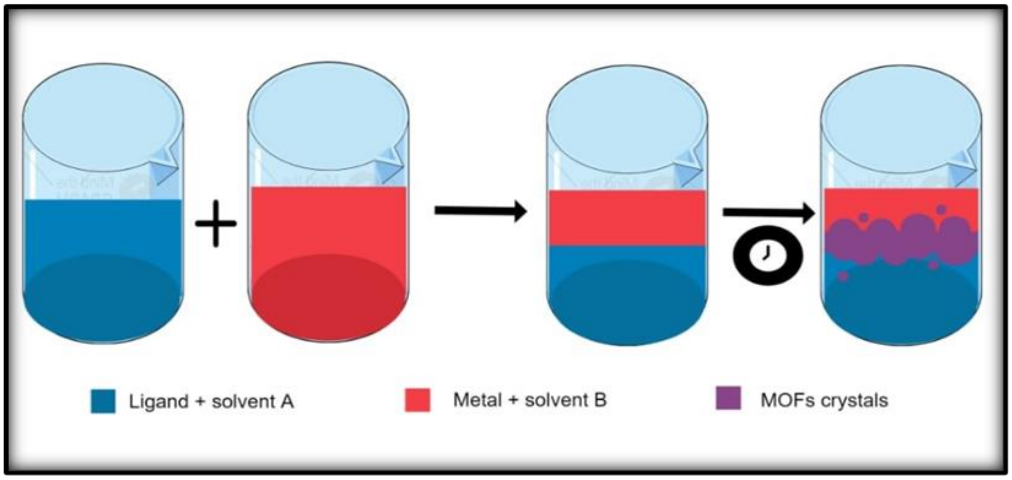


Figure 3. Schematic diagram for MOF synthesis by the liquid phase diffusion method[74].

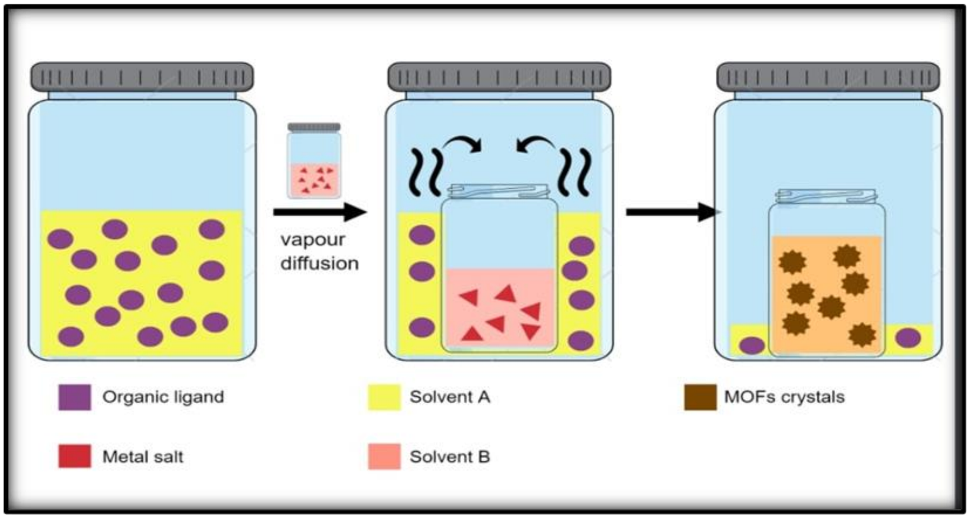


Figure 4. Schematic diagram for MOF synthesis by the gas phase diffusion method[74].

Solvothermal synthesis method

When the used solvent is water, the solvothermal method is also referred to as the hydrothermal synthesis method. This approach involves the continuous mixing of organic linkers, metal ions, and reaction solvent in a definite ratio takes place in a polytetrafluoroethylene liner (autoclave) under autogenous pressure for a specified period of time at a specific temperature that ranges from 80 to 260°C. After that, the mixture is placed in a high-temperature reactor where the reaction can initiate at the boiling temperature of the solvent or above. After the reaction takes place, the product is cooled at room temperature (Figure 5). It should be washed repeatedly by a deionized aqueous solution such as water to remove the contaminants from the product. After cleaning the product with alcohol or another solution, vacuum drying is employed to produce pure MOFs. By changing the reaction temperature, crystal growth and nucleation rate can be managed. MOF-5, MOF-74, MOF-177, UiO-67 and ZIP-8are some examples of solvothermal MOFs[76,79].

Advantages of this method

- It is simple to obtain single large crystals.
- Produce higher yields with better crystallinity of the product.
- Reproducible method, where the reaction conditions can be controlled over a long period of time.

Disadvantages of this method

- Products must self-assemble out of soluble precursors.
- If reaction times are prolonged, several unfavorable effects including crystallization loss and pore weakening occur.
- Regent dissolving requires high temperature and/or vigorous chemicals (acids, organic solvents, bases).
- Using potentially hazardous and corrosive chemicals (metal salts) and organic liquids, in addition to

generating waste byproducts such as strong acids or salts e.g., HCl, HNO_3.

- Heat-sensitive chemicals and solvents are not suitable.
- Extended reaction duration (solvothermal and hydrothermal procedures can sometimes last for several weeks or months)[80,81].

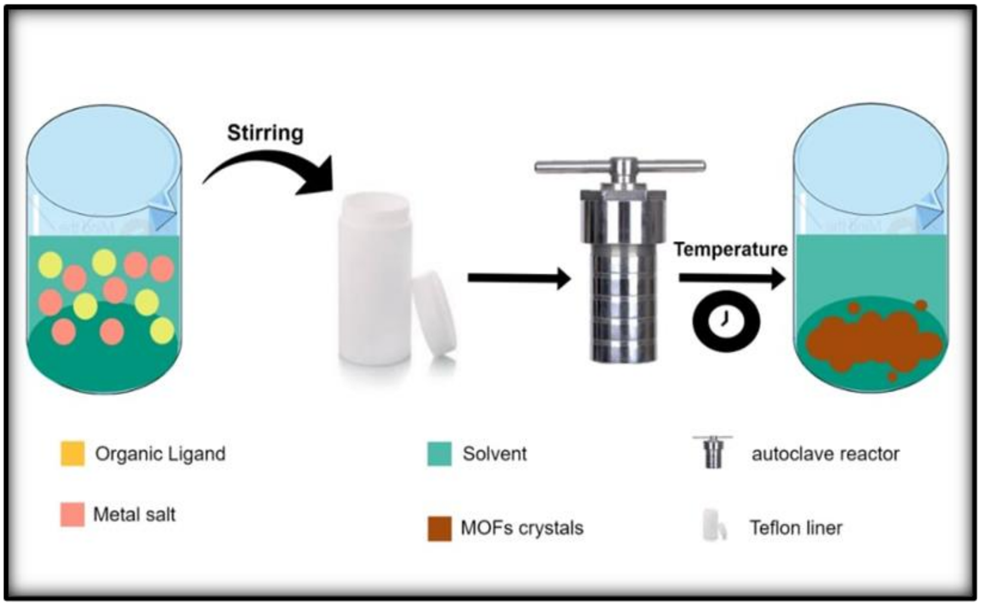


Figure 5. Schematic diagram for MOF synthesis by solvothermal method[74].

Microwave synthesis

The microwave synthesis technique is regarded as one of the best MOF synthesis procedures due to its many advantages. This method involves heating the solution for at least an hour with microwave radiation (with frequencies between 300 and 300 000 MHz) to form MOFs nanocrystals. The electromagnetic radiation from the microwave induces the solution molecules to arrange in an oscillating manner. As a result, the solution's temperature increases significantly and activates the interaction between the reactants (Figure 6). To catalyze the reaction, the starting materials are put into a mill with a stainless-steel ball. The mill is stirred at the same time as microwave radiation is introduced. After 30 to 60 minutes, the solution is filtered. Later, ethanol is added to the solid residue and stirred by magnetic stirrer. Suction is then used to filter and dry precipitates. Some MOFs that were synthesized by using the microwave method are Fe-MIL-53, ZIF-8, Fe-MIL-101-NH2, MIL-100 and UiO-66[83-85].

