

# Metal organic frameworks as promising sensing tools for electrochemical detection of persistent heavy metal ions from water matrices: A concise review

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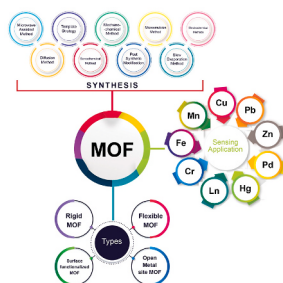
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## HIGHLIGHTS

- MOF as electrochemical sensing systems.
- Various synthetic approaches for synthesizing MOFs sensing materials.
- Landscape view for the sensing of different heavy metals.
- Challenges and detection mechanism of MOFs based sensors.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Water bodies are being polluted rapidly by disposal of toxic chemicals with their huge entrance into drinking water supply chain. Among these pollutants, heavy metal ions (HMIs) are the most challenging one due to their non-biodegradability, toxicity, and ability to biologically hoard in ecological systems, thus posing a foremost danger to human health. This can be addressed by robust, sensitive, selective, and reliable sensing of metal ions which can be achieved by Metal organic frameworks (MOF) based electrochemical sensors. In the present era, MOFs have caught greater interest in a variety of applications including sensing of hazardous pollutants such as heavy metal ions. So, in this review article, types, synthesis and working mechanism of MOF based sensors is explained to give general overview with updated literature. First time, detailed study is done for sensing of metal ions such as chromium, mercury, zinc, copper, manganese, palladium, lead, iron, cadmium and lanthanide by MOFs based electrochemical sensors. The use of MOFs as electrochemical sensors has attractive success story along with some challenges of the area. Considering these challenges, we attempted to highlight the milestone

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achieved and shortcomings along with future prospective of the MOFs for employing it in electrochemical sensing devices for HMIs. Finally, challenges and future prospects have been discussed to promote the development of MOFs-based sensors in future.

| Abbreviations                 |                                                                                                                                                   |                     |                                                                                                                                                                                                                                       |
|-------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------|---------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <i>Abbreviation Full name</i> |                                                                                                                                                   |                     |                                                                                                                                                                                                                                       |
| MOF-1                         | Metal <sub>3</sub> (TCOPM) <sub>2</sub> dpe]·6H <sub>2</sub> O·DMF} <sub>n</sub> dpe = 1,2-di-4-pyridylethene TCOPM = tris(p-carboxyphenyl)methyl | BPDC                | 4,4'-biphenyldicarboxylic acid                                                                                                                                                                                                        |
| SBU                           | Secondary building Unit                                                                                                                           | SDBA                | 4,4'-sulfonyldibenzoic acid                                                                                                                                                                                                           |
| MOF-2                         | Metal (BDC)·(DMF) (H <sub>2</sub> O) (BDC = 1,4-benzenedicarboxylate) (DMF = N,N'-dimethylformamide)                                              | PCN                 | Porous Coordination Network                                                                                                                                                                                                           |
| ppda                          | (pyridin-3-yloxy)-phthalate                                                                                                                       | QP                  | Quenching percent                                                                                                                                                                                                                     |
| npdc                          | naphthalene-1,4-dicarboxylate                                                                                                                     | BUT-14              | [Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>8</sub> (H <sub>2</sub> O) <sub>4</sub> (L <sup>1</sup> ) <sub>2</sub> ] L <sup>1</sup> = 5',5'''-bis(4-carboxyphenyl)-[1,1':3',1'':4'',1''':3''',1''''-quinquephenyl]-4,4''''-dicarboxylat |
| Eu                            | europium                                                                                                                                          | BUT-15              | [Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>8</sub> (H <sub>2</sub> O) <sub>4</sub> (L <sup>2</sup> ) <sub>2</sub> ] L <sup>2</sup> = 4,4',4'',4'''-(4,4'-(1,4-phenylene)bis(pyridine-6,4,2-triyl))tetrabenzoate                        |
| Tb                            | terbium                                                                                                                                           | FRET                | transition from acceptor is radiative                                                                                                                                                                                                 |
| TMB                           | 3,3',5,5'-tetramethylbenzidine                                                                                                                    | PET                 | transition from acceptor is non radiative                                                                                                                                                                                             |
| BTC                           | benzene tricarboxylate                                                                                                                            | UMCM(1)-NH(2)       | NH(2)-BDC derivative of UMCM-1 (University of Michigan Crystalline Material-1) BDC = 1,4-benzenedicarboxylic acid                                                                                                                     |
| (H <sub>2</sub> dbp)          | ligand 4'-(4-(3,5-dicarboxylphenoxy)phenyl)-4,2':6',4''-terpyridine (H <sub>2</sub> dbp)                                                          | bimb                | 4,4'-bis(1-imidazolyl)biphenyl                                                                                                                                                                                                        |
| LOD                           | Limit of detection                                                                                                                                | LLCT                | Ligand to ligand charge transfer                                                                                                                                                                                                      |
| CR                            | carboxylate                                                                                                                                       | AO                  | Atomic orbital                                                                                                                                                                                                                        |
| MOF-525                       | Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>4</sub> (TCPP-H <sub>2</sub> ) <sub>3</sub> TCPP = 5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin        | MO                  | Molecular orbital                                                                                                                                                                                                                     |
| MIL                           | Materials Of Institute Lavoisier                                                                                                                  | MFCs                | microbial fuel cells                                                                                                                                                                                                                  |
| ZIF-8                         | zeolitic imidazolate framework materials                                                                                                          | PANI                | polyaniline                                                                                                                                                                                                                           |
| BPEI                          | branched poly-(ethylenimine)                                                                                                                      | GCE                 | Glassy carbon electrode                                                                                                                                                                                                               |
| CQDs                          | Carbon quantum dots                                                                                                                               | MOF-5               | Zn <sub>4</sub> O(BDC) <sub>3</sub> , where BDC <sup>2-</sup> = 1,4-benzodicarboxylate                                                                                                                                                |
| ZIF-10                        | zinc imidazolate (mer-Zn(Im) <sub>2</sub> )                                                                                                       | tdca                | thiophene-2,5-dicarboxylate                                                                                                                                                                                                           |
| DHT                           | 2,5-dihydroxyterephthalic acid)                                                                                                                   | bppd                | N-bis(4-pyridylmethylene)-1,4-benzenediamine                                                                                                                                                                                          |
| DMF                           | Dimethyl formamide                                                                                                                                | NDC support         | Nationally determined contributons                                                                                                                                                                                                    |
| MOF-74                        | Metal = Mn, Co, Ni, Zn, MnCo, MnNi, and MnZn And 2,5-dihydroxyterephthalic acid network                                                           | DPTTZ               | N,N'-di(4-pyridyl)thiazolo-[5,4-d]thiazole                                                                                                                                                                                            |
| MLCT <sup>3</sup>             | Long lived Metal to ligand charge transfer                                                                                                        | IPA                 | isophthalic acid                                                                                                                                                                                                                      |
| bpy                           | 2,2'-Bipyridine                                                                                                                                   | CPNPs               | lanthanide coordination polymer                                                                                                                                                                                                       |
| Phpy                          | 2-phenylpyridyl                                                                                                                                   | Im                  | imidazole-4,5-dicarboxylic acid                                                                                                                                                                                                       |
| DPA                           | Di(2-pyridyl)amide                                                                                                                                | EPA                 | The Environmental Protection Agency                                                                                                                                                                                                   |
| bt                            | (2'-benzo [b] thienyl) pyridine                                                                                                                   | LMCT                | ligand-to-metal charge transfer                                                                                                                                                                                                       |
| DPTMIA                        | (5-(3,5-di-pyridin-4-yl-[1,2,4]triazol-1-ylmethyl)-isophthalicacid)                                                                               | BA                  | Boric acid                                                                                                                                                                                                                            |
| HPU-1                         | {[Zn(DPTMIA)](H <sub>2</sub> O) <sub>2</sub> (DMF)0.5} <sub>n</sub>                                                                               | BIPA                | (bis(4-(1H-imidazole-1-yl)phenyl)amine)                                                                                                                                                                                               |
| TPC <sub>4</sub> A            | 2,8,14,20-tetra-phenyl-6,12,18,24-tetra-methoxy-4,10,16,22-tetracarboxy-methoxy resorcin                                                          | HIP                 | (2 S)-2-amino-3-(3-phosphonoimidazol-1-ium-4-yl)propanoic acid                                                                                                                                                                        |
| TNC <sub>4</sub> A            | 2,8,14,20-tetra-phenyl-6,12,18,24-tetra-methoxy-4,10,16,22-tetracarboxy-methoxy resorcin                                                          | H <sub>2</sub> TCPP | meso-Tetra(4-carboxyphenyl)porphine                                                                                                                                                                                                   |
| MLCT                          | It involves electronic transition from a metal centered orbital to an organic linker-localized orbital                                            | TPE-COOH            | 2-(4-(1,2,2-triphenylvinyl)phenoxy) acetic acid                                                                                                                                                                                       |
| OBA                           | 4,4'-oxidibenzoic acid                                                                                                                            | MIL-121             | [Al(OH) (H <sub>2</sub> BTEC)·(H <sub>2</sub> O)] <sub>n</sub> BTEC = 1,2,4,5-benzenetetracarboxylic acid                                                                                                                             |
| BPTP                          | 3,5-bis(5-(pyridin-4-yl)thiophen-2-yl)pyridine                                                                                                    | bpydc               | 2,2'-bipyridine 5,5'-dicarboxylic acid                                                                                                                                                                                                |
|                               |                                                                                                                                                   | SWASVS              | Square wave anodic stripping voltammetry                                                                                                                                                                                              |
|                               |                                                                                                                                                   | ESPT                | excited state proton transfer                                                                                                                                                                                                         |
|                               |                                                                                                                                                   | DPA                 | Destructive Physical Analysis                                                                                                                                                                                                         |
|                               |                                                                                                                                                   | ICT                 | Intramolecular Charge Transfer                                                                                                                                                                                                        |

## 1. Introduction

During recent years, ecosystem and public health has been greatly affected by environmental pollution due to exponential increase in population and industrial development. Industrial pollutants mainly refer to Hg<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and other transition metal ions exceeding the allowable limits are toxic pollutants. It is, therefore, unavoidable to monitor accurate concentration of transition metal ions at ultra-low concentration. Some significant changeover metallic ion like Cu<sup>2+</sup>, Zn<sup>2+</sup>, Fe<sup>2+</sup> and other trace elements are essential for the metabolic

processes inhuman body. These ions can cause major environmental and health hazards when present in higher amounts (Mudgal et al., 2010; Tchounwou et al., 2012; Rasheed et al., 2019a, 2019b, 2019c). The ions have tendency to trap in the MOF structure and develop interactions/replace the existing metal ions and consequently detected. For example, higher concentration of Fe<sup>2+</sup> causes various physiological disorders in human body including anemia, insomnia, heart disease, cancer and Parkinson's disease and imbalance of iron homeostasis (Andrews, 2000). Excess of Zn<sup>2+</sup> can suppress the absorption of other essential metals such as copper and iron. That's why an efficient protocol for determination of very low concentration of transition-metal

cations is always needed.

Many techniques have been employed for sensing of metal ions which are categorized into three classes; electrochemical detection techniques (amperometry, voltammetry, potentiometry, impedance measurement and coulometry), spectroscopic detection techniques (atomic absorption spectroscopy, atomic emission spectroscopy, inductively coupled plasma mass spectrometry) and optical detection techniques (absorption, reflection or luminescence spectrometry). Spectroscopic methods are quite sensitive but are exclusive and need laborious pre-preparations (Harrington et al., 2011). Optical techniques are quite conventional one. Optical techniques has good selectivity because selective chromogenic reagents and indicator dyes can be used where they can interact with a specific metal ion (Oehme and Wolfbeis, 1997). In comparison, electrochemical methods are more cost-effective, fast, easy, reliable and suitable for in-field applications (Bansod et al., 2017). Many materials has been synthesized to detect metal ions such as carbon based materials (Raju et al., 2023), metal nanoparticles (Hyder et al., 2022), metal oxides (Dharmalingam et al., 2022), nanocomposites (Naushad, 2014; Batool et al., 2021; Ali et al., 2022b) and metal organic frameworks (MOFs) (Kajal et al., 2022).

Metal organic framework (MOFs) are chemically hybrid organic-inorganic crystalline frameworks with regular assortment of metal cations enclosed by organic linkers thus generating a hollow cage-like structure. The organic units are usually organic anions and heterocyclic compounds (Sharmin and Zafar, 2016), (Burtch et al., 2018). In the

beginning, MOFs caught chemists' attention due to their tunable structure with nanopores. Later on, the nonporous structure of MOFs utilized for different applications in catalysis (Majewski et al., 2018), optics, sensors (Campbell and Dincă, 2017), bio-reactors, drug delivery (Chowdhuri et al., 2017), to hold various pollutants and gaseous molecules like H<sub>2</sub> and CH<sub>4</sub> (VahidMohammadi et al., 2018), catalysis, energy storage (Choi et al., 2014; Yang et al., 2021) and others. MOFs have a huge porous surface area (about 90% free space) with tunable pores (Furukawa et al., 2013a). So far, the highest surface area of MOFs (7000 m<sup>2</sup>/g) has been recorded (Hönicke et al., 2018), which is significantly higher as compared to other porous materials.

Simple synthetic strategies such as ion thermal, solvothermal, diffusion, ultrasound assisted, microwave methods, template directed synthesis, and others are involved for the synthesis of MOFs (Butova et al., 2016). MOF's as well as MOF's based material have been shown to have high thermal and chemical stability (Li et al., 2019). The desired properties in relation of sensing can be introduced in MOFs by wise selection of metallic cations, organic ligands and reaction conditions (Furukawa et al., 2013b). Furthermore, MOFs are considered suitable as electrochemical sensors due to their properties such as uniform network structure, large surface area and unsaturated metal coordination sites. These properties make competent in catalytic efficiency and coating of electrode thus leading to efficient sensor. Moreover, large surface area and good porosity increase the mass transfer of analytes thus increasing electrical signal and eventually sensing sensitivity (Xinxin et al., 2017).

**Table 1**

Recently reported MOFs materials for different applications.

| MOFs                                                                                                                                                                                                                                        | abbreviation                                                                                                                       | Metal ion                                                                                                                   | linker                                                                                     | Method of synthesis                     | Application                                                     | Ref.                                                   |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------|-----------------------------------------|-----------------------------------------------------------------|--------------------------------------------------------|
| CeCo-MOF<br>(M <sub>2</sub> (imidazole) <sub>2</sub> Ce(H <sub>2</sub> O)<br>(C <sub>2</sub> O <sub>4</sub> ) <sub>1/2</sub> (4,5-ida) <sub>2</sub> ·2<br>(H <sub>2</sub> O),<br>(M = Zn, Cu);<br>(4,5-ida: 4,5-imidazole<br>dicarboxylate) | ZnCe-MOF@PANI and<br>CuCe-MOF@PANI<br>(PANI = polyaniline)                                                                         | Ce and Co<br>Zn, Ce, Cu                                                                                                     | Triethanolamine<br>4,5-imidazole dicarboxylate                                             | Thermal synthesis<br>Hydrothermal       | Hydrogen evolution<br>Supercapacitor                            | Li et al. (2022)<br>Sun et al. (2022)                  |
| Zinc-MOFs@ZIF-8<br>Fe-MOFs                                                                                                                                                                                                                  | Fe-MIL100                                                                                                                          | Zinc<br>Fe                                                                                                                  | terpolymer<br>trimesic acid organic linker                                                 | Diffusion<br>Heating                    | Super capacitor<br>Catalytic<br>Dehydrogenation of<br>Isobutane | Ali et al. (2022a)<br>Rodríguez-Gomez<br>et al. (2022) |
| Bi or multi-element<br>MOF@Carbon Cloth                                                                                                                                                                                                     | MOF74@CC                                                                                                                           | Mn <sup>2+</sup> ,<br>Co <sup>2+</sup> ,<br>Cu <sup>2+</sup> ,<br>Zn <sup>2+</sup> , Al <sup>3+</sup> ,<br>Fe <sup>3+</sup> | pristine organic ligand                                                                    | Solvothermal                            | Nickel–Zinc Batteries                                           | Chen et al. (2022b)                                    |
| Bi-metallic MOF-<br>phosphides-hollow<br>carbon nanofibers                                                                                                                                                                                  | (Ni-Fe)-P-C@HCNF                                                                                                                   | Ni, Fe                                                                                                                      |                                                                                            |                                         | Supercapacitor                                                  | Chhetri et al. (2022)                                  |
| Co <sub>2</sub> (L) <sub>2</sub> (azpy)] <sub>n</sub> (L = 5-<br>(pyridin-4-ylmethoxy)-<br>isophthalic acid), (azpy<br>= 4,4'-azopyridine)                                                                                                  | Co-MOF                                                                                                                             | Co                                                                                                                          |                                                                                            | Solvothermal                            | CO <sub>2</sub> Adsorption and<br>photo thermal<br>conversion   | Dang et al. (2022)                                     |
| N-heterocyclic carbene-<br>ligated Cu Single atom<br>site (SAS = single atom<br>site)                                                                                                                                                       | Cu-MOF-SAS                                                                                                                         | Cu                                                                                                                          | N-heterocyclic carbene                                                                     | –                                       | Methane electrolysis                                            | Chen et al. (2022a)                                    |
| Mixed-ligand-devised<br>anionic MOF with<br>divergent open Co(II)-<br>nodes                                                                                                                                                                 | CSMCRI-10                                                                                                                          | Co                                                                                                                          | H <sub>3</sub> TCA = 4,4',4''-<br>tricarboxytriphenylamine and<br>bpy =<br>2,2'-bipyridine | Solvothermal                            | electrochemical water<br>oxidation                              | Seal et al. (2022)                                     |
| viologen-derived host-guest<br>MOF material (Zn-MOF)                                                                                                                                                                                        | Zn <sub>3</sub> (IPA) <sub>4</sub> MV<br>(IPA = isopthalate)<br>(MV = 1,1'-dimethyl-<br>(4,4'-bipyridine)-1,1'-<br>dium dinitrate) | Zn                                                                                                                          | isophthalic acid, and 1,1'-<br>dimethyl-(4,4'-bipyridine)-1,1'-<br>dium dinitrate)         |                                         | Inkless printing                                                | Liu et al. (2022)                                      |
| Co nanoparticles-MOF and<br>ZnO nanoparticles-MOF                                                                                                                                                                                           | Co@ZnO@N doped<br>Carbon composite<br>, Carbon composite=<br>(graphitized nitrogen-<br>doped carbon<br>framework)                  | Co, ZnO                                                                                                                     |                                                                                            | Hydrothermal<br>and pyrolysis<br>method | Adsorbent                                                       | Yang et al. (2022)                                     |

Previously, review articles has been published describing types of MOFs, synthesis of MOFs (Soni et al., 2020), functionalization and designing of MOFs (Baumann et al., 2019). MOFs application in energy storage device (Baumann et al., 2019), tissue engineering and regenerative medicine has been reviewed (Shyngys et al., 2021). Applications of MOFs in catalysis, sensors, adsorption and separation has been studied (Chen et al., 2020). MOF as sensor has been studied briefly for detection of few biological metal ions (metal ions involved in biological processes) (Pamei and Puzari, 2019) but there has not been any compilation for electrochemical detection of metal ions by MOFs in such detail. This article has reviewed comprehensively electrochemical sensing of 10 metal ions. In this review article, synthesis, types and application of MOFs are described briefly with updated literature (2022) to give overview (Table 1). In future, more work can be done in manufacturing of MOFs materials which can enhance importance of electrochemical sensors for detection of metals ions to combat environmental problems by eradicating these metals.