Advantages of this method

- The microwave method provides several benefits, including rapid heating, excellent crystallinity, high purity, high yield, impressive phase selectivity, and controllable particle shape and size. Additionally, neither a temperature gradient nor a hysteresis effect exists.
- Using the microwave approach the resulting crystal was approximately 4 times smaller in size (100 nm) than the crystals created using the conventional heating approach (about 400 nm) because of the ability of microwave heating to accelerate nucleation, which reduces the crystals size and increasing the number of nuclei.
- This method is also characterized by rapid reaction rate where the synthetic duration can be significantly reduced from 24 hours to 30 minutes. Additionally, this process is cost-effective because of the use of energy-efficient synthetic devices that only generate minimal amounts of chemical waste[86].

Disadvantages of this method

- Temperature and reaction time are two further restrictions on reproducibility because various instruments cannot provide the same conditions.
- Volatile solvents are usually unsuitable to be used in this method[76,87].

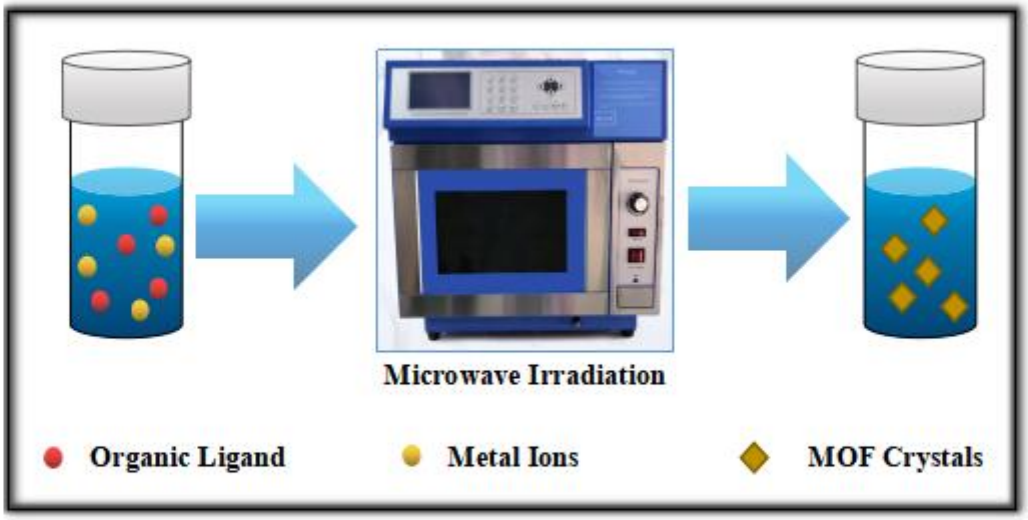


Figure 6. Schematic Diagram for MOFs synthesis by microwave method[82].

Sonochemical synthesis

Sonochemical synthesis is the term used to describe a method when high-energy ultrasound is employed as a heat source to initiate the reaction (a frequency between 20 kHz to 10 MHz). Ultrasonic sonicator uses ultrasonic cavitation (vapor formation and air release) to disperse agglomerated particles. The "cavitation" effect of ultrasonic waves forms high temperature, high pressure, and strong shock wave, which propagates in the form of standing waves. Micro jets are produced together with cavitation when a solid surface is nearby which leads to the destruction of the agglomerate structure in the system, the enlargement of the particle gap and the formation of separate particles (Figure 7). Additionally, ultrasonication can improve the solubility of the starting chemicals. The reaction is carried out by adding the starting materials solution to a horn-shaped Pyrex reactor that has an adjustable power output and a sonicator bar.Sonication causes the production and breakdown of bubbles (acoustic cavitation) which produce extremely elevated pressures (1000 bar) and temperatures (5000 K), which led to quick rates of heating and cooling (>1010 K/s) and this what generates the fine crystals. The first MOFs produced using this technique are Zn (Zinc) carboxylates $Zn_3(BTC)_2$ in 2008. Other MOFs produced using this technique are HUSK-1, Mg-MOF-74, IRMOF-9, and $Zn_4O(C_{14}H_8O_4)$: 4,4′-Biphenyl-dicarboxylic acid, and MOF-5 $[Zn_4O(BDC)_3]$[89-91].

Advantages of this method

- This approach stands out for being eco-friendly, energy-efficient, nanocrystalline particles synthesis, simple to operate and applicable at room temperature.
- Homogeneous and rapid nucleation decreases the time of crystallization and produces fine particle size, which is a significant feature for using this technique.
- High yield of product.

Disadvantages of this method

- One of the disadvantages of this method is that even though the synthesis is conducted at room temperature in some cases, it is not always possible to control the temperature near the reactive mixture area [92,93].

Electrochemical synthesis

This synthesis process uses cathode plates, a battery cell, and an anode. The electrochemical media contains the starting materials (Figure 8). In this method, the metal ions produced not from using metal salt but comes from the ongoing production of a metal ion by anodic dissolution. Utilizing protic solvents to prevent the deposition of metal close to the cathode. However, hydrogen gas is emitted when using this procedure. When synthesizing MOFs, it is essential to take the electrolyte, temperature, voltage-current density, synthesis yield, and textural features into account. In 2005, (HKUST-1) was the first MOF to be created using this technique. Some of other MOFs produced by electrochemical synthesis are HKUST-13, Al-MIL-53-NH_2, ZIF-8, and Al-MIL-100. Unlike other synthesis procedures, electrochemical method can be used to produce higher solid content of MOFs which makes it commercially viable. In addition, this approach has certain advantages over solvothermal synthesis, such as avoiding anions like metal nitrates salts, milder reaction temperatures, and incredibly quick synthesis[95].

Another advantage is that the generation of metal ions close to the support surface reduces the undesirable crystal deposition throughout the synthesis process. Additionally, MOF can generate more fine crystals compared to solvothermal techniques by adjusting the voltage or applying specific pulses due to its negative coefficient of thermal expansion. This method can produce both powders and films MOFs. On the other hand, MOF formation by anodic oxidation is only possible if the full metallic pattern is kept in constant electrical contact with the power source[94,96].

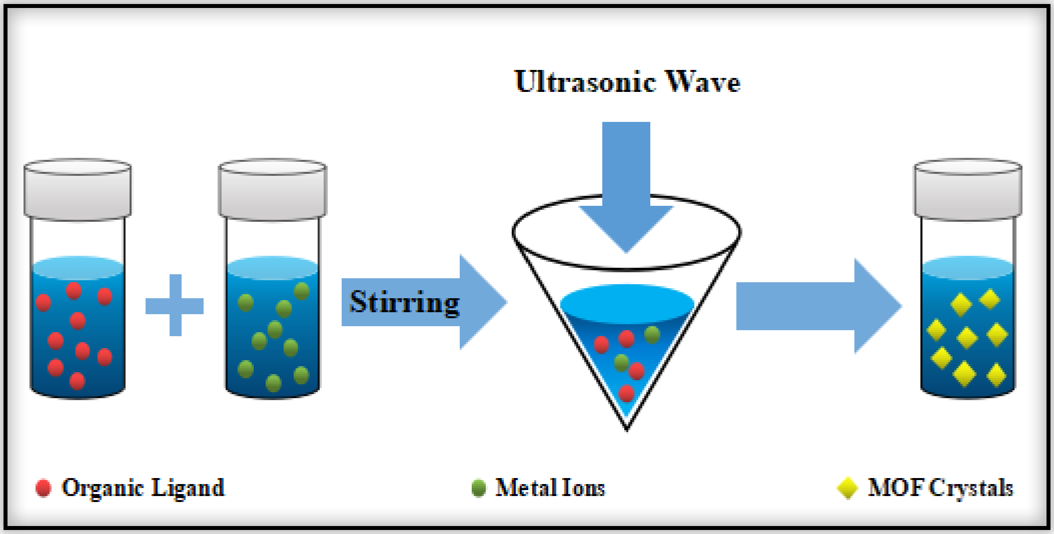


Figure 7. Schematic diagram for MOFs synthesis by sono-chemical method[88].