## 2. Types of MOF materials

MOFs classification on the basis of structural features is worth of discussion due to their effects on its activity as sensor. MOFs are classified as rigid groups, flexible frameworks, open metal sites and surface functionalized MOFs (Peng et al., 2022). Rigid frameworks are stable, robust, and porous framework. Its porous framework remain stable on adsorption and desorption of adsorbate. These MOFs are used as molecular sieve (Ghanbari et al., 2020) (Fig. 1) (see Fig. 2).

Flexible frameworks as depicted show flexible shape on inclusion or removal of adsorbate, due to different factors such as pressure, temperature. It is observed flexible nature is observed on removal of solvent molecules but porous structure was retained on adsorption or removal of gas molecule even at high pressure. There are some MOFs which exhibit this flexible nature during adsorption/desorption such as MIL-5 (Hamon et al., 2009a), MIL-8 (Serre et al., 2007b) and SNU-MIL (Serre et al., 2007b). There is change in unit cell volume is observed during adsorption/desorption of adsorbate.

There is open metal site MOFs, it can enhance the activity of MOFs. It is observed that presence of water molecules in open metal site of MOFs increase the capability of MOFs to capture CO<sub>2</sub> (Liang et al., 2009). Surface functionalized framework MOFs enhance adsorption ability of MOFs by linking functional groups upon surface of MOFs. Different functional groups such as arylamine (Millward and Yaghi, 2005), alkylamine (Demessence et al., 2009a) and hydroxyl (Serre et al., 2007a) has been grafted upon MOFs to increase adsorption of carbon dioxide upon surface of carbon dioxide. This grafting is done via either ligand modification or coordination of metal center. Here is recently synthesized MOF with their application in Table 1 to overview of recent development in relation of MOFs.

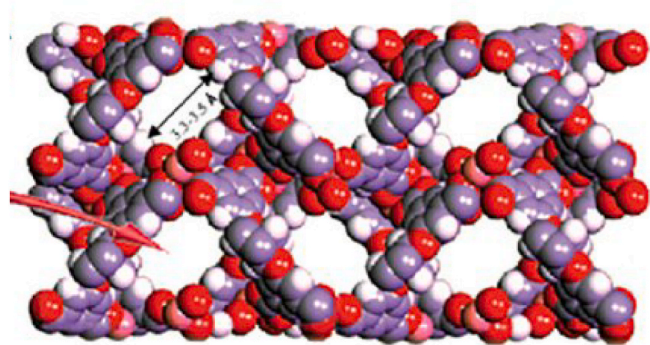


Fig. 1. Adsorption in rigid MOFs based on the molecular sieving effect. With permission from (Ghanbari et al., 2020) copyright©2019 Elsevier.

## 3. Synthesis of MOF materials

MOFs are synthesized by linking metal ion and organic bridging ligands. Simple combination of both metal ions and organic linkers can lead to crystalline and porous network of MOFs via modular synthesis method (Sumida et al., 2012). Different methods (Fig. 3) can be applied for synthesis which can be classified as conventional solvothermal method and unconventional method.

### 3.1. Conventional solvothermal/hydrothermal

A mixture of metal ions and organic linkers in solvent is heated in Teflon-lined autoclaves for temperature higher than 400 K (Wang and Ying, 1999) during conventional solvothermal synthesis, hydrothermal synthesis if solvent is water. Pressure, temperature, the makeup of the solvent, reagent concentration, etc. are synthesis parameters that can be modified for a particular structure. An essential variable in the synthesis of MOFs is the temperature of the reaction mixture. When a reaction occurs at a temperature greater than the solvent's boiling point, it is referred to as a solvothermal reaction, and when it occurs at a temperature lower than the solvent's boiling point, it is referred to as a non-isothermal reaction. Different MOFs such as MOF-5, MOF-74, MOF-177, HKUST-1 ZIF-8, have been stated to be synthesized by this method (Huang et al., 2003; Tranchemontagne et al., 2008; Biełmi et al., 2009; Cravillon et al., 2009). This method is also called upon as direct precipitation reaction. Temperature is the parameter which control the morphology of MOFs.

### 3.2. Unconventional methods

In mechanochemical method, metal salt and organic linker is grounded by mortar pestle and ball milling followed by its gentle heating to evaporate water and other volatile molecules in absence of solvent. A mixture of metal salt and organic linker is grinded in a mortar pestle or in a ball mill without using solvent after grinding the mixture is heated gently to evaporate water or other volatile molecules which are formed as by products in the reaction mixture (Nouar et al., 2009). There is breakage of intramolecular force by mechanical force followed by chemical transformation. This method is environmental friendly due to nontoxic solvents with the benefit of high yield (Braga et al., 2007). Pichon et al. first reported this method for synthesis of MOFs (Pichon et al., 2006). Bipyridene-based covalent organic framework (COF) has been synthesized by using both mechanochemical and solvothermal method. It was noted that proton conducting property is observed in COF which is formed by mechanochemical method. It is observed that addition of minor amount of solvents in reaction mixture quickens the mechanochemical reactions by enhancing the mobility of the reactants.

### 3.3. Alternative synthesis methods

Alternative routes have also been attempted in addition to these methods. Alternative routes can lead to different crystallization rate, particle size, size distribution and adsorption properties as well as morphologies that can have an influence on the properties of material. For example, diffusion of guest molecules in porous materials with different particle size can exhibit a direct effect on catalytic activity, adsorption and separation capacity of molecules. Important alternate routes can be categorized as microwave assisted method, electrochemical method, sonochemical synthesis and layer and layer synthesis. In microwave assisted method, microwave radiations are used to give energy for synthesis. This method gives advantage of fast crystallization, phase selectivity, morphological control and narrow particle size distribution. Several MOFs having Cr<sup>3+</sup>, Al<sup>3+</sup>, Fe<sup>3+</sup>, V<sup>3+</sup>, Ce<sup>3+</sup> have been synthesized by this method.

In electrochemical synthesis, metals ions are supplied through anodic dissolution of metal source instead of metal salt followed by

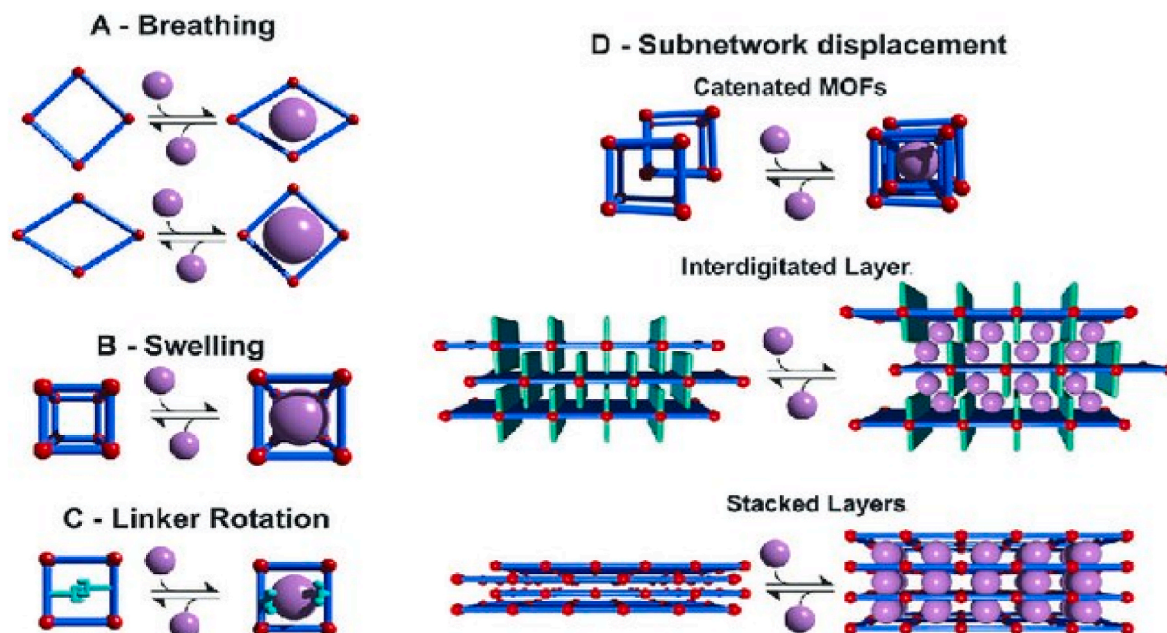


Fig. 2. Classification of different flexibility modes of MOFs with permission from (Schneemann et al., 2014) via license: CC BY 3.0.

reaction dissolved linker molecules and conducting salt in reaction medium. Most of time, protic solvents are used to prevent deposition of metal on cathode (Mueller et al., 2006). MOFs having ionic liquids as linker are also produced by electrochemical route (Richter et al., 2009). MOFs quality is observed to be compromised due to incorporation of linker molecules and/or conducting salt in the pores during crystallization.

In sonochemical synthesis, synthesis is rapid and environment friendly as ultrasonic radiation of about 20 kHz–10 MHz is employed. This method give advantage of homogenous and rapid nucleation thus leading to reduced crystalline time and smaller particle size as compared to conventional solvothermal method. In sonochemical method, there is cavitation process which involves creation, expansion and collapse of bubbles under high energy ultrasound which interacts with liquid and generates energy at high temperatures of 5000 K and pressures of 1000 bar (Sharanyakanth and Radhakrishnan, 2020). Microjets are created by the cavitation process when it comes to solids, and these microjets can clean, erode, or actuate the surface followed by dispersion of agglomerated small particles. When homogeneous liquid is exposed to ultrasonic waves, a chemical reaction may occur. The first MOF  $[\text{Zn}_3(\text{BTC})_2]$  (BTC = benzene-1,3,5-tricarboxylate) produced sonochemically in ethanol that demonstrates selective sensitivity towards organoamine was reported by Qiu et al. (2008).

The layer-by-layer approach is utilized to create MOF thin films. The procedure is based on surface chemistry and involves immersing a functionalized organic surface successively into metal ion and organic linker solutions. According to observations, the order in which the reactants are supplied affects the thin film's orientation (Zacher et al., 2011). The two main elements that influence the pace of growth of MOF film are the metal source and surface termination (Bai et al., 2011). For substrates functionalized with various functional groups like COOH and OH, highly oriented growth was seen. Other methods for fabrication of thin film MOFs are chemical solution deposition (Demessence et al., 2009b, 2010; Horcajada et al., 2009), post-synthesis modification (Stock and Biswas, 2012), and the ionothermal method (Cooper et al., 2004) (using ionic liquids).

#### 4. A brief overview of different applications of MOF materials

In MOFs, there is a simultaneous appearance of three characteristics,

viz. crystallinity, porosity and existence of strong metal-ligand interaction. The unique combination of these properties makes MOFs a very special class of materials (Corma et al., 2010). MOFs has application in catalysis, drug delivery, gas storage, nanoparticle precursor, luminescence, electrochemistry and sensing. There has been review articles in relation of different application such as energy storage (Ren et al., 2020; Peng et al., 2022), medical application (Bieniek et al., 2021), drug delivery (Cao et al., 2020), environmental applications (Zhang et al., 2017; Rasheed et al., 2020a, 2020b, 2022; Hao et al., 2021; Rego et al., 2021; Rasheed and Rizwan, 2022) and hydrogen production (Wu et al., 2020) but there has not been article in relation of detection of metal ions by MOFs materials as described below. Detection of metal ions also have a lot of importance for pollutant eradication as accurate sensing of non-desirable agent is first step of its eradication (Fig. 4).

#### 5. MOFs as sensing tools

MOF-based sensors have made rapid advances providing high sensitivity and selectivity in chemical analysis in agriculture, health care, industry, and environment monitoring and food safety. MOFs based sensors can exhibit luminescent enhancement or quenching up to certain degrees upon interactions between absorbed guest analyte and the framework. Large surface ranges of MOFs offer assistance to construct up higher concentration of analytes, which comes about in expanded affectability. MOFs materials have been found as photoluminescent materials due to aromatic units in linkers. This ability made MOFs suitable in cathode ray tubes, projection television, fluorescent tubes and X-ray detectors (Rocha et al., 2011), small-molecule sensors (Lu et al., 2011; Wang et al., 2022), pH sensors (Rozenberga et al., 2022), light concentrators for photovoltaic devices, antennae in photo-sensitive bioinorganic compounds and high-technology optics. In this, both the metal and the linker have ability to produce luminescence, and its antenna effect (interaction) increase the quantum yield and brightness. It is observed that Ln-MOFs having multiple lanthanide ions can be used as multicoloured light emitters. This mode can be useful in multiplexed detection and imaging of therapeutic cells (Lim et al., 2009).

Ln-MOFs have been employed in cation sensing, anion sensing as well as molecule sensing. Sensing can be done by observing a visible color change of material. In this context, a nanotubular MOF,

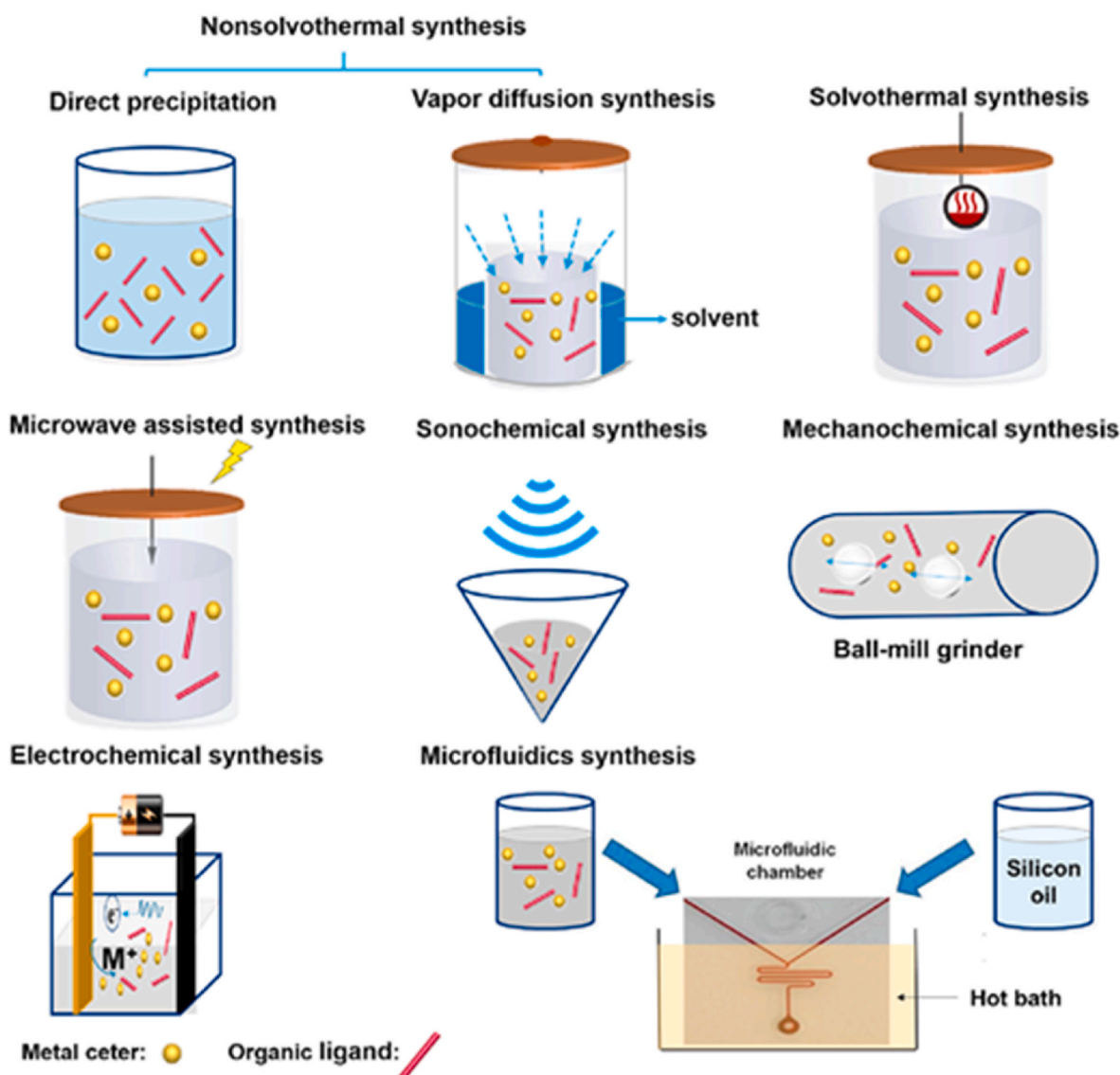


Fig. 3. Different methods for synthesis of MOFs. With permission from (Batool et al., 2023) copyright © 2023 Elsevier.