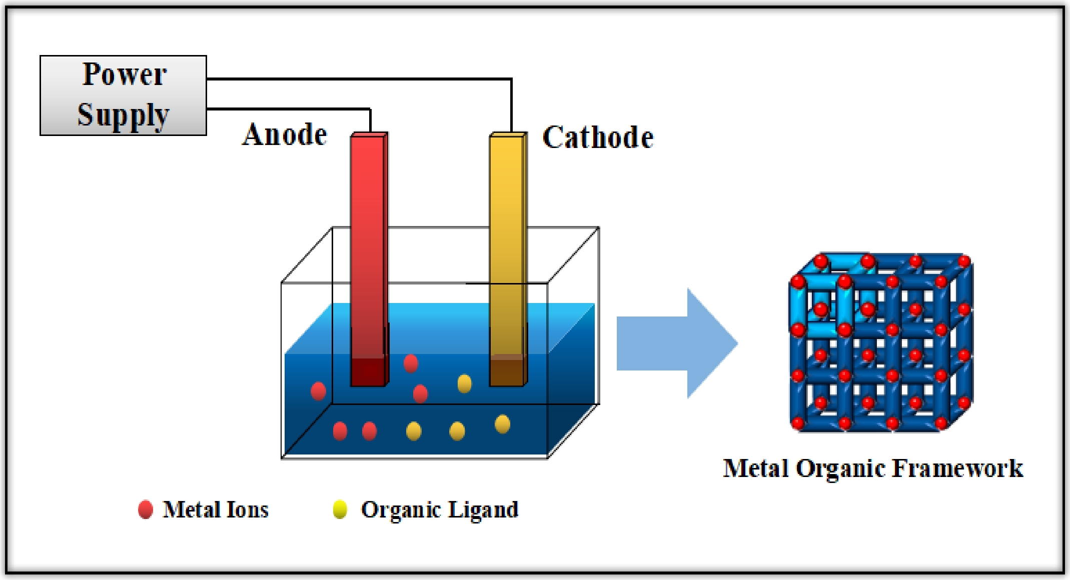


Figure 8. Schematic diagram for MOFs synthesis by electrochemical method[94].

Iono-thermal process

Instead of using an organic solvent, this method uses an ionic liquid medium. In addition to producing a pure ionic environment, using an ionic liquid also serves as an excellent template or charge balance group. Ionic liquid is a form of salt that contains both cations and anions, and it has a liquid phase that is at or almost at room temperature. It is characterized by having low melting point (less than 100ºC),a wide variety of liquids, recyclability, negligible vapor pressure, superior solvating, and excellent thermal stability[97].

Ionic liquids such as [Bmim] [BF_4] have a variety of uses; it can be utilized as a solvent, catalyst promoter, fluoride supply, and structure-directing agent. Using choline chloride/dimethyl as the solvent, HUSK-1 was produced using this method (Anumah et al., 2019). This technique also enabled the production of Cd_3F-based MOFs by using BF_4^- anions to fill in channels and/or holes during in situ ion thermal oxidation and hydrolysis[98].

Advantages of this method

- By altering the ionic liquid's composition, it is possible to change the physicochemical characteristics of MOFs.
- By modifying the ionic liquid's size, polarity, and hydrophilicity, it is possible to further increase MOF yields and controllability.
- It is a green synthesis technique.
- Excellent thermal stability.

- Synthesis is achieved without a reflux condenser, where moderate to higher temperature synthesis can be performed[71].

Disadvantages of this method

- If ionic liquid has even a small quantity of contaminant or residue, the thermal stability is reduced[99].

Mechanochemical method

The mechanochemical method (Grinding method) uses mechanical agitation or collision between substances to synthesize MOFs. Mechanical force can achieve chemical reactions by mechanical breakage of bonds. Mechanical MOF synthesis has sparked interest for a variety of reasons. One of the important points is related to environmental issues. This is especially useful when we can avoid using organic solvents or only use a small amount of them. Also, reactions can be carried out at ambient temperatures. In just 10 to 16 minutes of reaction time, MOFs can be synthesized with quantifiable yields (Figure 9). Manganese-based MOF, or Mn-MOF produced by liquid diffusion method took almost 24 h to complete but the mechanochemical technique only requires 10 minutes.

Water is only formed as a byproduct when metal oxides are used in place of metal salts. reducing energy use and promoting green production. Additionally, while employing the mechanochemical approach, Mn_2O_3 had a greater impact on the catalytic degradation of ammonium perchlorate, which was able to reduce the temperature of pyrolysisby 158 °C, hence lowering the energy need. The first time this approach is used was in 2006 to synthesize $Cu(INA)_2 . xH_2O . yAcOH$. Also this method is used to produce HKUST-1[101,102].

Advantages of this method

- It is highly regarded for using little energy and has recently emerged as a hotspot for research for being a green synthesis process. Liquid-assisted grinding (LAG), a method that requires a small amount of solvents, is likewise straightforward, quick, and very successful.
- Good yield of product with higher crystallinity.
- Additionally, The mechanochemical approach was faster than the liquid phase diffusion methodology[103].

Disadvantages of this method

- limited to low melting point and hydrated metal salts[104].

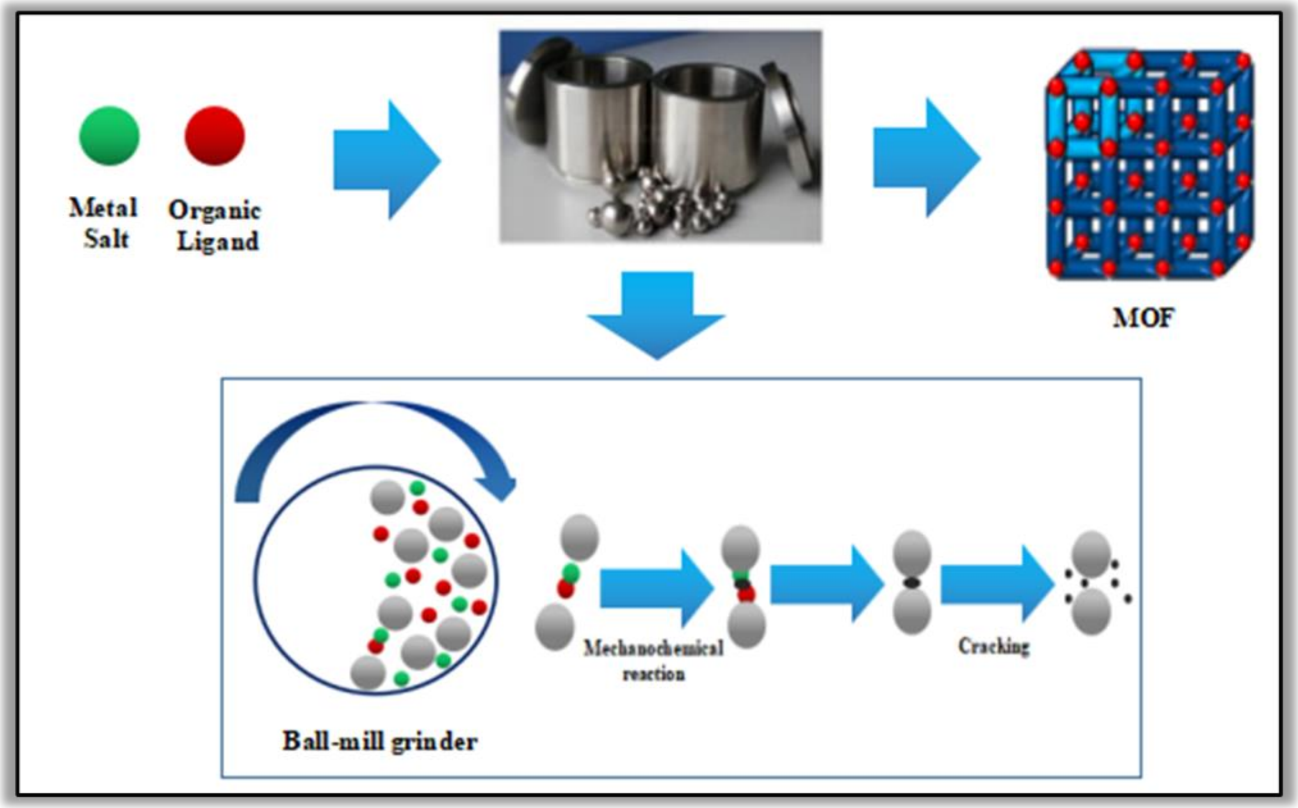


Figure 9. Schematic diagram for MOFs synthesis by mechanochemical method[100].

2.Types of MOFs and detection mechanism

2.1 Types of MOFs

2.1.1 Fluorescent MOFs:

Fluorescence can come from a variety of items, including metal ions, organic linkers, and guests. Fluorescent metal organic framework-based materials can be categorized into four classes depending on the different sources of fluorescence: Ln-MOFs, Transition metal-based MOFs, fluorescent ligand MOFs, and fluorescent MOF complexes.

A) Ln-MOFs

They are made up of lanthanide ions and organic linkers. Ln-MOFs exhibit antenna effects through energy transfer from the linkers to the lanthanide ions and notable fluorescence intensity increases. As a result, by varying the efficiency of energy transfer and antenna effect from linkers to lanthanide ions through host-guest interactions, sensing of chemical species is made possible. Lanthanide MOFs are of great interest because of their significant Stokes shifts, good quantum yields, and long luminescence lifetimes[105].

Fluorescence often results from the ligands' absorption of energy into more excited states, followed by their emission of light into the ground state. However, in the case of Ln-MOFs, inter system crossing allows the energy absorbed by the ligand to be transferred from the singlet excited state (S_1) to the triplet state (T_1). The energy is then transferred to Ln^{3+} higher excited state, $S_1 > T_1 > Ln^{3+}$, and then released into the ground state of Ln^{3+}. The lanthanides are garnering increased attention among other metal ions because of their unique behavior. Recent researches have shown that using mixed metal Ln-MOFs which feature two or more lanthanide metal ions as fluorescence sources to build ratiometric fluorescence sensors is a promising method. Mixed metal Ln-MOFs have excellent sensitivity, and many pronounced colour changes seen with the naked eye compared to single metal Ln-MOFs[106].

B) Transition metal-based MOFs

Issues like high synthesis costs, high toxicity, secondary contamination, etc. are limitations for Ln-MOFs. Transition metal ions, on the other hand, are simpler to obtain less expensive, and less dangerous. They are suitable for small molecule and ion sensing. They have so attracted the interest of scientists, and their applications are being thoroughly investigated[107].

C) Fluorescent ligand MOFs

Fluorescent ligand-based MOFs based on aromatic or -conjugated linkers to reduce the gap between the HOMO–LUMO, limit the non-radiative decay and enhance the radioactive decay. The fluorescent organic linker (called fluorophore or antenna) should be sensitive and selective towards target molecules (called substrate unit).The fluorescence emission is caused by the interaction of the analyte with the -electron-rich fluorescent aromatic ligand[108].

D) Fluorescent MOF complexes

To create photo-functionalized MOF-based materials, a variety of fluorescent guests such as organic dyes, quantum dots (QDs), carbon dots (CDs), and metal nanoclusters can be encapsulated within, adsorbed on, or linked to non-emissive MOFs which can then be used to make fluorescent MOF-based composites. Zeolite imidazole frameworks (ZIFs) don't exhibit fluorescence, but the fluorescence properties can be introduced by enclosing various fluorescent nanomaterials or molecules in their pores[109].

E) Multiple fluorescence sources

Research has revealed that materials with only one fluorescence frequently perform less well in applications and have a smaller application scope than fluorescence sensing techniques that integrate two or more fluorescent sources. Many emissive mechanisms, such as metal-to-ligand charge transfer (MLCT), ligand-to-metal charge transfer (LMCT) and guest-induced luminescence are viable thanks to the multicomponent design of MOFs. Additionally, several non-photo functional MOF-based materials can be employed for fluorescence detection by catalyzing the fluorescence reactions or acting as a quencher to reduce fluorescence reactions[110].

2.1.2 Colorimetric MOFs

MOFs can be utilized as colorimetric sensors as well[111]. Different ways of combining chromophores with MOFs can result in MOF-based colorimetric sensors. A chromophore is a molecule that can absorb specific visible light wavelengths, which causes variations in electron density following the excitation process. Organic chromophore compounds have distinctive properties, such as high charge carrier mobility, light absorption, thermal stability, and availability for the coordination with metal ions. One of the most popular detection methods, colorimetric sensing, has been shown to be capable of detecting multiple-colored targets via UV-Vis spectroscopy. Due to their simple design structures, MOFs have attracted a lot of interest as a interesting class of materials for colorimetric sensing. There are two MOF-based colorimetric sensing techniques. The first technique is done by changing the color of the MOF-based materials itself, The second technique is established by using MOF-based complexes to catalyze colorimetric reactions[112].

Certain factors, such as the aggregation or decomposition of nanoparticles, catalysis of nanozymes, and ligand-receptor interactions, are related to colorimetric sensing mechanisms towards metallic cations, anions, small molecules, drugs, biomolecules, bacteria, and other toxic pollutants in water systems[113]. Some of the drawbacks of MOF colorimetric sensing is the low selectivity of the sensor also the MOFs employed in colorimetric sensors are unstable, which is a significant restriction. These MOFs are frequently unstable in water or at high pH levels[114].

2.2 Detection Mechanism

There are different sensing mechanisms as illustrated in Figure 10.

A) Collapse of a metal organic framework

In the sensors in which the organic ligand is responsible for the luminescence response of the sensor towards the target ions, a certain analyte may cause a collapse of the MOF resulting in releasing of the ligands which leads to a change in the luminescence signal of the sensor [115].

B) Cation exchange process

When the target metal ion exchanges with the cations in the host MOF's metallic nodes, a luminescence signal is produced [116].

C) Host-guest interactions

Analyte may interact with the functional groups or coordinating Lewis acidic sites on the MOF, changing its optical characteristics [117].

D) Energy transfer mechanism

Occurs when analytes absorb either the energy emitted by the LMOF or competes with the MOF to absorb the excitation energy. both cases result in a quenching effect. Förster resonance energy transfer (FRET) is one of the energy transfer mechanisms that is predominant in many MOF based sensors. When the analyte and the MOF's fluorophore are located within a few nanometers of each other the analyte's absorption band and the fluorophore's emission band substantially overlap, making it easier for the analyte to absorb fluorescence resonance energy. Depending on the system's energy transfer direction, fluorescence may be enhanced or quenched. In addition to spectral overlaps, non-linear S-V graphs are a typical indicator of the presence of FRET [118].

E) Electron transfer processes

Electron transfer processes include metal to ligand charge transfer (MLCT), ligand to metal charge transfer (LMCT), ligand to ligand charge transfer (LLCT) and photoinduced electron transfer (PET). Many MOF sensing responses are based on PET mechanism. PET occurs when there is a donor atom and acceptor atom located closely to each other which leads to an orbital overlap. The redox reaction is responsible for quenching or enhancing the luminescence response in the PET mechanism in which an electron moves from the donor to acceptor. When the lowest unoccupied molecular orbital LUMO of the excited donor atom is more energetic than the LUMO of the acceptor atom, electron transfer takes place from the LUMO of the excited donor atom to the LUMO of the acceptor atom. On the other hand, electron transfer occurs from the HOMO of the donor to the HOMO of the excited acceptor when the highest-occupied molecular orbital (HOMO) of the donor is doubly occupied and more energetic than the singly filled HOMO of the excited acceptor. Both types of electron transfers lead to a singly occupied HOMO in the donor and a completely occupied HOMO with a single occupied LUMO in the acceptor (Figure 11). Analytes can hinder or facilitate a PET, which can result in fluorescence enhancement or quenching [119] .