$\{[(\text{WS}_4\text{Cu}_4)_{12}(\text{dptz})_3]\cdot\text{DMF}\}_n$  ( $\text{dptz} = 3,6\text{-di-(pyridin-4-yl)-1,2,4, 5-tetrazine}$ ,  $\text{DMF} = N,N\text{-dimethylformamide}$ ) was found very efficient in detecting small solvent molecules. Small solvent molecules inclusion was shown by visible color change depending on the solvent guests (Lu et al., 2011). Recently, a cationic MOF (Bai et al., 2011; Desai et al., 2016) is reported which has ability to adsorb oxoanionic pollutants.

Some characteristic features of MOFs such as ease of preparation, good adsorption capacity, enhanced catalytic efficiency, tunable chemical properties, high surface area, and diverse structure make them potential sensing materials to be used in chemical sensors (Chidambaram and Stylianou, 2018; Rasheed and Nabeel, 2019; Chen et al., 2022a). The physicochemical properties and structural adaptation in MOF on attachment of incoming particles are used as a sensing tool for detection of various metals in recent years (Stavila et al., 2014). MOF functionalized with particular bunches can identify focused on substance with upgraded selectivity through host-guest intuitive or estimate prohibition; and adaptable as well as tunable porosity or structure that permits the reversible absorption and elude of substrates to extend recovery and reusing [17].

Literature gave insight into four sorts of MOFs-based materials which have been utilized as sensors counting crystalline MOF materials, MOF-based composites, nanoscale MOFs (NMOFs) and MOF membranes. It

was found that obvious changes were observed on entrance of visitor particles inside the pores of the MOFs such as shift in crests of the outflow range, altering of color, and improvement or extinguishing of fluorescence which is named as “turn-on” and “turn-off” reactions (Cui et al., 2014). There have been different types of sensor such as electrochemical sensor, colorimetric sensor, optical sensor, piezoelectric sensor and field effect sensor. In this review our focus will be on electrochemical sensor because of its extensive use due its good selectivity, robustness, easy miniaturization and excellent detection limits.

### 5.1. Electrochemical sensor

Electrochemical sensor is constructed to have a redox reaction. Electrochemical sensor model is presented in Fig. 5. A sensor is usually made up of a transduction and a detecting electrode which converts the detected information to an electrical or visual sign (Nandasiri et al., 2016). The critical features of a sensor depend on the sensitivity, selectivity, response time, sustainability, limit of detection (LOD) and cost. In this regard, the selection of correct material during the development of a particular sensor is key point towards sensor performance. Sensitivity is a key feature, which can be defined as the minimum fluctuation of exterior stimulus inducing a noticeable signal variation

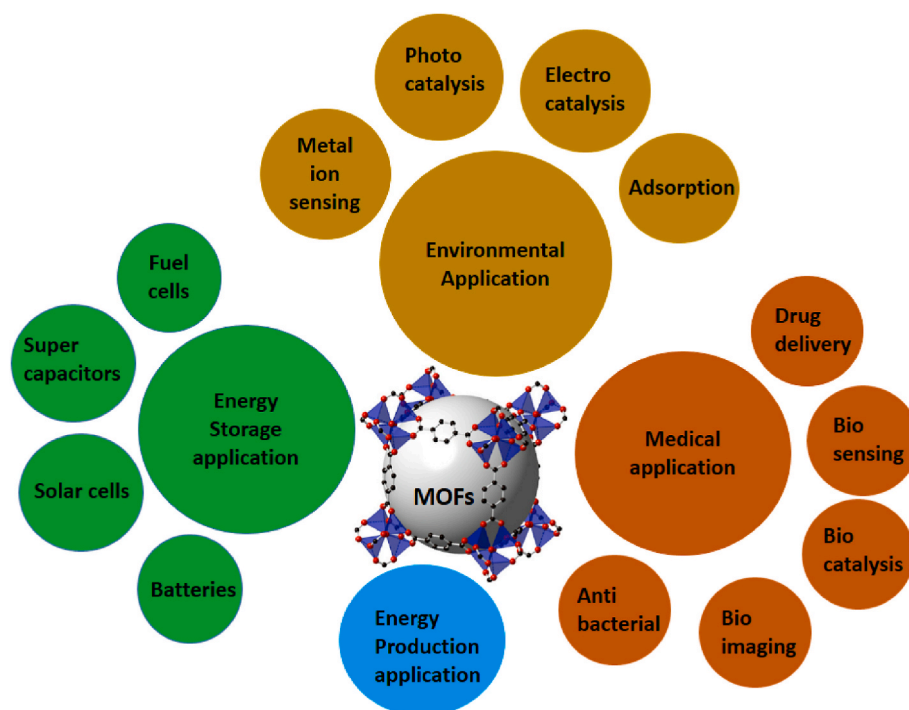


Fig. 4. Applications of MOF materials.

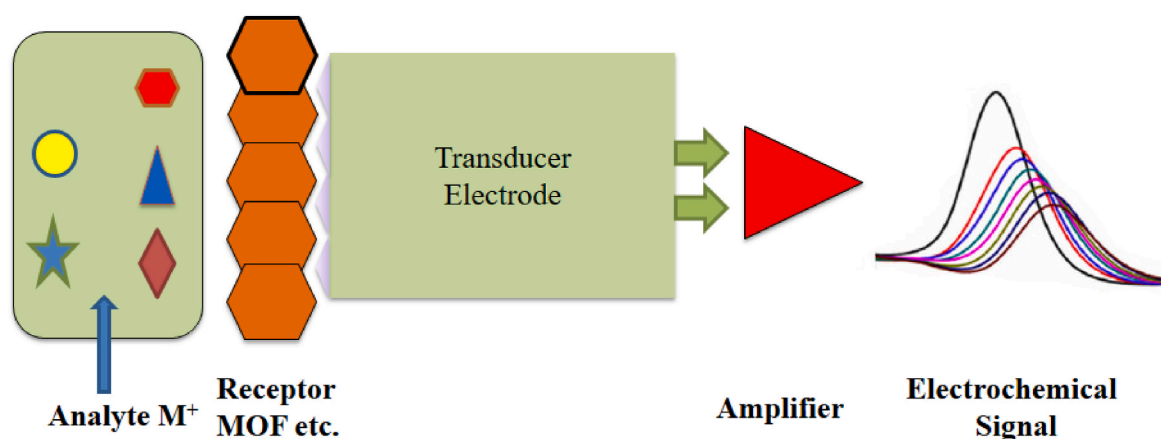


Fig. 5. Working principle of electrochemical sensor.

(Zhang et al., 2020). Literature survey reveals that a number of materials including carbon nanomaterials, metals as well as metal oxides etc. having different sensing properties have been used in chemical sensors (Al-Juboori et al., 2020; Sher et al., 2020; Al-Shara et al., 2021).

## 6. Sensing of transition-metal cations by MOFs

Some recent MOFs based materials used for sensing of transition metal cations is discussed in detail in upcoming sections.

### 6.1. MOFs as sensors for $\text{Cr}^{3+}$ and $\text{Cr}^{6+}$ detection

Chromium's widespread usage in industrial and chemical processing has resulted in major contamination of the air, land, and water. In nature, chromium exists in two valence states:  $\text{Cr}^{3+}$  and  $\text{Cr}^{6+}$  and the toxicity of chromium in both states vary considerably.  $\text{Cr}^{3+}$  is a vital trace element for human life and health.  $\text{Cr}^{3+}$  ions that surpass a particular threshold attach not-especially to DNA that might result in

genetic factor alterations and cancerous lumps. As a result, chromium determination must be precise and selective in order to protect human health and the environment. Chen and colleagues developed a 3D Ca-MOF with micropores holding  $[(\text{CH}_3)_2\text{NH}_2]\text{I}$  cations, a Secondary building Unit (SBU) of  $[\text{Ca}_5(\text{O}_2\text{CR})_{10}]$  (CR = carboxylate ligand) and 3-connected ligands, forming a unique topology network (Chen and Xu, 2019). In the solid form, the fluorescence emission of (MOF-1) was minimal. Surprisingly, limiting fluorescent dyes as a guest luminous object gave MOFs a bright glow. Tb (III) was obtained by ion exchange in the post-synthetic process. Tb (III) emitted the typical Tb (III) emission spectra and exhibited excellent  $\text{Cr}^{3+}$  detection abilities. Furthermore, the detection limit was  $0.27 \mu\text{g}$  per milliliter. Because the UV-Vis spectra of  $\text{Cr}^{3+}$  ions overlapped more with excitation spectrum of Tb (III), thus competing absorption of excitation wavelength energy of Tb (III) and  $\text{Cr}^{3+}$  might be due to slaking.

Zhan et al. created a well ordered and stable Eu-MOF by  $[\text{Ln}(\text{npdc})]_2$ , (npdc = naphthalene-1,4-dicarboxylate) which form single dimensional double nuclear chain which joined repeatedly to form a 2D

layer by the organic ligand (pyridin-3-yloxy)-phthalic acid (Zhan et al., 2019). In aqueous media with pH 2 to 13, it displayed outstanding fluorescence stability. As a result, researchers looked into the compound's fluorescence sensing experiment with various metal ions. Except for tri-positive cations like  $\text{Cr}^{3+}$ ,  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ , most of cations exhibited no discernible quenching impact. The quenching effectiveness was 98.5%, 62.2%, and 58.1% when the  $\text{Cr}^{3+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Al}^{3+}$  concentrations were  $2.1 \times 10^{-2}$  M. Chromium (III) has a detection limit  $6.17 \times 10^{-5}$  M. As,  $\text{Cr}^{3+}$  ion absorption excitation did not overlap, putative  $\text{Cr}^{3+}$  ion reducing mechanism was hypothesized.  $\text{Cr}^{3+}$  ions may induce energy degeneracy by collision hence lowering power transmission by ligand to core Eu (III) ions.

Li described series of same structure 3D Ln-MOFs. MOF-17 had good uses in luminescence sensors, which could swiftly and efficiently detect  $\text{Cr}^{3+}$ .  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  luminescence quenching effect due to stable presence of complexes in water. Eu-MOF and Tb-MOF emission spectra were recorded in varied absorptions of  $\text{Cr}^{3+}$  in order to identify their sensitivity to  $\text{Cr}^{3+}$  ions. Their brilliant intensity gradually decreased as the  $\text{Cr}^{3+}$  ion concentration increased. At low concentrations, the  $\text{Cr}^{3+}$  ion's quenching curve was practically linear, but the linear relation varied as concentration increased, confirming both active and passive quenching in this process. For  $\text{Cr}^{3+}$  ions, the detection limits were 1.5 and 1.9  $\mu\text{M}$  respectively. The slaking of Eu-MOF and Tb-MOF by  $\text{Cr}^{3+}$  may cause energy competition and absorption similarity between their excitation bands. Furthermore,  $\text{Cr}^{3+}$  might have a weak attraction on uncoordinated cyano groups, resulting in energy transfer and luminescence quenching. After  $\text{Cr}^{3+}$  introduction to Tb-MOF nitrogen 1s peak changed, showing weak connection between them, which was further validated by X-ray photoelectron spectroscopy (XPS). In brief, energy absorption and weak coordination contact resulted in the fluorescence intensity being quenched (Sun et al., 2017).

Hexavalent chromium ( $\text{Cr}^{6+}$ ) has widespread industrial applications such as used in tanneries, in electroplating as well as surface coating and making of alloys. The release of  $\text{Cr}^{6+}$  in water bodies causes numerous health hazard effects on human life counting interior gushing, asthma, diseases of kidney and neurological illnesses. In this regard, Cr (VI) determination and removal from water bodies is ever needed. Nano-sized MOF based materials have attained considerable application in monitoring and determination of Cr (VI).

Herein, in 2021, Wei Shi synthesized nanoscale MOF-199 by mixing benzene tricarboxylate (btc) triethylammonium solution and copper nitrate solution and stirring at room temperature for 10 min. The prepared MOF-199 shows the excellent catalytic activity of Cr (VI) catalytic oxidizing enzyme and the significant oxidation of 3,3',5,5'-tetramethylbenzidine (TMB) by Cr(VI) produces a deep blue color, as shown in Fig. 6b. In this way, a practical and cost-effective catalyst-based sensor for selective, fast and sensitive colorimetric detection of Cr(VI) has been developed. Furthermore, the proposed method has also been successfully used to monitor Cr(VI) in environmental water samples (Shi et al., 2021).

## 6.2. MOFs as sensors for $\text{Mn}^{2+}$ detection

In 2017, two MOFs were prepared in the presence of ligand 4'-(4-(3,5-dicarboxylphenoxy)phenyl)-4,2':6',4''-terpyridine ( $\text{H}_2\text{dbp}$ ) thus giving  $[\text{Zn}(\text{dbp})_n]$  and  $[\text{Cd}(\text{dbp})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ .  $\text{CH}_3\text{CN}$  which were recognized as rare detection tools for  $\text{Mn}^{2+}$  ion detection by (Wu et al., 2017). The luminescence reactions between Zn–Cd MOFs were studied and it was discovered that the luminescence strength reduced dramatically in occurrence of  $\text{Mn}^{2+}$  ion, having limit of detection (LOD) values of  $1.80 \times 10^4$  M and  $5.08 \times 10^6$  M for both respectively, minimal reactions with other competing metals and showing great specificity. The power engrossed by ligand  $\text{H}_2\text{dbp}$  is transported to incoming  $\text{Mn}^{2+}$  ion resulting in a quenching action.

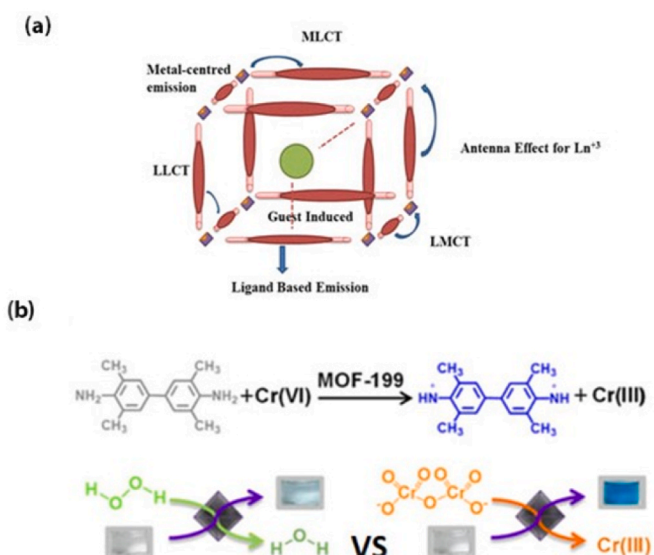


Fig. 6. (a) Schematic diagram of possible luminescence origin in MOF-199, (b) Schematic diagram of MOF to probe Cr(III) with permission from (Shi et al., 2021) under copy right © 2021 American Chemical Society.

## 6.3. MOFs as sensors for $\text{Cu}^{2+}$ detection

Copper is discharged into the environment in most industrial settings, having detrimental health consequences (Doebrich, 2009). Copper is also a crucial part for all living things, as it is one of the micronutrients required by the human body. It can keep internal organs' regular activities and metabolic processes going. Excessive copper consumption can cause health problem like stomach distress, serious liver and kidney damage. Cu(II) has a high thermodynamic affinity for oxygen and nitrogen-containing chelating ligands as well as quick metal-to-ligand binding kinetics hence previous attempts to detect  $\text{Cu}^{2+}$  were fairly effective (Bag and Bharadwaj, 2005), (Zheng et al., 2003). As a result, developing a simple, quick, and effective fluorescent probe for detecting  $\text{Cu}^{2+}$  is ever needed.

In 2010, Shujan Liu and his coworkers reported for the 1st time an anionic MOF  $[\text{NH}_4]_2[\text{Zn}(\text{ligand})] \cdot 6\text{H}_2\text{O}$  (Liu et al., 2010a). The stability of the MOF aqueous environment made it a suitable  $\text{Cu}^{2+}$  sensor for applications in biological and environmental studies. X-ray diffraction confirmed phase purity of prepared MOF and it was found that one dimension of polymer is occupied by water and  $\text{NH}_4^+$  counter ions. But the weight loss observed by thermogravimetric analysis after 185 °C was attributed to the chemical decomposition (V.A. Blatov et al., 2004 and <http://www.topos.ssu.samara.ru>).

When the polymer 1 was excited at 339 nm, strong photoluminescence was observed at 437 nm at room temperature (Zhao et al., and 149.). Polymer 1 was obtained from the hydrothermal self-assembly of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , pyromellitic dianhydride, and  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ . It was thought that photoluminescence might be due to chelation effect or from the photo induced electron transfer (PET) from the ligand to the fluorophore upon binding Zn(II), presenting the of polymer is potent sensor selective sensing of  $\text{Cu}^{2+}$  ions. The hydrolytic stability of anionic MOF,  $[\text{NH}_4]_2[\text{ZnL}] \cdot 6\text{H}_2\text{O}$  ( $\text{L} = 1,2,4,5\text{-benzenetetracarboxylate}$ ) made it a suitable sensor for applications biological and environmental studies (B. Zhao and 149.).

Porphyrin is a well-known heterocyclic compound has a small cavity that assists metal cations to coordinate (Santoro et al., 2012). It was used to create fluorescence probe MOF-525 for  $\text{Cu}^{2+}$  ion. Liu et al. reported the MOF-525 is formed by  $\text{Zr}_6\text{O}_4(\text{OH})_4$  cuboctahedral units linking to porphyrin (Fig. 7). MOF-525, a porphyrin-based chemical sensor with a unique capacity to detect  $\text{Cu}^{2+}$  ions. It is worth mentioning that detection limit of 67 nM was attained lower than the  $\text{Cu}^{2+}$  level permitted by

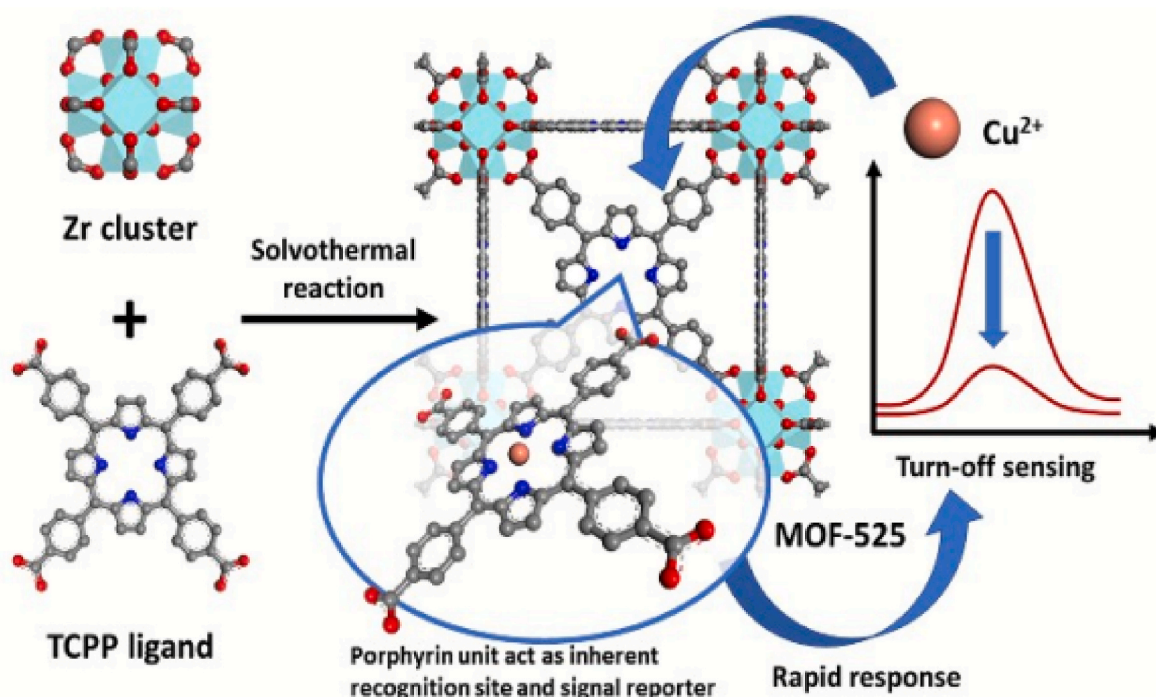


Fig. 7. A strategy of specific luminescent detection of Cu (II) ion with porphyrinic MOF with permission from (Li et al., 2017b) available via license: CC BY-NC 3.0.

world health organization (WHO) guidelines for drinkable water (Li et al., 2017b). The fluorescent intensity of MOF 525 was observed in the occurrence of other various metallic ion. These were because of fact that after interacting with  $\text{Cu}^{2+}$  ions, electronic structure of porphyrin ligand was appreciably modified, causing changes in the crystal's luminescence properties. Second, the MOF's uniform pores have tendency to absorb the analyte and to interact with complex identification position easily thus optimizing ion sensing potential. It was largely owing to their electrical characteristics that complex and metal ions had different quenching effects.

Usually transition metal ions with the filled-d subshell exhibit no quenching phenomenon. However, the charge transfer phenomenon may be attributed to the availability of the unsaturated energy states. The dynamic process is unique from static luminescence quenching because the fluorescence lifetime does not vary as the quencher concentration rises. Cu(II) porphyrin complex's excited state ( $t = 3.56$  ns) deteriorated more speedy as compare to free state ( $t = 6.01$  ns), indicating that quenching of fluorescence could be a continuous process. The porphyrin's electron density may drop after interacting with paramagnetic  $\text{Cu}^{2+}$  ions. Furthermore,  $\text{Zr}_6(\text{OH})_4\text{O}_4$  cluster has the ability to effectively block the  $\pi$ - $\pi$  interaction reduces the quenching effect caused by aggregation between the TCPP molecules (TCPP =  $\text{C}_{48}\text{H}_{22}\text{O}_8\text{N}_4$ ).

PCN-222-Pd (Hf) is another potential porphyrin-based MOF. The nanoscale Pd-PCN-222(Hf) was prepared by the reaction of metal complex of Pd(II) 5,10,15,20-tetrakis (4-carboxyphenyl) porphyrin (Pd-TCPP) and  $\text{HfCl}_4$  in dimethyl formide in the presence of  $\text{CF}_3\text{COOH}$  with heating at  $120^\circ\text{C}$  in an oil bath. Copper (II) ions typically use a fluorescence getting off process, but fluorescence turn on proved difficult due to the fact that metals with paramagnetic properties, such as copper, are excellent quenchers (see Fig. 8) (Chen and Jiang, 2016).

Yan et al. also devised a chemical sensor turn off with pyrene functionalized ligand (MIL53-L) that is a novel  $\text{Cu}^{2+}$  fluorescent MOF that is very efficient and selective (Liu et al., 2016). The organic ligand  $\text{H}_2\text{L}_1$  (L = ligand) was selected because terephthalic acid component can be utilized to build MOF framework, while imine component could be utilized to create binding sites for the MOF.  $\text{H}_2\text{L}_1$  was transformed from monomer of free  $\text{H}_2\text{L}_1$  to excimer of MIL-53 as a result of restricted space

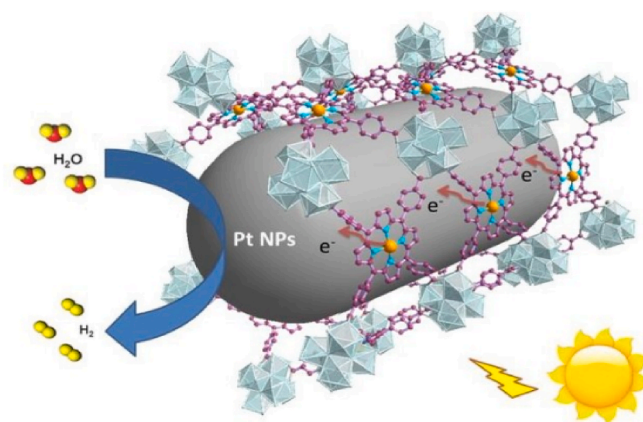


Fig. 8. The possible hydrogen evolution reaction (HER) mechanism of Pt@Pd-PCN-222(Hf). With permission from (Chen and Jiang, 2016) available via license: CC BY-NC 3.0.

inside the MOF (Fig. 9).

Fluorescence quenching was triggered by a conformational shift in the fluorophore produced by the interaction of  $\text{Cu}^{2+}$  ions with the binding sites in the complex. The fluorophore incorporated in the MOF was sterically adjusted throughout the sensing process, resulting in a unique fluorescence change sensing mechanism. It displayed a 567 nm emission band after synthesis of 10 under 337 nm stimulation. The overlaid interactions in the molecule were ascribed to the overlap of pyrene units, which resulted in additional emission bands. There may have been a restricting impact after the creation of MOF since all pyrene molecules were excimers rather than monomers. The suspended pyrene groups pushed together to create excimer due to MOF structure's internal space limitation. The unchangeable limiting effect in MOF, causes pendant group to change its structure, was discovered in this work. This product was appropriate for fluorescence sensing in aqueous conditions due to its water affinity. As a result, the luminous intensity of it was investigated under various metal ions.

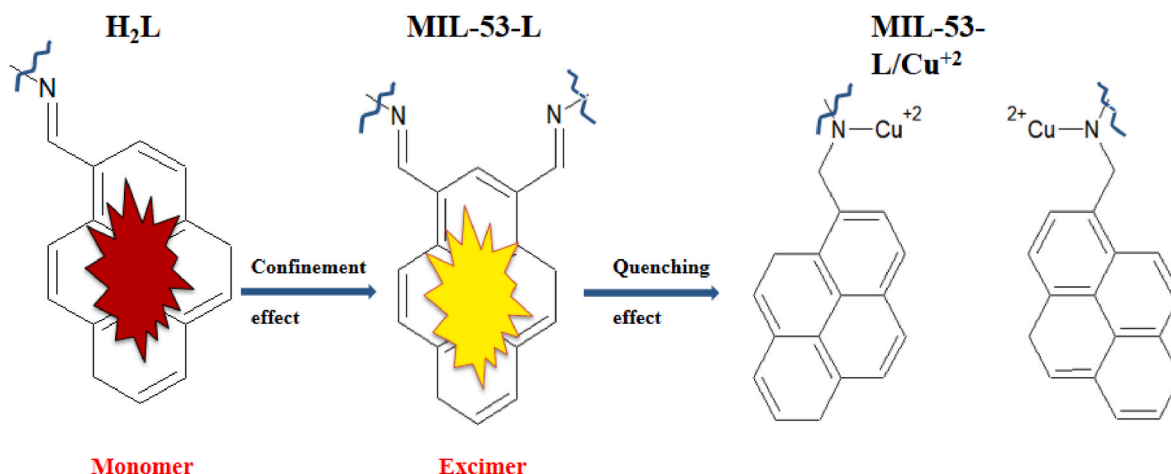


**Fig. 9.** The possible conformational changes of MIL-53-L during preparation of MOF and coordination with imine group after adding  $Cu^{2+}$  with permission from (Liu et al., 2016) © 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Except for  $Cu^{2+}$ , numerous metal ions had no influence on luminous intensity of it after adding  $Cu^{2+}$  ions, the lifespan of it ranged from 677 to 63  $\mu s$ .  $Cu^{2+}$  interacting with nitrogen atom of interior imine group was one probable mechanism for  $Cu^{2+}$  ion-induced light quenching (Fig. 10). After coordination of  $Cu^{2+}$  with amide groups, pyrene groups could not retain its excimer form. In XPS, N 1-S peak moved from 396.7 to 396.8 eV when  $Cu^{2+}$  was added, implying that  $Cu^{2+}$  ions are coordinated to the imine's Nitrogen. The s-s luminescence characteristics of ligand  $H_4L_2$  and MOF were thoroughly investigated above normal heat. Highest emission peaks for  $H_4L_2$  ligand (ex = 280 nm) and MOF (ex = 350 nm) were found at 414 nm, respectively. The emission spectra were found to be very similar to that of  $H_4L_2$  ligand, which was due to  $\pi-\pi^*$  electronic shift. It displayed a good impact on  $Cu^{2+}$  ions when luminescence response of various metal ions was tested. In process of varying  $Cu^{2+}$  ions concentration in solution, quantitative sensitization of quenching behavior was examined. The interaction of  $Cu^{2+}$  cations with the oxygen atoms of ligand, which caused light reduction, was therefore mainly linked to the odd quenching action.

Highly fluorescent branched poly-(ethylenimine)-capped carbon

quantum dots/zeolitic imidazolate framework materials (BPEI-CQD/ZIF-8-MOF) showed ultrasensitive and highly selective detection of  $Cu^{2+}$  ions present in environmental water samples (Dong et al., 2012). The coordination mechanism between  $Cu^{2+}$  ions and MOF was investigated by adding BPEI-CQDs/ZIF-8 to the blue  $Cu^{2+}$  ions in solution. It was clearly observed that almost all blue  $Cu^{2+}$  ions were adsorbed on the deposited BPEI-CQD/ZIF-8 particles. This high adsorption capacity of BPEI-CQDs/ZIF-8 for copper ions is associated with the cationic adsorption properties of the corresponding zinc imidazolate (ZIF-8) and the formation of a complex between the  $Cu^{2+}$  and imidazole moieties of the MOF. (Fig. 11a). Adjustments between  $Cu^{2+}$  ions and BPEI-CQD/ZIF-8 MOF showed that the addition of  $Cu^{2+}$  ions reduced the FL intensity of MOF at 440 nm. On the other hand, no effect on maximum fluorescence emission and excitation wavelength (curves (a), (b), (c), and (d) in Fig. 11b) was observed. UV-Vis absorption studies supported the presence of  $Cu^{2+}$  ions that cause reduced light absorption at 360 nm (curves (e) and (f) in Fig. 11b), which are the highest excitation wavelengths for CQD signal.  $Cu^{2+}$  ions tend to coordinate with amino groups on the surface of BPEI-CQD to form FL-inactive but

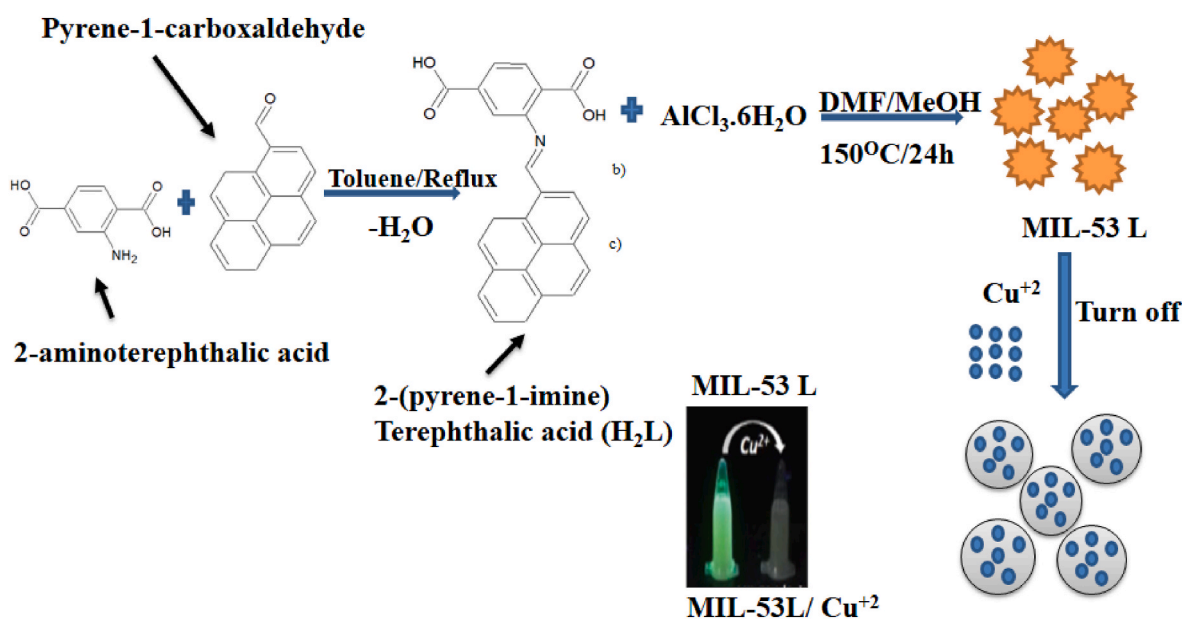


**Fig. 10.** Turn-off of fluorescent chemosensor of micro-sized MIL-53-L on  $Cu^{2+}$  with permission from (Liu et al., 2016) © 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

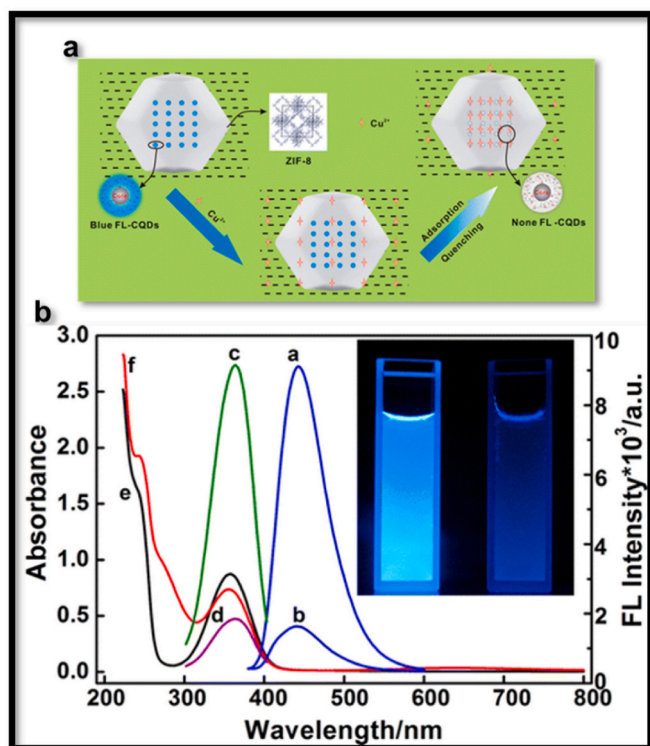


Fig. 11. (a) Mechanism of Cu Sensing on MOF, (b) Fluorescent spectra (emission spectra, a, b; excitation spectra, c, d) and UV-Vis absorption spectra (e, f) with permission of (Dong et al., 2012). Copyright © 2012, American Chemical Society.

UV-active complexes. These results confirm the dual role of the BPEI-CQD/ZIF-8 complex. It tends to strongly adsorb and accumulate Cu<sup>2+</sup> ions and shows a selective FL response to Cu<sup>2+</sup> ions.