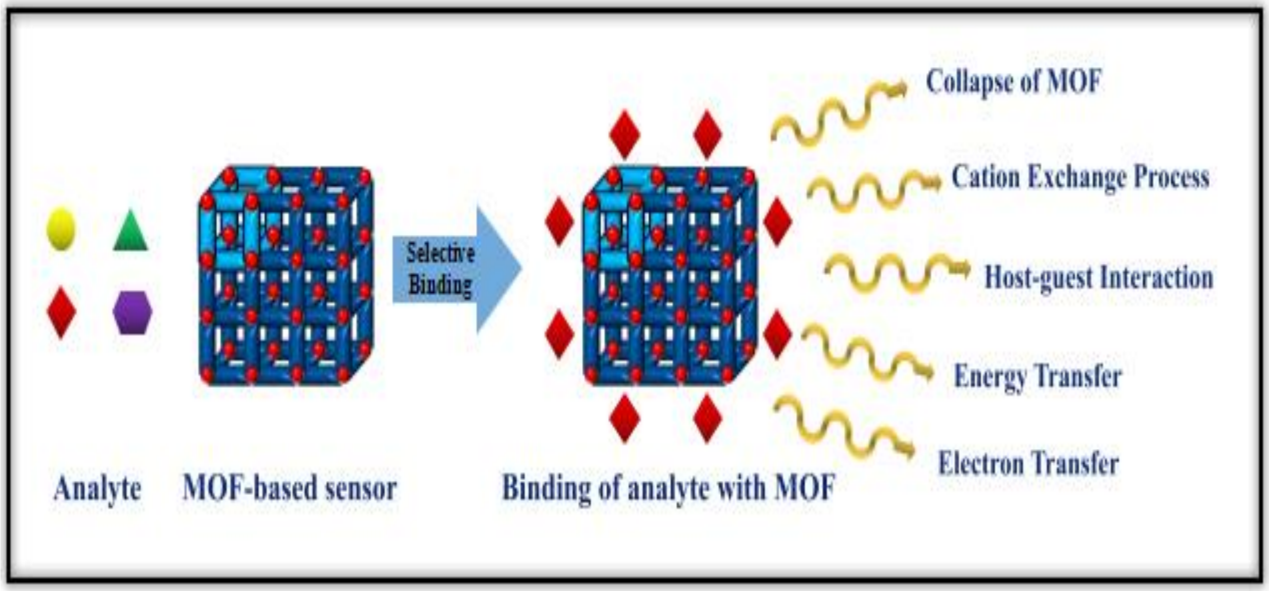


Figure 10. Metal organic framework sensing mechanism[8].

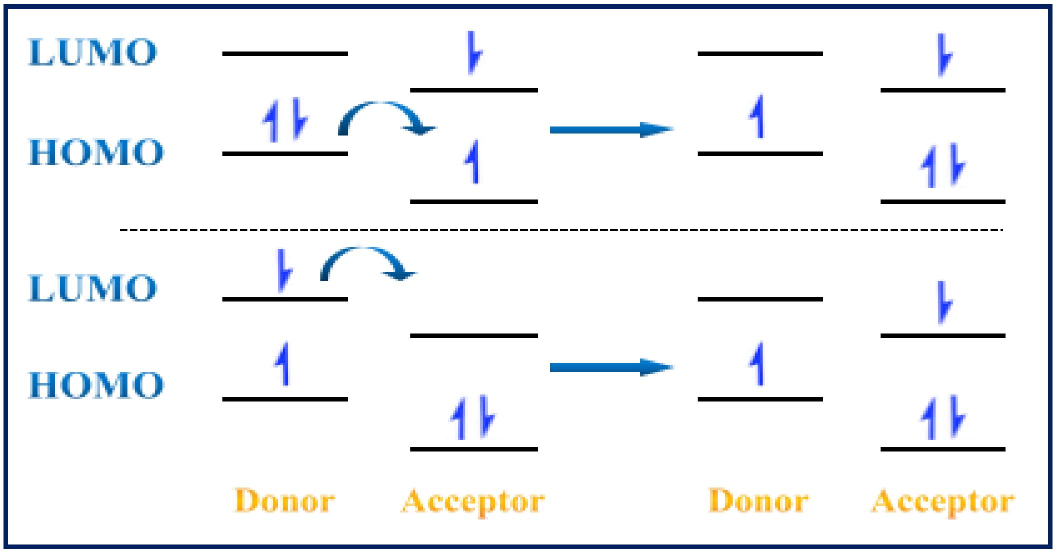


Figure 11. Representation of PET transpiring from donor to acceptor [8]

Inductively Coupled Plasma (ICP) analysis, powder XRD, FT-IR, UV-visible spectroscopy, and other methods have all been used to obtain insight into the mechanism of optical sensing by MOFs. While IR spectra are useful in understanding the nature of interactions, ICP analysis offers suggestions about the incorporation of the analytes into frameworks. UV-Vis and emission spectra analysis explain the presence of energy transfer[8].

3. MOFs for Detecting Hazardous Materials

3.1 Detection of metal ions

(Wang et al., 2022) proposed a novel Zn-MOF, namely, $[Zn_2(m\text{-}2mbix)(HEA)_2 \cdot 2H_2O]n$, The MOF was successfully produced by Solvothermal approach. The MOF is highly stable in water, and it can act as a turn-off luminescent sensor for the highly selective detection of trace quantities of Fe^{3+}, CrO_4^{2-}, and $Cr_2O_7^{2-}$ ions in aqueous solutions via luminescence quenching. It was assumed that energy transfer played a role in the quenching mechanism. The competition between the ions and the MOF framework for the emission energy determines the probability of fluorescence resonance energy transfer. The detection limits of $Cr_2O_7^{2-}$, CrO_4^{2-}, and Fe^{3+} ions are 1.13×10^{-7} M, 1.39×10^{-7} M and 1.01×10^{-7} M, respectively. Through experimentation, it was determined whether certain anions impurities, such as Cl^-, F^-, Br^-, SO_4^{2-}, PO_4^{3-} and SCN^- (the most prevalent anions in water), affected the sensing of $Cr_2O_7^{2-}$ and CrO_4^{2-} anions. These impurities did not appear to have any significant effects on the adsorption of $Cr_2O_7^{2-}$ and CrO_4^{2-} ions. Also, the impact of various metal ions on the sensing of Fe^{3+} was examined. Compared to other common metal ions, a significant luminescence change exhibited by Fe^{3+} ions could be seen. indicating good anti-interference performance of the MOF toward the detection of $Cr_2O_7^{2-}$, CrO_4^{2-}, and Fe^{3+}[120].

(Hou et al., 2022) developed a new dual-mode ratio metric sensor for the highly sensitive detection of copper ions. The fluorescent and colorimetric sensor is based on Zr MOF (Zr-Tetraphenylporphyrin Tetra sulfonic Acid Hydrate Metal-Organic Frameworks). Also, a ratiometric fluorescent probe employing fluorescein isothiocyanate (FITC) was developed. The fluorescence emission from ZTMs is noticeably quenched when exposed to varied concentrations of Cu^{2+}, but that from FITC is enhanced. The solution's fluorescence changes from red to green as a result. The ZTMs additionally exhibit a strong ratiometric colorimetric response for Cu^{2+}. The sensor has a linear range of 0.1 μM to 50 μM and a detection limit of 5.61 nM, the ZTMs FITC fluorescent probe demonstrates a broad range of detection. Additionally, a colorimetric ZTM-based sensor shows a linearity from 0.1 to 20 μM with a limit of detection of 4.96 nM. The sensor is used to monitor Cu^{2+} in water samples, demonstrating its utility in biological and environmental systems[121].

A cobalt-based metal-organic framework (MOF), $[Co_2(L1)(obc)_2]$.DMF, was proposed by (Kirandeep et al., 2021). The MOF can act as a selective sensor for detecting hazardous metal cation Zr^{4+} ions in water. By adding the metal ions, the sensor's fluorescence is turned off. The sensor showed a quick response time and a limit of detection that reaches to 0.067 μM. The fluorescence experiments demonstrated that the MOF' is extremely selective and sensitive towards Zr^{4+} ions with wide range of detection from 2–45 μM. The optimal pH range for the detection of Zr^{4+} ions is between 3 and 8. The MOF's turning on fluorescence toward Zr^{4+} ions can be attributed to absorbance-caused enhancement (ACE) mechanism. To study the effect of different interferences, metal ions were added to the sensor. Most metal cations had no effect on the intensity of the fluorescence except for mercury(II) ions[122].

A dual-emission ratiometric fluorescence and colorimetric sensing system based on Zr metal-organic frameworks (Zr-MOFs) and silver nanoclusters (AgNCs) was proposed by (Li et al., 2022) for the selective and sensitive detection of mercury ions (Hg^{2+}) in Porphyra samples with quick response time of 10 min and recovery range of 94.74%–101.1%. The MOF was synthesized solvothermally. When mercury ions were added to the sensor, it displayed fluorescence quenching, which was explained by the fluorescence resonance energy transfer (FRET) process. The sensor exhibit a low detection limit of 1.8 μg L^{-1} with wide range of fluorescence and colorimetric detection ranges of 0.10 to 0.50 μg.m^{-1} and 0.01 to 0.5 μg mL^{-1}, respectively. To test the MOF's sensing, variable interference ions were used, however none of these impurities seem to have a noticeable impact on the sensing[123].