Liu effectively developed luminous MOF of transition metal, [NH<sub>4</sub>]<sub>2</sub>[ZnL].6H<sub>2</sub>O, which demonstrates the cation exchange phenomenon in aqueous conditions. The quick exchange in this study happens between NH<sub>4</sub><sup>+</sup> and Cu<sup>2+</sup> ions rather than Zn<sup>2+</sup> ions via the quenching mechanism. [Mg (DHT) (DMF)<sub>2</sub>]<sup>n</sup> (DHT = 2,5-dihydroxyterephthalic acid) (DMF = Dimethyl formamide), an intriguing luminescent MOFs (LMOF) material with great Cu(II) specificity was presented (Li et al. 2014).

Despite presence of some interfering metal ions, the material's fluorescence emission is greatly reduced when exposed to Cu(II), however when free ligand is present this effect is not detected, suggesting that Cu(II) binding is due to OH-groups in tiny holes (Jayaramulu et al., 2012). Cd-MOF-74 was reported for discerning discovery and elimination of Cu ion from physiologically same fluids. MOF-74 is honey comb like network of metal ion and 2,5-dihydroxyterephthalic acid. When Cu ion added to solutions in water of different metallic ions quickly change color from yellow to dark red (Zheng et al., 2017).

Most rhenium-polypyridine complexes exhibit long lived metal-to-ligand charge transfer (MLTC<sup>3</sup>) emission characteristics. Four imine-functionalized bipyridine ligands and their rhenium (I) complexes 1–4 were synthesized and characterized by spectral techniques. They act as selective and sensitive sensors for Cu<sup>2+</sup> ions, as evidenced by changes in UV-visible absorption, emission, and excited state lifetimes. A huge boost is detected in emission intensity, quantum yield and luminescence lifetime with the addition of copper (II) ion due to the limitation of isomerization C=N in the Re(I) complexes (Fig. 12) (Ramdass et al., 2017b).

Taking advantage of its outstanding photophysical properties, numerous ruthenium (II) polypyridyl complexes have been developed and used as optical sensors for metal cations. One of the studies involved the use of ruthenium (II) complexes with heteroditopic 1,10-phenanthroline ligands named from 9 to 11 as an efficient and selective emission sensor for Cu<sup>2+</sup> ions. Reduction of 1,10-phenanthroline-5,6-dione dioxime with sodium dithionite or formamidine sulfinic acid and picolinic acid or its derivatives results in significant yields of the ligands H<sub>2</sub>L<sub>9</sub> and H<sub>2</sub>L<sub>10</sub> at 54% and 52%, respectively. It was generated. Ru<sup>2+</sup> complex named 9–11 was also synthesized by reacting RuCl<sub>3</sub>·3H<sub>2</sub>O or Ru (bpy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O (bpy = 2,2'-Bipyridine) with the appropriate ligand under reflux conditions. Complexes 9–11 show typical MLCT absorption and emission bands at 450 nm and 620 nm, respectively. The addition of Cu<sup>2+</sup> ions gradually reduce the emission intensity of 9–11. Adding 2 equivalents of Cu<sup>2+</sup> ions to 9–11 completely quenches the luminescence. To characterize the selectivity of complex 9 to Cu<sup>2+</sup> ions, changes in emission intensity as a function of pH were investigated with various metal ions. A significant reduction in emission intensity at pH 5 is achieved only in the presence of Cu<sup>2+</sup>, which contains complex 9. The addition of excess other metal ions with the Cu<sup>2+</sup> ions does not show a significant change in the emission intensity observed with complex 9 and Cu<sup>2+</sup> alone. Therefore, these complexes act as excellent on/off sensors for Cu<sup>2+</sup> ions (Ramdass et al., 2017a).

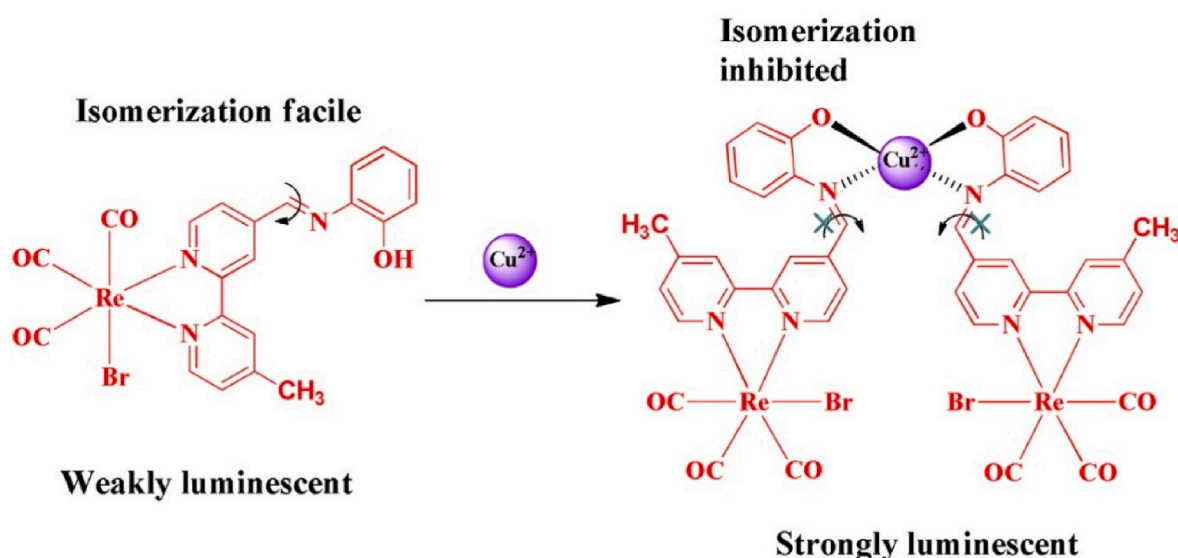


Fig. 12. Inhibition of Re(I) complex isomerization after incorporation of copper ion with permission from (Ramdass et al., 2017b) © 2016 Elsevier B.V.

A new class of cyclometallated iridium (III) complexes named 16 has emerged as a potential platform for use as phosphorescent sensors.  $[(\text{Phpy})_2\text{Ir}(\text{III}) (\mu\text{-Cl})]$  ( $\text{Phpy} = 2\text{-phenylpyridyl}$ ), this iridium based complex was prepared by heating a mixture of 2 (ppy = 2-phenylpyridine). An ion sensor is produced and 2- (benzo [b] thiophen-2-yl) -5- (di- (2-picoryl) aminomethyl) pyridine, as shown in the figure at 130 °C. (Fig. 12 c). The copper ion receptor di (2-picoryl) amine (DPA) is bound to a (2'-benzo [b] thienyl) pyridine (btp) ligand via a methylene linker (Ramdass et al., 2017a).

The green (470–570 nm) double phosphorescence from the bi pyridine (ppy) ligand and the red (580–700 nm) double phosphorescence from the (2'-benzo [b] thienyl) pyridine (btp) ligand appears in the absence of  $\text{Cu}^{2+}$  ions. When  $\text{Cu}^{2+}$  ions are added to complex 16, a complex is formed between complex 16 and Di (2-pyridyl)amide (DPA) and  $\text{Cu}^{2+}$  ions, so the red emission is preferentially extinguished. In addition, there was change in luminescence due to copper using the reduced phosphorescence lifetime of red luminescence. These studies confirmed the selective quenching of red phosphorescence which is due to the proximity of the btp ligand to the paramagnetic  $\text{Cu}^{2+}$  center (a simple energy transfer mechanism). The Joblonski plot shows that the stoichiometric ratio of  $\text{CuCl}_2$  to the DPA receptor is 1: 2. The reversibility of the  $\text{Cu}^{2+}$  ionic bond and the resulting changes in phosphorescence intensity ratio and lifetime value can also be investigated by adding  $\text{Na}_2\text{EDTA}$  to the 1: 2 ratios. Complex 16 exhibits moderate cytotoxicity to HeLa cells, but within the cell it produces a phosphorescent signal via both the green (510–560 nm) and red (>600 nm) channels. HeLa cells treated with  $\text{Cu}^{2+}$  ions selectively quench the red emission intensity of complex 16, but the green channel image remains relatively intact (Turba et al., 2008; Antonioli et al., 2009).

Porphyrin has interesting properties such as high absorption coefficient in the visible region, adjustable fluorescence emission, and high stability to light and chemical reactions, so it is an interesting class of luminescence chemical sensors used for specific analytes. In 2007, Ye et al. Synthesized 5- (p-N, N'-bis (2-pyridyl) amino) phenyl-10,15,20-tris (p-methoxyphenyl) porphyrin zinc complex (named as complex 17) by Ullmann coupling. Reaction of 5-(p-bromophenyl)-10, 15, 20-tris (pmethoxyphenyl) porphyrin zinc and 2,2'-dipyridylamine (dpa) by using Cu powder and  $\text{K}_2\text{CO}_3$  as catalysts and bases, respectively was performed. In complex 17, zinc porphyrins act as fluorophores, and dpa bound to zinc porphyrine act as metal ion recognition and binding sites [64, 65]. No significant change in the Soret band at 427 nm is obtained when transition metal ions are added to complex 17  $\text{CHCl}_3$  solutions. When excited at 435 nm, complex 17 emits sharp = 5.8%) with  $\text{CHCl}_3$ .  $\Phi$  The band is 608 nm, the shoulder is 656 nm, and the lifetime is 1.53 ns (the emission intensity of complex 36 is suppressed by 76% by the addition of  $\text{Cu}^{2+}$  ion, and the selective complex formation with  $\text{Cu}^{2+}$  ion is 1: 1 When ethylene diamine tetra acetic acid (EDTA) is added to the complex solution of  $6.31 \times 10^5 \text{ M}^{-1}$  binding constant 17 and  $\text{Cu}^{2+}$ , the fluorescence signal at 608 nm is restored, indicating that the sensor is reversible to  $\text{Cu}^{2+}$ . The  $\text{Cu}^{2+}$ -ion bond at complex 17 is much stronger (5x) than other metal ions (Callan et al., 2005).

#### 6.4. MOFs as sensors for $\text{Fe}^{3+}$ detection

$\text{Fe}^{3+}$  ions are among the most important metal ions in humans to transport oxygen to blood. It is also a redox enzyme promoter, as well as a component of hemoglobin and various enzymes. Abundance or deficiency of  $\text{Fe}^{3+}$  ions, for example, can cause illnesses including Alzheimer's, anemia and diabetes. As a result, many MOF-based sensors capable of identifying trace levels of  $\text{Fe}^{3+}$  have been reported. Due to its  $d^5$ -paramagnetic structure,  $\text{Fe}^{3+}$  is regarded as an effective quencher, as previously described (Varnes et al., 1972). As a result, the majority of MOFs used to detect iron are "turn-off" sensors.

Based upon cation exchange quenching effect, a highly selective and strong fluorescent MIL-53 was prepared. The MIL-53 structure consists of inorganic  $[\text{M} - \text{OH}]$  chains, which are connected to four neighboring

inorganic chains by terephthalate-based linker molecules.  $\text{Al}^{3+}$  present on fluorescent MOF was swapped with target ion, iron in water media, changing structure into a weak fluorescent MIL-53 (Liu et al.). Another example of a cation exchanger is a stable Zn-based HPU-1. (HPU-1 =  $\{[\text{Zn}(\text{DPTMIA})(\text{H}_2\text{O})_2(\text{DMF})0.5]\}_n$ ,  $\text{DPTMIA} = (5-(3,5\text{-di-pyridin-4-yl-}[1,2,4]\text{triazol-1-ylmethyl})\text{-isophthalic acid})$ ). The quenching effect is caused by the transition of the parent framework to  $\text{Fe}^{3+}@\text{HPU-1}$ , verified by the powder XRD data of  $\text{Fe}^{3+}$  treated HPU-1 compared to parent MOF. Within the framework, the exchange of  $\text{Fe}^{3+}$  ions with  $\text{Zn}^{2+}$  ions decreases energy transmission from ligands to  $\text{Zn}^{2+}$ , resulting in a dramatic quenching effect (Fig. 13) (Li et al., 2017a).

A competitive absorption process causes luminescence to be quenched by overlapping the metal ion's absorption and excitation band of host material. Zhao developed two luminous 2D  $[\text{Zn}_2(\text{TPC}_4\text{A})(\text{DMF})(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$  and 3D  $\{[(\text{CH}_3)_2\text{NH}_2]_2[\text{Zn}(\text{TNC}_4\text{A})]\}[(\text{CH}_3)_2\text{NH}_2]_2[\text{Zn}(\text{TNC}_4\text{A})]\}[(\text{CH}_3)_2\text{NH}_2]_2[\text{Zn}(\text{TNC}_4\text{A})]\} \cdot 4\text{H}_2\text{O}$  MOFs having phenyl and naphthyl functional groups for selective detection of  $\text{Fe}(\text{III})$  and  $\text{Fe}(\text{II})$ . Both ions cause limitation of framework's fluorescence strengths (Zhao et al., 2016). A hydrophilic MOF with a twofold describing 3D transition to metal framework, exhibits spectacular stability in water and have enhanced selectivity for  $\text{Fe}^{3+}$  ion with resistance to other interfering metal ions. The quenching action occurs as a result of the  $\text{Fe}^{3+}$  ion and the framework competing for excitation wavelength energy absorption (Hou et al., 2016).

There are three MOFs which have various coordination ways (Han et al., 2017),  $[\text{Zn}_2(\text{OBA})_2(\text{BTP})]$  ( $\text{OBA} = 4,4'\text{-oxidibenzoic acid}$ ,  $\text{BTP} = 3,5\text{-bis}(5\text{-(pyridin-4-yl)thiophen-2-yl)pyridine}$ )  $[\text{Ni}(\text{OBA})_2(\text{BTP})_2(\text{H}_2\text{O})_2]$  and  $[\text{Cd}_2(\text{OBA})_2(\text{BTP})](\text{H}_2\text{O})]$  were investigated to see how various coordinating environments affected their sensing abilities. The nitrogen available at the terminal position of ligand BTP in Zinc MOF, whereas nitrogen in central part is exposed in holes inside the

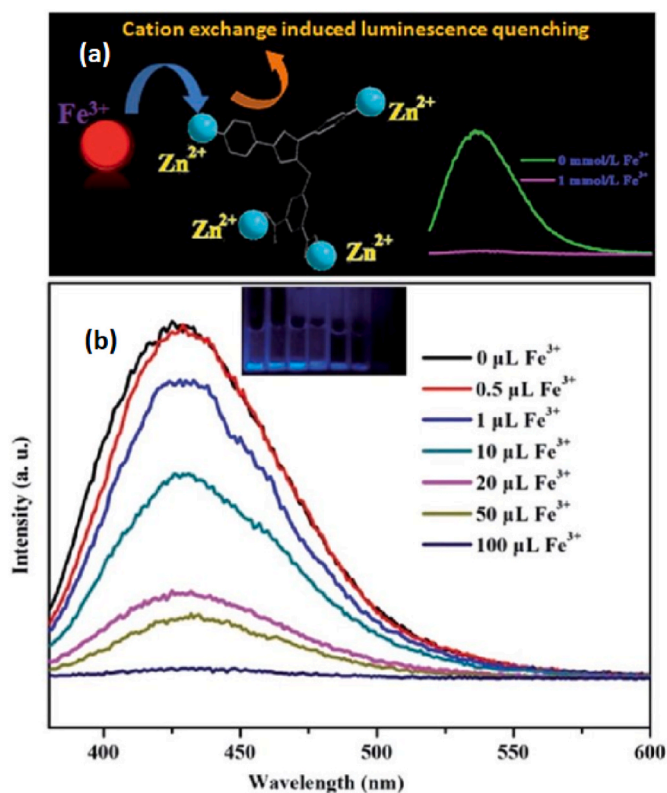


Fig. 13. (a) Schematic representation of the sensing mechanism. (b) Fluorescence emission spectra of HPU-1 (2 mg) in aqueous solutions of various concentrations of  $\text{Fe}^{3+}$  (Li et al., 2017a). Figure reproduced under permission (Li et al., 2017a), Available via license: CC BY 3.0.

framework for ion sensing. The center nitrogen atoms in Ni-MOF were coordinated to the core Nickel, while terminal nitrogen atoms are for detection of ions, but in Cadmium-MOF, all nitrogen atoms are attached to  $\text{Cd}^{2+}$  cations, generating deformed two folds 3D network. Different outcomes are obtained as a result of the variations in coordinating sites. When three MOFs were submerged in metal solutions, the  $\text{Fe}^{3+}$  metal ion had significant impact on luminescence quenching especially in the Cd-MOF, which had LOD 0.36 M.

Overlapping of  $\text{Fe}^{3+}$  ions absorption band with Cd MOF excitation wavelength of accounts for strong quenching effect observed in Cd-MOF, whereas partial overlapping occurs in the other two MOFs, resulting in mild quenching. Chen et al. prepared two luminous MOFs, [Cd(L)(BPDC)]( $\text{H}_2\text{O}$ )<sub>2</sub> (BPDC = 4,4'-biphenyldicarboxylic acid) and [Cd(L)(SDBA)( $\text{H}_2\text{O}$ )]( $\text{H}_2\text{O}$ )<sub>0.5</sub>, (SDBA = 4,4'-sulfonyldibenzoic acid) with good dual fluorescence characteristic and considerable luminosity reduction along slaking % quenching oercent (QP) of 57 and 52.5 percent in  $\text{Fe}^{3+}$  presence, which is greater than quenching percent (QP) of other ions (Chen et al., 2017). Another fluorescent sensor composed of a novel 3D porous Cd-MOF for  $\text{Fe}^{3+}$  ions detection from aqueous phase was developed (Gai et al., 2018). The titration studies on  $\text{Fe}^{3+}$  revealed that the fluorescence sensor has a rapid identification for  $\text{Fe}^{3+}$ , with a limit of detection  $10^{-5}$ . Furthermore, the power transmission pathway since ligand network to Cd (II) ion may responsible for luminescence caused by addition of  $\text{Fe}^{3+}$ . In difference,  $\text{Fe}^{3+}$  is frequently detected using lanthanide luminous MOFs (Ln-MOFs) that are water stable.

Two MOFs luminous such as [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>8</sub>(H<sub>2</sub>O)<sub>4</sub> (L<sub>1</sub>)<sub>2</sub>] (BUT-14) and [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>8</sub>(H<sub>2</sub>O)<sub>4</sub> (L<sub>2</sub>)<sub>2</sub>] (BUT-15) were developed by Wang et al. are a great illustration of the FRET and PET. In aqueous media, both MOFs have a strong fluorescence that can only be suppressed by a modest amount of  $\text{Fe}^{3+}$  ions. As for FRET, high spectrum overlaps between  $\text{Fe}^{3+}$  ion's absorption and emission bands of BUT-14 and BUT-15 is comparable with the reducing efficiency seen for  $\text{Fe}^{3+}$ , BUT-15, on the other hand, has a larger quenching impact than BUT-14 in comparison. This finding proves that fluorescence quenching isn't only due to FRET. Electrons on the eager condition moved toward the lowest occupied molecular orbital (LUMO) of  $\text{Fe}^{3+}$  ions when they were added into systems then returned to ground state of ligands through a radiation channel, results in substantial fluorescence. The availability of N atoms in pyridine rings, which may give electrons to  $\text{Fe}^{3+}$  ions, contributes to BUT-15's increased quenching efficiency (Wang et al., 2017).

Wang prepared a functionalized UMCM-1-  $\text{NH}_2$ , UMCM-1-NH(2) is an NH(2)-BDC derivative of UMCM-1 (University of Michigan Crystal-line Material-1), a MOF having both NH(2)-BDC and BTB (BTB = 4,4',4''-benzene-1,3,5-triyl-tribenzoate) linkers with Zn (4)O SBUs. This MOFs with amine group are a good choice for usage as an extremely delicate metallic ion probe (Wang et al., 2009). Ligand to ligand charge transfer is responsible for the luminescence of UMCM-1 and UMCM-1-NH<sub>2</sub>. Because of amino binding sites existence inside porous framework, amino modified MOF material has a greater capability for sensing  $\text{Fe}^{3+}$  ions. Fluorescence quenching in this study is mediated by  $\text{Fe}^{3+}$  ions attributed to donor acceptor electron transfer pathway. The first innovative photo luminescent cadmium MOF, [Cd (5-asbraz (bimb))]<sub>n</sub>, built employing a various-functional ligand along receptive detecting characteristics for sensing very low concentration of  $\text{Fe}^{2+}$  ion (1 ppm) in environment. Response to fluorescence was quenched (turned off), and the spectrum overlap between the  $\text{Fe}^{3+}$  ion's absorption and emission band of complex, reveals that stronger quenching effect is attributable to energy transfer mechanism. MOFs having a high sensitivity for iron due to interaction of guest metal ions with host structures are preferred (Liu and Yan, 2016).

To detect  $\text{Fe}^{3+}$  in aqueous solution, a 3D Tb-MOF was developed (Jin et al., 2019). In addition, despite the presence of several other ions, it showed specific sensing abilities of  $\text{Fe}^{3+}$  and unaffected. The quenching mechanism revealed that  $\text{Fe}^{3+}$  ion arrived station to impede projection effect, causing quenching. Chen and his colleagues too produced a Tb-MOF along a high transmittance quenched  $\text{Fe}^{3+}$  well. Some

functionally connected elements, such as  $\text{Fe}^{3+}$  ions and Vitamin B significant for living organisms, as we all know (Lustig et al. 2017). Xie created novel kind of stable Zirconium MOF with strong fluorescence emission (FRET and PET) for  $\text{Fe}^{3+}$  detection (Jin et al., 2021).

Vittal reported a water stable Zn-MOF having blue luminescence for  $\text{Fe}^{3+}$  detection. Under acidic and alkaline (pH 4–11) settings, the structure of this chemical was remained intact. MOF was an appropriate chemical sensor for  $\text{Fe}^{3+}$  ions because of high fluorescence emission and great hydrolysis (Rath and Vittal, 2020). The solid-state luminescence of MOF at normal temperature mostly related to d-10 transition obtained from pure ligands. Inadequate organization geometry of Zn(II) with dicarboxylate and tpeb (1, 3, 5- tri-4-pyridyl-1, 2-ethenylbenzene) ligands, stimulating process of ligand to ligand charge transfer (LLCT), might explain blue shift emission as compared to the free ligand. The improved weak contact between nearby ligands was responsible for the considerable rise in luminescence. Adding traces amount of  $\text{Fe}^{3+}$  ions to the solution at 365 nm transformed the color from blue to black, with a quenching effect of 97 percent. Furthermore,  $\text{Fe}^{3+}$  ions had a detection limit of 0.882 M, indicating that it had exceptional sensing capability. Because the analyte's absorption band and excitation band of MOF overlapped significantly, it was possible that analyte may compete with compound for excitation light absorption in the quenching mechanism. As a result of the presence of competitive absorption, excitation efficiency was lowered, and emission quenching could be observed with the naked eye.

#### 6.5. MOFs as sensors for $\text{Zn}^{2+}$ detection

In human system Zinc come at second after calcium and plays essential part in numerous metabolic pathways. It is vital element for immunity and for proper working of sense of smell and taste. Zn may greatly affect the absorption of other essential elements if present in excess (Pamei and Puzari, 2019).  $\text{Zn}^{2+}$  ions are spectroscopic ally inactive due to its filled d<sup>10</sup>-configuration. It is therefore tricky to detect zinc using ordinary spectroscopic techniques. In this regard, fluorescent MOFs have been shown of being an operative alternative tool. Cadmium based LMOFs, [Cd(C<sub>12</sub>N<sub>2</sub>H<sub>8</sub>)(C<sub>7</sub>N<sub>1</sub>O<sub>4</sub>H<sub>3</sub>)] was prepared for discerning recognition of  $\text{Zn}^{2+}$  ions from watered media based on turning on mechanism. This Cd-MOF also helps to distinguish  $\text{Zn}^{2+}$  form counterpart i.e.  $\text{Cd}^{2+}$  ion. The strong linkage between sensed  $\text{Zn}^{2+}$  ion and ligand in complex could be linked to mechanism of sensing. This coordination makes make ligand hard, limiting non-radioactive degeneration by electronic means eager state and cause increased fluorescence. Absorption of  $\text{Hg}^{2+}$  ion into same MOF network leads luminescence decrease which is usually exhibited by the metals having completely filled d subshell (d-10 configuration). This unusual response of  $\text{Hg}^{2+}$  is related to the fact that the charge transfer may exhibit in two ways: one from  $\pi$ -MO of ligand to vacant 6s AO of  $\text{Hg}^{2+}$  and second way is from filled 5 d atomic orbital of  $\text{Hg}^{2+}$  to the lowest vacant molecular orbital of the ligand.

Microbial fuel cells (MFCs) having Zirconium MOFs showed super-microporosity, UiO-66 was applied for targeted sensing of  $\text{Zn}^{2+}$  ions (Fig. 14). UiO-66 is a crystal having metal nodes made of a zirconium oxide complex bridged by terephthalic acid ligand. The mechanism of ion ( $\text{Zn}^{2+}$ ) is based on decomposition of C=N isomerization at a high energy state when  $\text{Zn}^{2+}$  ions coordinate to ligand. The rigidity of complex increases chelation of ligand with  $\text{Zn}^{2+}$  ion, results in intensified fluorescence emission (Pamei and Puzari, 2019).

#### 6.6. MOFs as sensors for $\text{Pd}^{2+}$ detection

A flake like NH<sub>2</sub>-MIL-53(Cr) MOFs was synthesized under reflux conditions and then it was applied for electrochemical lead ( $\text{Pd}^{2+}$ ) finding in the watered solution. Square wave anodic stripping voltammetry (SWASV) method was utilized for the lead ion sensing by using acetate buffer having pH 6.0 under the stirring condition, −0.8 V

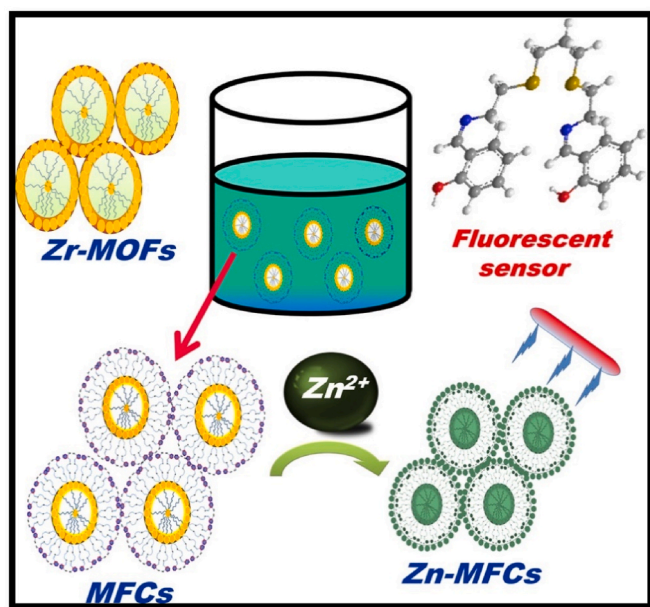


Fig. 14. Super microporous Zirconium Based immobilized with fluorescence for sensing Zinc reproduced with permission of (Pamei and Puzari, 2019) under license of Creative Commons CC-BY-NC-ND.

regeneration potential was applied to working electrode for about 330s (Xu et al., 2013). Between -1 V and -0.2 V, the anodic stripping voltammetry response was recorded. About 1 V desorption potential was applied about 100s for removing the residues. The modified electrode exhibits higher sensitivity, and selectivity towards lead ions detection under the optimum conditions.

The modified and the virgin electrode were poured into  $1 \times 10^{-3}$  mol/litter of metallic ion and 0.2 mol/litter potassium chloride solutions. In order to electrochemical characterization of modified electrode, cyclic voltammetry was performed with potential range and the scanning speed of -0.2 to +0.6 V and 0.1 V/s respectively. Characterization of bare and modified electrode was done by electrochemical impedance spectroscopy. The modified electrode showed decreased in oxidation and reduction peak currents because of poor electrical conductance. Moreover, according to EIS curve, in case of modified electrode, the Ret resistance sharply increased because of forming the blocking layer by  $\text{NH}_2\text{-MIL-53}(\text{Cr})$  results in slow electron migration.

Electrode performance of MOFs for lead ions was compared with  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Zn}^{2+}$  while the concentration used for these ions was 10 times higher as compare to  $\text{Pb}^{2+}$  ions. The results showed mercuric ions gives the largest peak current change and the magnitude of signal introduced by mercuric ions was 16.7% of magnitude induced by lead ions. This result gives the conclusion that this modified electrode is highly selective for lead ions detection. Quantitative determination of lead ions at different concentrations even at micron level can also be performed by using the optimum conditions by using the  $\text{NH}_2\text{-MIL-53}(\text{Cr})$  based MOFs.

Reproducibility of  $\text{Pd}^{2+}$  ions sensing was also evaluated by utilizing the five modified electrodes and lead ions concentration was detected all from these. Peaks currents were observed of  $-8.07 \times 10^{-6}$ ,  $-8.05 \times 10^{-6}$ ,  $-8.18 \times 10^{-6}$ ,  $-8.23 \times 10^{-6}$  and  $-8.10 \times 10^{-6}$  A for all of these and the standard deviation noted was 0.93%. The results indicate the reproducibility measurement of concentration of lead ions (Hamon et al., 2009b).

#### 6.7. MOFs as sensors for $\text{Cd}^{+2}$ detection

$\text{Cd}^{2+}$  is highly poisonous metal for environment as well as for human being. Prolonged gasp of Cd leads towards long-lasting exterminating

and make kidney failure. In this regard, monitoring and detection of  $\text{Cd}^{2+}$  is of great importance.  $\text{Cd}^{2+}$  is detected by minor enhancement technique. Hong created dual interpenetrating Zn-MOF with  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  ions selectivity, which sensed Cadmium and Copper ions through switch on and turn off processes (Lim et al., 2017). Ligand's nitrogen might be employed as a Lewis site to cooperate along incoming metallic ion dispersion toward framework holes. Surprisingly, 60 times rise in fluorescence intensity was observed as compared to without  $\text{Cd}^{2+}$  ions. This was greatest luminous MOF sensor improvement yet documented. As a result, this material might be utilized to create a chemical sensor that is ready to use.

Another electrochemical sensor,  $\text{UiO-66-NH}_2/\text{PANI}$  ( $\text{PANI}$  = was synthesized for  $\text{Cd}^{+2}$  sensing, by MOFs  $\text{UiO-66-NH}_2$  functionalized with poly aniline ( $\text{PANI}$ ) (Wang). The responses of 100  $\mu\text{g/L}$ –1 Cd (II) in terms of oxidation peaks was observed by using differential pulse voltammetry (DPV).  $\text{UiO-66-NH}_2$  with coated electrode surface displayed significant increase in oxidation peak. Electrochemical analysis results of Cd(II) at the  $\text{UiO-66-NH}_2/\text{PANI}/\text{GCE}$  at different attentions displayed a linear relation between oxidation peak currents and concentration of Cadmium (II) in a wider range of 0.5 to 600  $\mu\text{g/L}$ –1 having a detection limit 0.3  $\mu\text{g/L}$ –1 (Xiao et al., 2014). The selective detection of the sensor towards  $\text{Cd}^{+2}$  was performed by addition of interfering cations and anions into cell containing 10  $\mu\text{g/L}$ –1 of Cd(II). The results in the presence of other related ion displayed that tolerance level up to  $\pm 5\%$ . Feasibility of this sensor was for practical detection of Cd(II) in various water sources was verified. Experimental outcomes proved that  $\text{UiO-66-NH}_2/\text{PANI}$  modified GCE is quite promising sensor for Cd(II) in environmental and biological examples.

A MOF based sensor  $\text{CH}_3\text{NH}_3\text{PbBr}_3/\text{MOF-5}$  ( $\text{MOF-5} = \text{Zn}_4\text{O}(\text{BDC})_3$ , where  $\text{BDC}^{2-} = 1,4\text{-benzodicarboxylate}$ ) having appropriate moisture resistant characteristics and enhanced luminescence sense to probe  $\text{Cd}^{2+}$  was developed by inserting perovskite quantum dots ( $\text{CH}_3\text{NH}_3\text{PbBr}_3$ ) into MOF-5 (Zhang et al., 2018). Another porphyrinic zirconium-based LMOF was developed by Moradi et al. obtained a highly selective sensing of  $\text{Cd}^{2+}$ . In this MOF, the pyrrole Lewis base site as a luminescent moiety which interact with  $\text{Cd}^{2+}$  thus resulting in a luminescent quenching (Moradi et al., 2020). In 2020, Mandal and his coworkers reported Exceptional fluorescent MOF-based probe for selective and sensitive detection of  $\text{Cd}^{+2}$  using ligand thiophene-2,5-dicarboxylic acid ( $\text{H}_2\text{tdca}$ ) and  $\text{N}_0\text{-bis}(4\text{-pyridylmethylene})\text{-1,4-benzenediamine}$  (bppd) and zinc nitrate salt thus giving MOF of  $[\text{Zn}_2(\text{tdca})_2(\text{bppd})_2]$ . The number of LMOF-based sensors has been reported as a potential probe for detecting  $\text{Cd}^{2+}$  ions, but is primarily used in dimethyl formide (DMF) due to its poor water stability. Further investigation is needed to detect  $\text{Cd}^{2+}$  in water (Yang et al., 2021).

#### 6.8. MOFs as sensors for $\text{Hg}^{+2}$ detection

Mercury ions ( $\text{Hg}^{+2}$ ) are considered as highest toxics and dangerous metallic ion. Saha with colleagues mimicked the natural light system's design idea and created a column-type paddle wheel of Zn MOF, with NDC support as power providers and  $\text{N,N'-di}(4\text{-pyridyl})\text{thiazolo-[5,4-d]thiazole}$  (DPTTZ) columns working as power receivers. It maintained a distinctive fluorescence signal for  $\text{Hg}^{+2}$  ions demonstrating that it can be detected  $\text{Hg}^{2+}$  ions preferentially. Another novel fluorescent sensor was described by Chen et al. utilizing the lanthanide based MOF for mercury ion sensing (Li et al., 2016). Briefly, fluorescent Eu-MOF was prepared, and its coordination complex was developed with imidazole-4, 5-dicarboxylic acid. The addition of mercury ions to the developed MOF resulted in strong coordination of imidazole with the mercury ions resulting in the release of imidazole from the MOF therefore reinstating the release. It modified sensor was also reported to sense  $\text{Ag}^{+}$  ions.

$\text{Ru-MOF}$  was prepared and allowed to interact with various metal cations, and it was observed that only  $\text{Hg}^{2+}$  have tendency to eliminate the yellow component ( $\text{Ru}(\text{bpy})_3^{2+}$ ). Experimental data demonstrated that, when  $\text{Ru-MOFs}$ ,  $\text{H}^{+}$ , other metal ions, anion and even Methyl

mercury ion ( $\text{CH}_3\text{Hg}^+$ ) were allowed to interact with MOF moreover, no release was observed in pure water as well as in acid media. These findings represented that there is an extra ordinary selective coordination between  $\text{Hg}^{2+}$  and the Ru-MOFs (Lin et al., 2015b) (Fig. 15). Sudden release of  $\text{Hg}^{2+}$  may be related to the porosity available in MOF, leading to absorption and coordination of  $\text{Hg}^{2+}$  and Ru ( $\text{bpy}$ ) $_3^{2+}$ . Ru ( $\text{bpy}$ ) $_3^{2+}$  can be trapped in the framework by electrostatic interaction with negatively charged MOFs [90]. When  $\text{Hg}^{2+}$  is added to the medium, adenine tends to form a complex [91], increasing the positive charge near Ru ( $\text{bpy}$ ) $_3^{2+}$  and the electrostatic repulsive force from the structure to Ru ( $\text{bpy}$ ) $_3^{2+}$  can be eliminated. As a result, the release of large seeds (ie, Ru ( $\text{bpy}$ ) $_3^{2+}$  ions) cleaves the MOF. Degradation of the outer Ru-MOF layer exposed the inner part to  $\text{Hg}^{2+}$  further degrading the inner framework until Ru-MOF was completely decomposed. These features make Ru-MOF-based sensors suitable for measuring ultra-trace  $\text{Hg}^{2+}$  ions at high concentrations of other metal ions. A real application was run to detect the amount of  $\text{Hg}^{2+}$  ( $2.49 \pm 0.075$  nM) in the Min River sample. These results confirm the legitimacy of this MOF-based sensor that detects  $\text{Hg}^{2+}$  in real-world.