By combining blue fluorescent carbon dots with red bi-ligands Eu-MOF (BiL-Eu-MOF), (Ameen et al., 2022) successfully created a unique and highly selective fluorescent ratiometric probe for the detection and quantification of silver ions (Ag^+) in water samples. The MOF was synthesized solvothermally. When exposed to UV light, the visual sensor showed a clear change in color from blue to red along with an increase in Ag^+ concentration that was visible to the naked eye and by using RGB analysis on smart phones, the multi color visual-based ratiometry detection of Ag^+ was carried out. The sensor has a wide linear range of detection from 0 to 660 μM with a low limit of detection of 2.1 μM. The selectivity of sensor was examined by adding common ions . The interfering ions have no effect on the sensing which indicates the selectivity of the sensor to silver ions. Also, the sensor is used to detect cysteine in human serum samples as discussed in detail[124].

In order to reduce interference from the surroundings, (Yi et al., 2020) successfully created a dual-emissive ratiometric fluorescence (RF) metal-organic frameworks-based sensor for selective and sensitive detection of Pb^{2+} with recovery rate of 94.0–106.5 %. CDs/QDs@ZIF-8 has been effectively created by trapping carbon dots (CDs) and CdTe quantum dots (QDs) into the metal-organic frameworks ZIF-8 which was generated using a conventional method. The fluorescence turn off was attributed to the electron transfer mechanism between QDs and Pb^{2+}.The sensor offers a large linear concentration range from 0.04 to 60 μmol/L and detection limit of 2.35 nmol L^{-1}. Different interferences were utilized to test the sensor's selectivity, and it is clear that the interferent substances have no impact on the detection of Pb^{2+}, demonstrating the sensor's high Pb^{2+} selectivity[125].

(Zhan et al., 2019) Proposed a novel water-stable sensor-based terbium-MOF for the sensing of Al^{3+} ions. Under solvothermal conditions, a terbium metal-organic framework involving both 4-(pyridin-3-yloxy)-phthalic acid and oxalic acid has been developed. Among several inorganic cations in aqueous solution, the sensor can act as a sensor for Al^{3+} ions with good selectivity and sensitivity with low detection limits of 5.66 μM. The energy transfer mechanism from the ligands to the Tb^{3+} ion is responsible for the antenna effect, which is the cause of the fluorescence characteristic of the sensor. The sensor's ability to detect Al^{3+} ions was tested using a variety of interfering cations, and it was revealed that the sensor exhibit high selectivity towards Al^{3+} ions[126].

(Moradi et al., 2020) successfully developed PCN-224, a novel zirconium-based MOF luminescent sensor, which has a response time of one minute and is highly sensitive and selective for the detection of Cd^{2+}. The MOF was prepared under solvothermal approach. The sensor displayed fluorescence enhancement towards Cd^{2+} cation with detection limit of 0.002 μM. A variety of interfering cations were used to study the sensor's sensing capabilities. The interfering ions were shown to have no impact on the MOF sensing[127].

Using a direct solvothermal method and modification with naphthylamine via the Schiff-base reaction, (Dong et al,. 2022) developed a novel fluorescent Zr-MOF with a quenching effect and high selectivity for the detection of Fe^{3+} ions. The sensor has a detection limit of 0.54 μM[128].

A dual-emission fluorescent sensor based Eu^{3+} MOF with a high-water stability used for selective detecting and quantifying ferric ions and Al^{3+} in wastewater as proposed by (Xia et al., 2022). The obtained MOF has dual emission at 450 and 614 nm and is extremely stable in pH range from 4 to 11 in aqueous environments. The Sensor was synthesized via conventional method. Various metal ions were added to the sensor to investigate its selectivity, and it was discovered that they had no significant effect on the emission. However, the fluorescence was significantly reduced when Fe^{3+} was added. Whereas when Al^{3+} was added, the fluorescence color shifted from blue color to purple. These findings show that the sensor has a strong selectivity towards ferric ions and Al^{3+} in aqueous media. Al^{3+} LOD was detected to be 0.36 μM, while Fe^{3+} LOD was detected to be 0.12 μM[129].

(Pavadai et al., 2022) created a new trimetallic-MOF (Ni/Zn with $K_3[Co(CN)_6]$) as an ultra-sensitive and selective fluorescence biosensor for Ag^+ and Hg^{2+} ions with good reproducibility. When the Ag^+ ion is introduced into the sensor, the fluorescence signal is reduced (Turned OFF). Yet, when Hg^{2+} ions are added to the above-mentioned quenched system, the fluorescence signal increases (Turn-ON). The sensor obtained detection limits of 0.29 nM for Ag^+ and 0.10 nM for Hg^{2+}, respectively. The co-precipitation technique was used to create the Sensor. The experimental investigation on this sensor system's selectivity was accomplished by adding various metal ions to the sensor. These metals exhibit negligible change on fluorescent intensity. In general, fluorescence bio-sensing activity is accomplished through DNAzyme breakage and the FRET mechanism[130].

A novel highly luminous sensor for the simultaneous detection of chromium (VI) has been proposed by (Yuan et al., 2022). AgNP-NCs@ZIF-8) was produced by incorporating D-penicillamine (DPA) capped silver nanoparticle-nanoclusters (AgNP-NCs) into zeolitic imidazolate frameworks (ZIF-8) produced via conventional method. Because of the high electron transfer, the luminescence intensity decreased as the Cr ion concentration increased. The detection limit was found to be (23.5 ± 0.8) μM. Aqueous solutions of various metal ions were tested for selectivity experiments, and it was discovered that except for Cu^{2+}, these metal ions had no effect on the sensor's luminescence[131].

(Li et al., 2022) suggested A novel sensor based metal-organic framework [Zn(CPA)(DMF)] based on Zn(II) with a sensitive detecting characteristics for of Hg(II) and Cr(VI). The sensor was manufactured using conventional methods and has a high stability over a wide range of pH from 3 to 12. By exploring the selectivity of the sensor several metal ions were introduced to it, and it was observed that the majority of metal ions have minimal influence on the fluorescence of the sensor except for In^{3+}, Al^{3+} and Cr^{3+}ions. The limit of detection was detected to be 7.90×10^{-7} mol·L^{-1}, 5.26×10^{-7} mol·L^{-1} and 6.32×10^{-7} mol·L^{-1} for Hg(II), CrO_4^{2-} and $Cr_2O_7^{2-}$, respectively. The process of Hg^{2+} quenching is primarily attributed to the ion exchange and fluorescence resonance energy transfer[132].

(Cui et al.,2023) proposed unique dual-function sensor-based Tb-MOF/Tb-AG with exceptional selectivity and sensitivity towards uranium with a detection limit of 5.1 pmol/L. (1.2 ppt). The sensor was created utilizing the solvothermal approach. The fluorescence signal reduced as the concentration of uranium ions increased, which was attributed to synergistic coordination, hydrogen bonding, and ion exchange. By investigating the selectivity of the sensor using different cations and anions, it is shown that except for Fe^{3+}, no noticeable quenching effect can be noticed by the various metal ions and anions [133].

(Luo et al., 2023) proposed A novel fluorescent sensor was produced by europium (III)-organic framework (Eu-MOF) for selective and sensitive sensing of $Cu^{2+}$with a detection limit of 1.98 μM. The sensor was produced by solvothermal method. To test the sensor's ability to detect metal ions, metal ions such as Cd^{2+}, Na^{+}, Zn^{2+}, Mg^{2+}, K^{+}, and Ca^{2+} were put to it. Except for Pb^{2+}, Ni^{2+}, and Ag^{+}, it was demonstrated that they have no discernible effect on fluorescence strength. The strongest quenching occurs when Cu^{2+} is added to the sensor showing that the sensor can be an effective luminescent sensor for detecting Cu^{2+}. The energy transfer process is primarily responsible for the quenching mechanism[134].

(Zhu et al., 2023) developed a very sensitive sensor for detecting Fe^{3+} ions composed of Tb-based MOF. The MOF was created solvo-thermally. The sensor has a strong selectivity towards Fe3+ ions in the presence of many interferences such as metal ions (K^{+}, Li^{+}, Ca^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Al^{3+}, and Fe^{3+}). Furthermore, the detection limit for Fe^{3+} is 0.78 μM, 7.73 × 103 M^{-1}. The high luminescence quenching effect was attributable to the competitive energy absorption process, which causes the great sensitivity and selectivity[135].

3.2 Detection of hazardous organic pollutants

Using a dual-emission reverse change ration fluorescence nanoprobe, (Kong et al., 2022) created a (Tb based MOF)/bovine serum albumin capped gold nanoclusters (BSA@AuNCs) for fluorimetric and colorimetric detection of heparin (Hep) and chondroitin sulphate (CS). The MOF was created using the solvothermal process, and the sensor was created by combining the MOF with (BSA@AuNCs). The sensor alone has bright green color fluorescence. By adding heparin or CS, the Tb-MOF dissociates, releasing BSA@AuNCs in the solution. This lead to turning off the green fluorescence of the sensor and turning on the red fluorescence of BSA@AuNCs. Overall, the color of the fluorescence changed from green to red. Additionally, by utilizing the RGB value information, heparin and CS can be calorimetrically detected using a smartphone. It was established through experiments whether specific contaminants, such as DNA, glucose, protamine, S^{2-}, SO_4^{2}, Ac^{-}, PO_4^{3-} and F^{-}, affected Hep and CS sensing. Except for DNA, none of these contaminants significantly affected the sensing. The sensor had a low detecting limit that can reach to 0.018 μM for heparin and 0.167 μg.m^{-1} for CS. Since the sensor has a high sensitivity and precision, it can be used in biological diagnosis to analyse Hep and CS[136].

For the detection of 4-nitrophenol, (Fu et al., 2022) developed a VIS/NIR dual-response ratiometric fluorescent sensor by using carbon dots@zeolitic imidazolate framework-8 (CDs@ZIF-8) and cadmium telluride (CdTe) quantum dots. The sensor-based on turn off mechanism. The quenching effect is related to the photoinduced electron transfer (PET) mechanism between CDs@ZIF-8/CdTe@MIP and 4-NP. The MOF (ZIF-8) was created via a solvothermal technique, and the CDs@ZIF-8 was created by incorporating carbon dots into the MOF. After that, CDs@ZIF-8 were used to trap CdTe QDs. Finally, a one-step sol-gel polymerization process was used to generate an imprinted layer on the surface of the MOF. The sensor had a good linearity range from 0.1 pM to 3.0 pM and 0.05 μM to 30 μM with a low detecting limit of 0.08 pM and 0.05 μM, respectively. To test the MOF's sensing, five analogues and interfering ions were used, however none of these impurities seem to have a noticeable impact on the sensing. Since the sensor has increased sensitivity and accuracy, it can be employed for Np detection of pollutants in real environments[137].

To accomplish precise, sensitive detection of thiamphenicol (TAP), (Fu et al., 2022) successfully developed a novel ratiometric fluorescence sensor based on carbon dots metal organic framework (bCDs@SiO_2@aCDs@ZIF-8@MIP) with down/up-conversion dual-excitation multi-emission. A one-pot method was used to successfully synthesize the sensor. The first step was to build down/up-conversion fluorescent bCDs and aCDs. Then, silicon was applied to the bCDs and aCDs, and ZIF-8 generated solvo-thermally. By using the one-pot sol-gel method, the imprinted layer was able to be placed on the surface of the fluorescent nanomaterial. The sensor's fluorescence quenching process was attributed to PET rather than FRET. At pH 7.0, the sensor efficiency was at its maximum. To test the sensor's selectivity, four analogues to (TAP) coexisting interference compounds were utilized. It was discovered that the sensor has anti-interference characteristics, indicating that it could detect TAP with selectivity and sensitivity in actual complex samples. The sensor responded to TAP throughout a wide linear range from 5.0 nM to 26.0 μM, and a limit of detection that reaches to 1.9 nM for down-channel and 0.9 nM for up-channel. TAP in milk and meat were analyzed using a the sensor, with recoveries ranging from 95.0 to 105.0%[138].

A novel Cobalt-based MOF sensor with aggregation-induced emission (AIE) features was created by (Zhu et al., 2022) to detect nitrogen heterocyclic compounds (NRHCs). The MOF was synthesized via conventional method where Tetraphenylethylene linkers and Co nodes were used to create the MOF that exhibits both fluorescence and colorimetric dual responses to single- and dual-ring NRHCs. Turn-on emission enhancement detection is displayed by the sensor. The sensor offers a wide detecting range from 5 μM to 7.5 mM within 25 seconds. The limit of detection reaches to of 4.31 and 1.14 μM for 3,3′-dinitro-5,5′-bis (1H-1,2,4-triazole) (DNT) and B_5-Nitro-2,4-dihydro-3H-1,2,4-triazole-3-one (NTO), respectively. According to calculations the limit of detection for colorimetric sensing reaches to 0.059 and 0.011 mM, respectively. The sensor demonstrates good selectivity of NRHCs in the presence of many interferent substances such as metal ions, organic solvents, nitroaromatics/nitramines explosives, and others, making it a suitable tool for creating multichannel detection strategies[139].

(Li et al., 2023) successfully prepared fluorimetric sensor based on cerium and polyacrylic acid metal organic framework (PCN-224@PAA-Ce) for selective detection of ascorbic acid (AA). The MOF was created using a sono-chemical technique, and the sensor was created using a simple post-synthesis modification. The inner filter effect (IFE) plays a significant role in the sensor fluorescence "off" detecting mechanism. The sensor has a wide linearity range (0.5- 100) μM and limit of detection (LOD) of 0.73 μM. In the matrix of biological samples, common interfering substances have been investigated. When compared to other interfering compounds and ions such glucose, lactose, K^+, Na^+, Zn^{2+}, Mg^{2+}, L-cys, Arg, Ala, Leu, Thr, Lys, and Ser, the fluorescence detection sensor demonstrated a greater selectivity for AA. With the exception of glutathione, the interfering compounds have not affected the sensing[140].

(Ameen et al., 2022) suggested a innovative fluorescent ratiometric sensor for detecting cysteine in human blood samples by combining blue fluorescent carbon dots with Eu-MOFs. Smartphone-based visual detection was performed using RGB analysis. A single-step solvothermal procedure was used to prepare the Eu-MOF. The visual probe clearly changed colour from red to blue as Cys concentration increased. The sensor exhibited excellent linearity towards cysteine within 0-405 μM range and low limit of detection of 0.15 μM. When interfering amino acids like (Tyr, His, Lys, Ser, Trp, Glut, Asp, and Cys) and potentially saccharides like (Gluc, Fru, and Suc) were added to the Eu-MOF to explore its selectivity, there was no noticeable effect on the sensing of the MOF. Also, the sensor is used to detect silver ion in water samples as discussed in detail[141].

By encapsulating gold nanoclusterswithin a metal-organic framework, (Cai et al., 2021) successfully created a fluorescent and colorimetric biosensor for detecting organophosphorus pesticides.The sensor has a significant fluorescence effect. The interaction of acetyl-cholinesterase (AChE) and choline oxidase (CHO) results in acetylcholine (ACh) hydrolysis and the production of H_2O_2, which alters the structure of the sensor and reduces its fluorescence. The MOF was synthesized using sono-chemical approach. The ideal pH for detecting organophosphorus pesticides was 7.4. The fluorimetric detection has a wide linear range of detection from 0.75 μg/L to 75 mg/L, with a detection limit of 0.67 μg/L. While the colorimetric detection was has a linear range from 0.75 μg/L to 100 mg/L, with a detection limit of 0.3 μg/L. Glyphosate, malathion, parathion, pirimiphos-methyl, and fenitrothion were examined to check the response of the sensor to other OPs. It was shown that the sensor was effective to identify several OPs. Moreover various commercial non-OPs pesticides, such as thiamethoxam, cyantraniliprole, spirotetramat, tebuconazole, and hymexazol were tested andit was revealed that the sensor has a high selectivity towards OPs[142].

(Xie et al., 2021) proposed a novel ratiometric fluorescent sensor composed of europium and terbium doped metal-organic framework for accurate antibiotics detection (98%). The sensor has exceptional quantitative performance for the mixture of antibiotics and was utilized to detect 48 unknown samples in water. With the presence of interfering chemicals, eight of the 25 different antibiotic types were identified. Using a solvothermal technique, the MOF was produced, and it is believed that the fluorescence was reduced by the inner filter effect. The sensor's detecting range extends from 0.4 to 200 μM, and the detection limit was 0.06 μM. The sensor was employed to monitor food and drugs safety[143].