The Eu/IPA CPNPs (CPNPs = lanthanide coordination polymer, IPA = isophthalic acid) was prepared by solvothermal method and was used for electrochemical sensing of  $\text{Hg}^{2+}$  present in biological samples (Li et al., 2016). Imidazole, a heterocyclic compound has tendency to coordinate with  $\text{Hg}^{2+}$  and oxygen atom. Greater binding constant of imidazole with  $\text{Hg}^{2+}$  and availability of carboxylate groups tends to form stable complexes of imidazole with metal cations (J. M. Thomas, 2004).

Selection of Eu/IPA-Im (Im = imidazole-4,5-dicarboxylic acid) to form stable complex with  $\text{Hg}^{2+}$  would be a brilliant choice as compared to other metal ions. The compound exhibited a strong red fluorescence due to  $\text{Eu}^{3+}$  electronic transitions of  $5D_0$  to  $7F_1$  as presented in Fig. 16. The results indicated that the absorbed radiation can be transferred to  $\text{Eu}^{3+}$ . However, on adding Im, Eu/IPA CPNPs fluorescence decreases. The transfer of Fluorescence resonance energy from Eu/IPA CPNPs to Im can be omitted because there is no spectral overlapping (Li et al., 2016).

The fluorescent of MOF increases rapidly with the addition of  $\text{Hg}^{2+}$  approached a constant value in a time span of 2 min. The fluorescent

intensity of MOFs complex exhibited a linear correlation ranging 2 nM - 2  $\mu\text{M}$  and detection limit about 2 nM, lower than allowable  $\text{Hg}^{2+}$  level in normal water (10 nM) allowed by The Environmental Protection Agency (EPA) (U. S. EPA). The fluorescent behavior of Eu/IPA-Im complex was studied, and it was observed in the presence of other metal ions it was deduced that only addition of  $\text{Hg}^{2+}$  can lead a substantial increase in fluorescence of Eu/IPA Im complex. The experimental outcomes proved that Eu/IPA-Im complex displayed high sensitivity towards for  $\text{Hg}^{2+}$ . Practical application of Eu/IPA-Im complex was conducted to measure the levels of  $\text{Hg}^{2+}$  in urine samples. The results displayed those recoveries of  $\text{Hg}^{2+}$  in urine were >95%. This indicated that targeted  $\text{Hg}^{2+}$  could be measured with good precision and the described sensor can be used for  $\text{Hg}^{2+}$  in urine samples.

In 2018, Samanta, P. and coworkers designed UiO-66@butyne luminescent MOF having excellent physicochemical stability to detect  $\text{Hg}^{2+}$ . The MOF was designed by the coordination of a  $\text{Zr}^{4+}$  with 2,5-bis (but-3-yn-1-yloxy) terephthalic acid. The butyne moiety in the MOF served as active site to trap  $\text{Hg}^{2+}$  through oxymercuration process. The MOF exhibited good selectivity for  $\text{Hg}^{2+}$  with a pronounced LOD of 10.9 nmol and a quick response time of 3 min (Samanta et al., 2018).

Zhang et al. reported a series of organically modified LMOFs having central metals ( $\text{Al}^{3+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Ti}^{4+}$ ) in high oxidation states. They used amino group to modify LMOFs which served the purpose to detect  $\text{Hg}^{2+}$  by the effect of ligand to metal charge transfer (LMCT). It was observed that Al based  $\text{NH}_2\text{-MIL-53(Al)}$  exhibited tremendous ability to probe  $\text{Hg}^{2+}$  with high selectivity over a wider range of pH and LOD (0.15  $\mu\text{M}$ ) and high anti-interference capacity. (Zhang et al., 2019).

Khatun et al. fabricated a LMOF;  $\text{Zn}_2(\text{NDC})_2$  (DPTTZ) with  $\text{Hg}^{2+}$  detection function. MOF photoluminescence showed a significant red-shift to 450 nm and then quenched in the presence of  $\text{Hg}^{2+}$ . The average fluorescence lifetime of MOF by using different  $\text{Hg}^{2+}$  concentrations was recorded as 9.57, 7.89, and 7.25 ns, respectively [97]. Recently, a fluorescent “turn-on” probe (BA-Eu-MOF) is used to probe  $\text{Hg}^{2+}$  and  $\text{CH}_3\text{Hg}^+$ . In BA-Eu-MOF, boric acid (BA) as an electron-withdrawing group showed a passivation “antenna” effect, causing a weak red emission in water. In this way, the “antenna” effect of the ligand was affected and red emission increased. As the concentration of

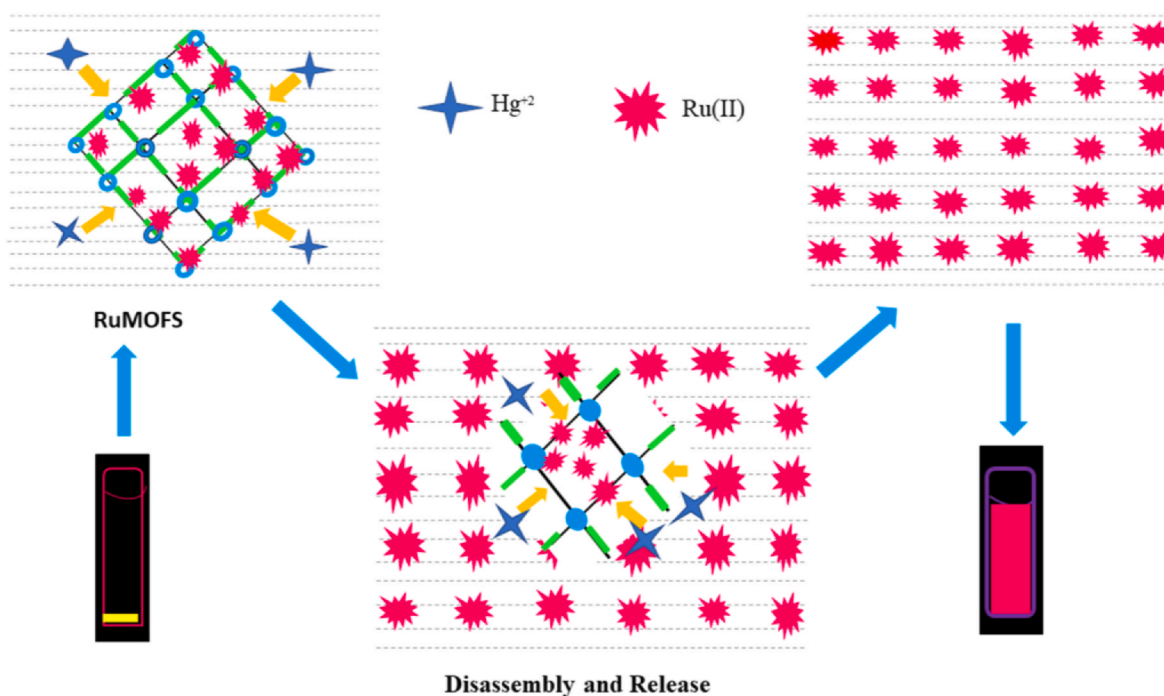


Fig. 15. Selective  $\text{Hg}^{2+}$ -Triggered Disassembly and Release Based on Ru-MOF with permission from (Lin et al., 2015b) Copyright © 2015 American Chemical Society.

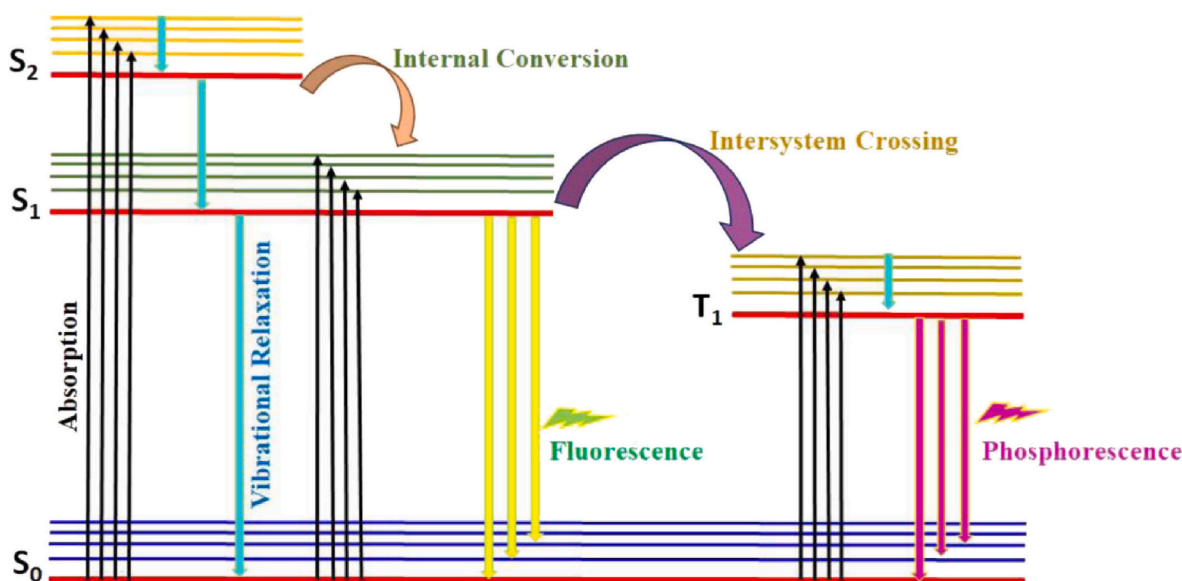


Fig. 16. Brief Overview of Jablonski Diagram with permission from (Pamei and Puzari, 2019) Under a Creative Commons license.

Hg<sup>2+</sup> and CH<sub>3</sub>Hg increases, the red emission increases, so the chromaticity can be confirmed with the naked eye under the ultraviolet rays of 365 nm (Wang et al., 2020).

Recently, fluorescein hydrazide-fabricated Ni(MOF); [Ni<sub>3</sub>(BTC)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>](DMF)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub> was reported to detect Hg<sup>2+</sup> ions. It has been confirmed that upon mixing this MOF with Hg ions could produce a new peak in absorption at 583 nm, with a chromogenic change to pink. The experiments with this sensor also confirmed that it is reversible and reproducible. In addition, the concentration of Hg<sup>2+</sup> ions in various types of water samples was detected (Helal et al., 2021).

#### 6.9. MOFs as sensors for Pb<sup>2+</sup> detection

Pb<sup>2+</sup> is considered as in one of the leading pollutant transition metals which can induce lethal effects on human health. It is therefore ever needed to monitor and detect the concentration of Pb<sup>2+</sup> ions. Ji et al. developed a lanthanide-based MOF sensor to detect the Pb<sup>2+</sup> ion (Ji et al., 2017). Tb-MOF namely [Tb(L)(H<sub>2</sub>O)<sub>5</sub>]n (H<sub>2</sub>L = 3,5-dicarboxyphenol) exhibited a quite sensitive green luminescence incited by the efficient antenna effect of the ligands, and the detection limit for Pb<sup>2+</sup> ions was as low as 10<sup>-7</sup> M. Subsequently, the researchers fabricated three Cd(II) MOFs namely [[Cd(BIPA)(IPA)]·DMF]<sub>n</sub>, [[Cd(BIPA)(HIPA)]·DMF]<sub>n</sub>, and [[Cd(BIPA)(NIPA)]·2H<sub>2</sub>O]<sub>n</sub> to probe Pb<sup>2+</sup>. The fluorescence detection studies displayed that MOF and [[Cd(BIPA)(IPA)]·DMF]<sub>n</sub> and [[Cd(BIPA)(HIPA)]·DMF]<sub>n</sub> have dual response towards detection of Hg<sup>2+</sup> and Pb<sup>2+</sup> ions (Wang et al., 2018, 2021a).

Wang et al. successfully developed an excellent fluorescent Zn-TCPP-MOF (H<sub>2</sub>-TCPP = meso-Tetra (4-carboxyphenyl)porphine) by combining Zn<sup>2+</sup> with H<sub>2</sub>TCPP and 2-(4-(1,2,2-triphenylvinyl)phenoxy) acetic acid (TPE-COOH) to probe Pb<sup>2+</sup> ions present aqueous bodies. In the present study, the MOF having a dark red color changed to colorless upon entry of Pb<sup>2+</sup> ions, which is visible with naked eyes. A comparative behavior Zn-TCPP-MOF with other MOFs depicted that it can detect Pb<sup>2+</sup> up to (LOD) of 4.99 × 10<sup>-8</sup> M. (Wang et al., 2021b). Another study reported that SO<sub>3</sub>H-UiO-66(Zr) MOF system usually applied in the last-end of a visual strength, have tendency to detect Pb<sup>2+</sup> in water at 27.3, 45.5, and 66.0 ppm levels. The plausible mechanism suggested that development strong electrostatic attraction adsorption of [Pb(OH<sub>2</sub>)<sub>6</sub>]<sup>2+</sup> in water on SO<sub>3</sub>H-UiO66(Zr) which leads to removal of Pb<sup>2+</sup> (Nazari et al., 2021).

#### 6.10. MOFs as sensors for lanthanides

MOFs composed of Lanthanides metal ions have ability to serve as a host and antenna wire to develop an unbending framework that can shield lanthanide cations from dissolvable extinguishing, furthermore, sharpen them to frame tunable fluorescent materials. For sensing of Eu<sup>3+</sup> and Tb<sup>3+</sup>, Dong et al. discovered a MOF (Majee et al., 2019) with typified [Mn(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> cations (Li et al.). The MOF has tendency to sense lanthanide ions through cation exchange phenomenon. The findings of Sun and Liu explored the Cd-MOFs can be employed for selective detection of Tb<sup>3+</sup>. Liu et al. discovered that Mg-MOF can sense Eu<sup>3+</sup> (Wang et al., 2007).

#### 6.11. MOFs as sensors for detection of miscellaneous transition metal ions

A robust MOF, Eu<sup>3+</sup>MIL-121 was reported for selective sensing of aqueous Ag<sup>+</sup> ions. The MOF exhibited tremendous luminescent enhancement within 5 min and ultra-sensitive detection limit (0.1 mM). 2,2'-bipyridine 5,5'-dicarboxylic acid (bpydc) is a well known aromatic compound has tendency to develop coordination with transition metal ions. Two metal organic frameworks (MOFs), UiO-bpydc and Eu-bpydc functionalized with bpydc were utilized to develop electrochemical sensors for transition metal ion (L. Li and Zhao; Lin et al., 2015a). The UiO-bpydc is composed of Zr<sub>6</sub> (μ<sub>3</sub>-O)<sub>4</sub> (μ<sub>3</sub>-OH)<sub>4</sub> nodes and bpydc bridging ligands (R.-B. Lin and Chen, 2013). The bpydc serve the purpose of accumulation of cations through chelation as well as fluorescent read out signal. The extraordinary stability of UiO makes its promising sensor for applications in aqueous as well as organic solvents. The Eu-bpydc is comprised of Eu<sup>3+</sup> ions and bpydc ligands to produce one dimensional open channel. Eu<sup>3+</sup> is an ideal luminescent reporter because of narrow emission line width. The fluorescence response of UiO-bpydc in the presence of 4.95 μM of metal ions.

The experimental results confirmed that Fe<sup>3+</sup> and Cu<sup>2+</sup> have highest effect on the fluorescence quenching of UiO-bpydc and Eu-bpydc. Luminescence quenching of the MOFs at various metal ion concentrations was studied by using Stern-Volmer equation

$$(I_0 / I_1) = 1 + K[M^{n+}]$$

In the equation, I<sub>0</sub> and I<sub>1</sub> stands for luminescent intensities before and after addition of metal ions and K represents the Stern-Volmer constant. From the equation, it as depicted that a detection limit of 3.2 ppb was found for Fe<sup>3+</sup> and <6.4 ppb for Cu<sup>2+</sup>. Particularly, Cu<sup>2+</sup>

produced more quenching response in Eu-bpydc MOF, but not in UiO-bpydc. The reason for no response in case of Eu-bpydc is related to the two adjacent bpy moieties, which are very close to each other and tend to coordinate with same cation in a square planar geometry. Single crystal to metalation of the Eu-bpydc was exhibited by soaking single crystal in  $\text{Cu}^{2+}$  solution. The crystal structure of Eu-bpydc-Cu (I) crystal. An overview of the MOF-based sensors for sensing transition metal ions discussed in this review is presented in Table 2, which depicted that majority of sensing mechanism is cation exchange mechanism between metal ions and MOFs.