To specifically detect trinitrophenol (TNP) explosives in aqueous media, (Wu et al., 2020) successfully created a novel sensor based on 2D Cadmium metal-organic framework. The sensor was prepared by using solvo-thermal approach. Fluorescence quenching is mostly caused by ligands to ligands charge transfer transition, as shown from the emission spectrum. The detection limit of the sensor reaches 0.119 μM. Further investigation to test the sensing performance of the MOF was done by using other nitrophenol compounds like nitrobenzene (NB), 2-nitrophenol (2-NP), 2-nitrotoluene (2-NT), 3-nitrotoluene (3-NT), 4-nitrophenol (4-NP), 4-nitrotoluene (4-NT), 2,6-dinitrotoluene (2,6-DNT), 2,4-dinitrotoluene (2,4-DNT) and 2,4,6-trinitrotoluene (TNT). The fluorescence intensity of other nitrophenol compounds is only slightly affected, but TNP exhibits a fully quenching response, indicating the MOF's ability for TNP-specific detection[144].

(Han et al., 2020) proposed a novel selective and sensitive fluorescent sensor based on Europium MOF for the accurate detection of Malachite Green (MG). The MOF was synthesized solvo-thermally. According to luminescence experiments, Eu-TDA sensor can quickly identify MG with a detection limit that reaches 0.0221 μM.

The probe exhibit fluorescence quenching effect by adding MG, this is caused by spectral overlapping and energy transfer mechanism. To test the sensitivity of the sensor, investigations were done by using various interferences like metal cations and anions. Out of 25 metal cations and anions, only MG totally quenched the fluorescence of the sensor, demonstrating the strong ability of the sensor for selective and sensitive detection of MG[145].

(Yuan et al., 2022) proposed a novel optical Cu based sensor for sensitive detection of glyphosate. The sensor can detect glyphosate via fluorescence and colorimetric methods with low detection limits that can reach 0.070 µg mL^{-1} for fluorescence and 0.092 µg mL^{-1} for colorimetric techniques. The sensor was used for glyphosate degradation monitoring in the soil and water[146].

(Luo et al., 2022) proposed a new ratiometric fluorescence and colorimetric Zr based MOF dual mode sensor for sensitive detection of glyphosate (GLP). To synthesize the sensor, carbon dots were encapsulated into the MOF that was produced via solvothermal method. By adding glyphosate to the sensor, the fluorescence of the sensor decreased where a photo-induced electron transfer (PET) mechanism was responsible for the fluorescence quenching mechanism. Also, the colorimetric sensing was achieved by changing the color of the sensor and turning it from purple to green under light. The sensor has a wide range of detection from 0.01 to 6.67 mg/L with a detection limit that can reach to 9.06 µg/L. The selectivity of the MOF was tested by using some interference like ions, amino acids, and saccharides. Except for Fe^{3+} and imidacloprid (IMI) none of the interfering substances has a noticeable effect on the sensing of the MOF indicating that the sensor is suitable for selective detection of glyphosate[147].

(Lin et al., 2021) created a colorimetric Cu based MOF sensor for the detection of glucose. The MOF was prepared via conventional technique. The sensor has a wide range of detection from 30 µM to 0.8 mM with low limit of detection that can reach to of 0.01 mM. The sensor’s selectivity was tested by using various interfering substances such as galactose, fructose, D-sucrose, chitosan, L-cysteine, mannose, glutathione and carbamide. It was revealed that none of them affect the MOF's sensitivity to glucose[148].

3.3 Detection of hazardous other pollutants:

(Yu et al., 2022) suggested a ratiometric fluorescence sensor for fluoride ion detection based on an amino-functionalized europium metal-organic framework. The sensor has excellent interfering ability, high selectivity, and sensitivity. Based on host-guest interactions, that is, hydrogen bonds formed between the free amino groups and F^- ions, EuTPTC-NH_2 was developed as a ratiometric fluorescence probe for F^- detection. EuTPTC-NH_2 was discovered to have a great linear response to F^- ranging from 0–80 µM with a low limit of detection that reaches 11.26 µM. The sensor was used for detecting F^-ions quantitatively in water[149].

(Gogoi et al., 2021) effectively developed a novel sensor metal-organic framework based on Zr metal with a Tri-fluoro acetamido-functionalized linker for fluorescence turn on detection of the cyanide ion in aqueous medium with fast response time (2 min). The MOF was produced via a sono-chemical technique. Photo induced electron transfer (PET) mechanism is responsible for the turn-on fluorescence. It was determined that the limit of detection reached 0.23 µM. Cyanide ions were detected via the sensor in solutions with pH values between 3 and 9. The sensor's affinity for the CN ion was also studied by adding several interfering anions that compete with it. Except for cyanide (CN^-), no anions' fluorescence intensity increased significantly, indicating that the sensor's fluorescence turn-on behavior is highly selective and sensitive toward the cyanide (CN^-) ion. The sensor is a useful for detecting CN^- in actual water samples[150].

Turn off fluorescent sensors based on transition metal (Zn^{2+} and Cd^{2+}) metal-organic frameworks were developed for sensitive and selective hydrogen sulphide detection. The solvothermal approach was used for both MOFs. The charge transfer between metal-to-ligand (MLCT) mechanism is responsible for the MOF's fluorescence. Both of which have good selectivity and sensitivity for H_2S detection when used as fluorescence "turn-off" sensors with detection limits of 7.9 µM for Zn MOF and 0.2 µM for Cd MOF. The attack of S^{2-} ions on metal ions, which results in framework disintegration, is what causes fluoresce turn-off response. The fluorescence response of the sensor was evaluated in the presence of a variety of potentially interfering pollutants, including biomolecules like alanine, serine, glutathione, and cysteine) and frequent anions like Cl^-, Br^-, I^-, NO_2^-, and NO_3^-). The results of the experiments reveal that the sensors have a high selectivity for H_2S detection[151].

A novel fluorescent terbium-MOF sensor for rapid and sensitive detection of CO_3^{2-} anions was proposed by (Zhan et al., 2019) The sensor has a wide pH range of 2 to 13, high fluorescence stability, and was synthesized under solvothermal conditions. The sensor also exhibits a low detection limit that reach to 0.38 µM for CO_3^{2-} ions. The antenna effect, which occurs as a result of the energy transfer from the ligands to the Tb^{3+} ion, is responsible for the sensor's fluorescence characteristics. A number of anions were utilized to study the MOF's sensing behavior. The fluorescence decrease only When the CO_3^{2-} ions were added, indicating the high selectivity of the sensor[126].

A successful water-stable luminous europium-MOF sensor based on mixed ligands for PO_4^{3-}ions detection was developed by (Zhan et al., 2019) The sensor was synthesized under solvothermal conditions. In aqueous media, the sensor showed outstanding fluorescence stability over a wide range of pH (2-13) and low limit of detection of 1.42×10^{-5} M. Some interfering anions were used to investigate the sensing behavior towards PO_4^{3-}. It was discovered that the MOF can function as a sensitive sensor for detecting phosphate ions since the PO_4^{3-} ion has a significant quenching effect on the sensor's emission, whereas other anions only cause a modest reduction in luminescence intensity.[152].

(Moradi et al., 2020) synthesize a sensitive luminescent sensor based on zirconium metal organic framework for detecting Bromide ions through fluorescence enhancement effect. The MOF was produced by solvo-thermal approach. The fluorescence enhancement is caused by ligand-to-metal charge transfer effect. It was revealed that the sensor has high sensitivity with low limit of detection that can reach to 0.0018 μM. Different anions were tested to investigate the sensing property of the sensor towards Br^-. It was discovered that whereas CrO_4^{2-} and F^- presented a minor drop in luminescence, SCN^-, ClO_4^-, MnO_4^-, CN^-, ClO_3^-, Cl^- and I^- showed a little fluorescence increment. However, bromide ions was able to significantly increase the sensor fluorescence luminescence which indicated the excellent selective behavior towards Br- anion[127].

(Wang et al., 2018) successfully synthesized a zirconium-based MOF as a colorimetric sensor for detecting oxidizing gases. The sensor was produced via post synthetic linker exchange route, the sensor was able to detect toxic nitrous gases like (NO, NO_2) and Bromine gas by changing the color of the sensor from yellow to pink[153].

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