## 7. Challenges with MOF based sensors

As discussed earlier that the efficiency of a sensor depends on its sensitivity towards the targeted analyte which is strongly related to the kinetics of the electrochemical process exhibiting in the analyte. Most of the MOFs exhibit decomposition in aqueous media (Burtch et al., 2014) and their electrochemical sensing operation are conducted in aqueous electrolytes. However, Hydrolytic stability of MOFs becomes one of the most critical considerations for their use in electroanalysis. The water molecules have tendency to cleave the metal-ligand linkage and leading to the formation of metal hydroxides/oxides (He et al., 2018). Furthermore, it is well recognized that most MOFs have poor electrical conductance (Hendon et al., 2012). Some strategies for improving electrical conductivity and stability of MOFs during electrochemical processes have been developed. Furthermore, the particle size of MOFs usually lies in micron range which results in poor adhesion between MOFs and the electrode surface. The problem of electrical conductance was solved by the growth of MOF based composites which hold advantages of both MOF and conducting material (such as metal oxides and carbon). The sensitivity of the corresponding electrochemical sensors is expected to improve with the use of MOF-based materials. Generally, it is observed that MOFs composed of ligands containing nitrogen have better hydrolytic stability as compared to the carboxylate-based MOFs so challenge of hydrolytic stability of MOFs can be solved by this. Chemically stable MOFs are developed by careful selection of metal cations with higher oxidation states as nodes and organic linkers (Yuan et al., 2018).

## 8. Mechanism of metal ions detection by MOF based sensors

MOF Based sensors detect various types of cations and anions through fluorescence enhancement or quenching phenomenon and is described as “turnoff” or “turn-on” mechanism respectively. This phenomenon is visible with the naked eye under ultraviolet radiations and exhibits due to molecular interactions between MOFs and analytes. The detected analyte when comes in contact with MOF framework, it interferes with the electronic arrangement of the ligand. Once electrons present in eager singlet state ( $S_1$ ) come back to previous stage ( $S_0$ ), they release photons inducing luminescence. The fluorescence mechanism from a substance can be visualized by Jablonski Diagram as displayed in Fig. 16 (Pamei and Puzari, 2019). Fluorescence enhancement or quenching is stems from the following factors, such as the effect of cation exchange quenching, the effect of competitive absorption quenching and metal-to-host interaction.

Ion exchange is one of the most common methods for detection of cations by MOFs. Metal cations absorb in the MOFs channel and lead towards the blocking, the “antenna effect”. A case study presented that by inserting  $\text{Fe}^{3+}$  into the original Eu-MOF structure, the content of  $\text{Eu}^{3+}$  was significantly reduced which resulted in reduction of fluorescence (Weng and Yan, 2016). Fluorescence enhancement is applied to check marked ions, for instance, Lu-MOF which emits mild red color light at first (due to electron attracting effect, ligand’s antenna effect was doped), but after absorbing  $\text{Hg}^{2+}$  ions it can sense and emit sharp red light (Wang et al., 2020). Another factor responsible for fluorescence enhancement or quenching is modest absorbance of excited light b/w

**Table 2**

Recent overview of MOF-based sensors for transition metal ions and their mechanism of sensing.

| Transition Metal Ion | MOF-Based Sensor                                                                                                                                                                                                                         | Detection Mechanism                     | References               |
|----------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------|--------------------------|
| $\text{Cr}^{+3}$     | 3D Ca-MOF                                                                                                                                                                                                                                | Competitive absorption mechanism        | Chen and Xu (2019)       |
| $\text{Cr}^{+3}$     | Eu-MOF                                                                                                                                                                                                                                   | Cation exchange Quenching Mechanism     | Zhan et al. (2019)       |
| $\text{Cr}^{+3}$     | Eu-MOF                                                                                                                                                                                                                                   | Cation exchange Quenching Mechanism     | Sun et al. (2017)        |
| $\text{Cr}^{+3}$     | Tb-MOF                                                                                                                                                                                                                                   | Cation exchange Quenching Mechanism     | Sun et al. (2017)        |
| $\text{Cr}^{+6}$     | MOF-199                                                                                                                                                                                                                                  | Oxidoreductase                          | Shi et al. (2021)        |
| $\text{Mn}^{+2}$     | MOFs [Zn (dbp)] <sup>n</sup>                                                                                                                                                                                                             | Competitive absorption                  | Wu et al. (2017)         |
| $\text{Mn}^{+2}$     | [Cd (dbp) ( $\text{H}_2\text{O}$ )]<br>2 $\text{H}_2\text{O}$ - $\text{CH}_3\text{CN}$ ] <sup>n</sup>                                                                                                                                    | Competitive absorption                  | Wu et al. (2017)         |
| $\text{Mn}^{+2}$     | $[\text{NH}_4]_2 [\text{ZnL}] \cdot 6\text{H}_2\text{O}$                                                                                                                                                                                 | Host-guest Interaction                  | Liu et al. (2010a)       |
| $\text{Mn}^{+2}$     | MOF-525                                                                                                                                                                                                                                  | Cation exchange quenching mechanism     | Li et al. (2017b)        |
| $\text{Mn}^{+2}$     | PCN-222-Pd                                                                                                                                                                                                                               | Cation exchange quenching effect        | Liu et al. (2016)        |
| $\text{Cr}^{+3}$     | MIL53-L                                                                                                                                                                                                                                  | LLCT mechanism                          | Liu et al. (2016)        |
| $\text{Cr}^{+3}$     | BPEI-CQDs/ZIF-8-MOFs                                                                                                                                                                                                                     | Cation exchange quenching effect        | Lin et al. (2014)        |
| $\text{Cr}^{+3}$     | $[\text{NH}_4]_2 [\text{ZnL}] \cdot 6\text{H}_2\text{O}$                                                                                                                                                                                 | Host-guest Interaction                  | Liu et al. (2010b)       |
| $\text{Cr}^{+3}$     | (Lin et al.) <sup>n</sup>                                                                                                                                                                                                                | Cation exchange quenching mechanism     | Jayaramulu et al. (2012) |
| $\text{Cr}^{+3}$     | Cd-MOF-74                                                                                                                                                                                                                                | PET/FRE mechanism                       | Zheng et al. (2017)      |
| $\text{Cr}^{+3}$     | MIL-53                                                                                                                                                                                                                                   | MLCT mechanism                          | (Liu et al.)             |
| $\text{Cr}^{+3}$     | Zn-based HPU-1                                                                                                                                                                                                                           | UV-Vis, XRD                             | Li et al. (2017a)        |
| $\text{Cr}^{+3}$     | 2D $[\text{Zn}_2 (\text{TPC}_4\text{A}) (\text{DMF}) (\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$                                                                                                                                  | Cation exchange quenching mechanism     | Zhao et al. (2016)       |
| $\text{Fe}^{+3}$     | 3D $[[(\text{CH}_3)_2\text{NH}_2]_2 [\text{Zn} (\text{TNC}_4\text{A})] [[(\text{CH}_3)_2\text{NH}_2]_2 [\text{Zn} (\text{TNC}_4\text{A})] ] [(\text{CH}_3)_2\text{NH}_2]_2 [\text{Zn} (\text{TNC}_4\text{A})] \cdot 4\text{H}_2\text{O}$ | Cation exchange quenching mechanism     | Zhao et al. (2016)       |
| $\text{Fe}^{+3}$     | NNU-1                                                                                                                                                                                                                                    | Cation exchange quenching effect        | Hou et al. (2016)        |
| $\text{Fe}^{+3}$     | $[\text{Zn}_2(\text{OBA})_2(\text{BPTP})]$                                                                                                                                                                                               | Competitive absorption quenching effect | Chen et al. (2017)       |
| $\text{Fe}^{+3}$     | [Ni (OBA) <sub>2</sub> (BPTP) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]                                                                                                                                                             | Competitive absorption quenching effect | Chen et al. (2017)       |
| $\text{Fe}^{+3}$     | $[\text{Cd}_2(\text{OBA})_2(\text{BPTP}) (\text{H}_2\text{O})]$                                                                                                                                                                          | Competitive absorption quenching effect | Chen et al. (2017)       |
| $\text{Fe}^{+3}$     | $[\text{Cd}(\text{L}) (\text{BPDC})] (\text{H}_2\text{O})_2$                                                                                                                                                                             | Competitive absorption quenching effect | Chen et al. (2017)       |
| $\text{Fe}^{+3}$     | $[\text{Cd}(\text{L}) (\text{SDBA}) (\text{H}_2\text{O})] (\text{H}_2\text{O})_{0.5}$                                                                                                                                                    | Competitive absorption quenching effect | Chen et al. (2017)       |
| $\text{Fe}^{+3}$     | Cd-MOF                                                                                                                                                                                                                                   | FRET/PET mechanism                      | Gai et al. (2018)        |
| $\text{Fe}^{+3}$     | BUT-14                                                                                                                                                                                                                                   | RET/FRET mechanism                      | Wang et al. (2017)       |
| $\text{Fe}^{+3}$     | BUT-15                                                                                                                                                                                                                                   | RET/FRET mechanism                      | Wang et al. (2017)       |
| $\text{Fe}^{+3}$     | UMCM-1- $\text{NH}_2$                                                                                                                                                                                                                    |                                         |                          |

(continued on next page)

Table 2 (continued)

| Transition Metal Ion                | MOF-Based Sensor                                                                                             | Detection Mechanism                 | References                          |
|-------------------------------------|--------------------------------------------------------------------------------------------------------------|-------------------------------------|-------------------------------------|
|                                     |                                                                                                              | Fluorescence quenching mechanism    | Wang et al. (2009)                  |
| Fe <sup>3+</sup>                    | [Cd (5-asbaz (bimb))] <sup>n</sup>                                                                           | FRET/PET mechanism                  | Liu and Yan (2016)                  |
| Fe <sup>3+</sup>                    | 3D Tb-MOF                                                                                                    | FRET/PET mechanism                  | Jin et al. (2019)                   |
| Fe <sup>3+</sup>                    | Zirconium MOF                                                                                                | FRET/PET mechanism                  | Jin et al. (2021)                   |
| Fe <sup>3+</sup>                    | Zn-MOF                                                                                                       | LLCT mechanism                      | Rath and Vittal (2020)              |
| Zn <sup>2+</sup>                    | [Cd(C <sub>12</sub> N <sub>2</sub> H <sub>8</sub> )(C <sub>7</sub> N <sub>10</sub> H <sub>3</sub> )]         | MLCT mechanism                      | [125]                               |
| Zn <sup>2+</sup>                    | Zirconium MOFs                                                                                               | Interaction metal and host material | [127]                               |
| Zn <sup>2+</sup>                    | [(Ln (PDA) <sub>3</sub> Mn <sub>1.5</sub> (H <sub>2</sub> O) <sub>3</sub> ].3.25H <sub>2</sub> O             | PET/FRET mechanism                  | Xu et al. (2013)                    |
| Pd <sup>2+</sup>                    | NH <sub>2</sub> -MIL-53(Cr)                                                                                  | PET/FRET mechanism                  | Xu et al. (2013)                    |
| Cd <sup>2+</sup>                    | Zn-MOF                                                                                                       | LMCT mechanism                      | Lim et al. (2017)                   |
| Cd <sup>2+</sup>                    | UiO-66-NH <sub>2</sub> @PANI                                                                                 | LMCT mechanism                      | (Wang)                              |
| Hg <sup>2+</sup>                    | ZnMOF                                                                                                        | Cation exchange quenching effect    | Li et al. (2016)                    |
| Hg <sup>2+</sup>                    | EuMOF                                                                                                        | PET/FRET mechanism                  | Lin et al. (2015b)                  |
| Hg <sup>2+</sup>                    | RuMOF                                                                                                        | PET/FRET mechanism                  | Lin et al. (2015b)                  |
| Hg <sup>2+</sup>                    | Eu/IPA CPNPs                                                                                                 | PET/FRET mechanism                  | Li et al. (2016)                    |
| Lanthanides                         | {[GdIII <sub>2</sub> L <sub>64</sub> ](Mn(H <sub>2</sub> O) <sub>6</sub> ).XH <sub>2</sub> O] <sub>n</sub> } | Cation exchange quenching effect    | Wang et al. (2007)                  |
| Lanthanides                         | CdMOFs                                                                                                       | PET/FRET mechanism                  | Wang et al. (2007)                  |
| Lanthanides                         | MgMOF                                                                                                        | PET/FRET mechanism                  | Wang et al. (2007)                  |
| Miscellaneous Transition Metal Ions | Eu <sup>3+</sup> @MIL-121                                                                                    | PET/FRET mechanism                  | (L. Li and Zhao; Lin et al., 2015a) |
| Miscellaneous Transition Metal Ions | UiO-bpydc                                                                                                    | PET/FRET mechanism                  | (L. Li and Zhao; Lin et al., 2015a) |
| Miscellaneous Transition Metal Ions | Eu-bpydc                                                                                                     | PET/FRET mechanism                  | (L. Li and Zhao; Lin et al., 2015a) |

MOF and analyte and MOFs. This competition often happens when there is a there is a good agreement between overlapping of absorption and excitation bands of metal cation and LMOFs respectively. This phenomenon of competitive absorption results in reduced excitation leading towards the quenching of fluorescence (Tan et al., 2018). Depending upon the structure of MOFs and the analyte, a number of factors are involved for enhancing luminescence intensity during coordination which includes formation of complexes at ground state, interaction between luminophore and sample, and many processes happening at higher energy states, like a FRET (Cao et al., 2017), PET (Ooyama et al., 2017), ICT (Feng and Du, 2020) and ESPT (Tong et al., 2018). MOFs are made up of organic linkers and inorganic metal lumps (Lin et al., 2015a).

The Review about sensing of transition metal ions will be a useful addition to the existing literature. Attention of the current project is based on categorization of MOFs on the basis of their transition metal ions sensing. Recent advances in MOFs and their future research opportunities have been discussed in relation of detection of transition metal ions.

## 9. Conclusion and future prospective

Nowadays attention of researchers to fast and delicate sensing of

transition metallic ion significantly increased MOFs based electrochemical sensors. As compared to other detection techniques MOFs based sensor have more applications in industry, food safety and environment pollution detection due to their high adsorption capacity and the relaxed identification of generated light signals. In this review, we briefly introduce MOFs, electrochemical sensor, especially the strategies for development of water-stable MOFs, as well as the applications of MOF based sensors in transition metal ions sensing in recent years. This review will bear some addition to researchers who are creating MOF based sensors for detection of transition cations. MOFs are classified as rigid groups, flexible frameworks, open metal sites and surface functionalized MOFs. Rigid one has good stability during adsorption/desorption. Flexible MOFs show flexibility only when there is adsorption/desorption of solvent molecules. Performance of MOFs can be enhanced by the presence of open metal site. MOFs can be synthesized by several methods such as solvothermal, hydrothermal, mechanical method, microwave method, sonochemical method, chemical deposition method and ionothermal method. Among these, solvothermal and hydrothermal method is most common one that's why its termed as conventional method for MOFs synthesis. MOFs have been employed for several applications such as catalysis, drug delivery, gas storage, nanoparticle precursor, luminescence, electrochemistry and as sensor in technology. MOF Based sensors detect various types of cations and anions through fluorescence enhancement or quenching phenomenon and is described as "turnoff" or "turn-on" mechanism respectively. The detected analyte when comes in contact with MOF framework, it interferes with the electronic arrangement of the ligand. Here, in this review we compiled data on electrochemical sensing of metal ions such as chromium, copper, zinc, lanthanide, iron, cadmium, palladium, lead, manganese and mercury. Furthermore, MOFs are considered suitable as electrochemical sensors due to their properties such as uniform network structure, large surface area and unsaturated metal coordination sites. These properties make competent in catalytic efficiency and coating of electrode thus leading to efficient sensor. Moreover, large surface area and good porosity increase the mass transfer of analytes thus increasing electrical signal and eventually sensing sensitivity.

There is challenges in relation of hydrolytic stability of MOFs materials which cause formation of metal hydro-oxide. So future, there can be work on stability of MOFs in water by formation of MOFs composed of ligands containing nitrogen which have better hydrolytic stability as compared to the carboxylate-based MOFs. Chemically stability MOFs can be attained by careful selection of metal cations with higher oxidation states as nodes and organic linkers. There is challenge in relation poor electrical conductance of MOFs which can be tackled by the growth of MOF based composites which hold the advantages of both MOF and conducting material (such as metal oxides and carbon). Thus, sensitivity of the corresponding electrochemical sensors is also expected to be improved by this. Further, micron sized MOFs has challenge of adhesion with sensing electrode so in future there can be either micron sized MOFs can be improved in term of adhesion or bigger size particle can be made without compromising their performance.

Further, there are still significant gaps in understanding of structure, stability and properties of MOFs. Detailed investigations are required to study reason of deterioration of MOFs with time along with mechanism. There should be study to increase reliability and stability of MOFs to commercialize MOFs based sensors. Because there is issue related to yield of MOFs material which make them less desirable for commercial usage. Different unique combinations such as carbon based (Naushad et al., 2019), quantum dots (Lei et al., 2014; Yang et al., 2018; Pirot and Omer, 2022) and membrane based MOF composites can be synthesized for metal ion detection (Ahmad et al., 2022; Rehman et al., 2022). So, special attention should be given to this issue by experimenting with different methods, metal ions and ligand component. Alternative ligands can be used which can enhance the yield without compromising its sensing activity. There is very less work on Nano-MOF based electrochemical sensor (Pumera et al., 2007; Wei et al., 2009; Feng et al.,

2021). Nano MOFs (NMOFs) has been employed for sensing pesticides. In this regard, Akash Deep et al. (2015) was the first one who showed biosensing application of Nano MOF for the detection of organo-phosphate pesticide, this can be explored further in future.

### Author contributions

Conceptualization, Syed Salman Shafqat, Tahir Rasheed; Literature review, Syed Salman Shafqat, Muhammad Rizwan; Writing—Original Draft Preparation, Syed Salman Shafqat, Muhammad Rizwan, Maria Batool, Syed Rizwan Shafqat, Ghulam Mustafa, Muhammad Nadeem Zafar; Writing—Review and Editing, Muhammad Rizwan, Tahir Rasheed, Revisions and Final editing, Tahir Rasheed. All authors have read and agreed to the published version of the manuscript.

### Declaration of competing 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.

### Data availability

No data was used for the research described in the article.

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