

# INVESTIGATION OF METAL-ORGANIC FRAMEWORK

## Abstract

The metal-organic framework (MOF) family includes zinc imidazole framework-8, often known as ZIF-8. Zinc metal is properly coupled with an organic ligand or fragment in ZIF-8's chemical structure, creating a cage-like three-dimensional network with distinctive porosity. ZIF-8 has lately been explored in several applications, including gas storage, catalysis, electrochemical sensing, drug administration, and so on, due to its distinctive design and physicochemical features.

**Keywords:** ZnO, Biomedical Applications, Antibacterial Activity, Biosensor

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## I. INTRODUCTION

Over the past 50 years, porous materials have gained a great deal of research attention because of their natural properties, notably their enormous surface areas, massive pore volumes, and tunable hole sizes [1]. As base porous materials, they are described as any solid that possesses pores and voids. Microporous, mesoporous, and macroporous materials are the three categories of porous materials. In microporous materials, micropores with widths or diameters of 2 nm can be discovered [2-3]. Pore widths in macroporous materials are greater than 50 nm, although those in mesoporous materials range from 2 to 50 nm. The term "nanoporous" has lately become popular. Moreover their catalytic activity and absorption, porous materials have attracted the interest of many researchers to be developed for commercial application [4]. Zeolites, which are now widely employed in commercial water softening and purification as well as hydro-cracking catalysts in the petrochemical sector, are an example of a success story of this evolution and have grown into a giga-dollar international market. Metal-organic frameworks (MOFs), which are made up of metal ions and organic ligands, are a form of nanoporous material with fascinating properties, tuneable topologies, and a wide range of applications [5]. Zeolitic imidazolate frameworks (ZIFs), a distinct and distinctive kind of MOF made up of metal ions and imidazolate linkers, have recently been discovered. ZIFs have a variety of structures that are similar to those of standard aluminosilicate zeolites.  $M^{2+}$  ions normally perform the function of silicon in zeolite frameworks, whereas imidazolate anions form bridges that serve the role of oxygen, with the M-Im-M angle being approximately  $145^\circ$  [6-7]. Because of their intrinsic porous characteristics, diverse functions, and excellent thermal and chemical stabilities, many ZIF materials have a wide range of potential applications. Because of their intrinsic porous characteristics, diverse functions, and excellent thermal and chemical stabilities, many ZIF materials have a wide range of potential applications.

**1. Development of metal-organic framework (MOF):** Due to their tremendous uses, metal-organic frameworks, or MOFs, are incredibly dynamic materials. When an inorganic component is joined to organic ligands by coordination bonds, MOFs organic-inorganic crystalline porous materials are developed. Two of the many intriguing aspects of these materials are their high and persistent porosity, as well as their flexibility in pore design and function. Due to their qualities, they may be used for a wide range of tasks, including encapsulation, medication administration, gas detection, and catalysis. The surface area per gram of the MOFs developed by researchers is around 7800 square meters. For example, a full soccer field's worth of surface area may be filled with just a teaspoon-sized amount of this MOF compound [9].

Numerous activities, including gas storage and separation, liquid separation and purification, electrochemical energy storage, catalysis, and sensing, make use of the cage-like structure of MOFs. In addition to their direct uses, MOFs have been investigated as outstanding precursors for the synthesis of inorganic functional materials with unmatched design potentials, such as carbons, metal-based compounds, and their composites, as well as for the fabrication of MOFs. Adsorption, catalysis, batteries, fuel cells, supercapacitors, administration of drugs, and imaging are a few of the many uses for carbonaceous materials. Since they are so tied directly to human health, many sensors are essential applications for carbonaceous materials [10–11].

Some of the essential ideas guiding the development of MOFs were derived from concepts found in the more venerable domains of coordination chemistry and zeolite chemistry [12].

Alfred Werner is credited with developing coordination chemistry, a branch of chemistry that concentrates on the interactions of organic and inorganic ligands with metal centers and explores issues like isomerism and bonding in coordination compounds (1913 Nobel Laureate). Werner is also credited with founding the field of chemistry. Some of the earliest MOFs feature an inorganic component that contains lone polyhedral or tiny clusters similar to what is seen in coordination chemistry. Zeolite chemistry pioneered the idea of SBUs, leading to the creation of over 40 naturally occurring and 190 artificial zeolite frameworks with distinctive structural and topological characteristics. This pertains to the architecture of the elements indicated by the point of expansion in the setting of MOFs, which includes the carboxylate C atoms in the vast majority of carboxylate MOFs [13–14].

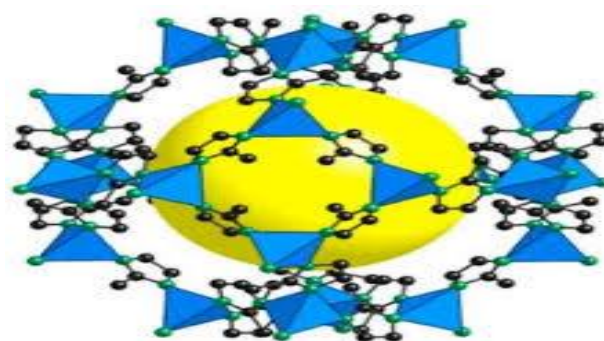
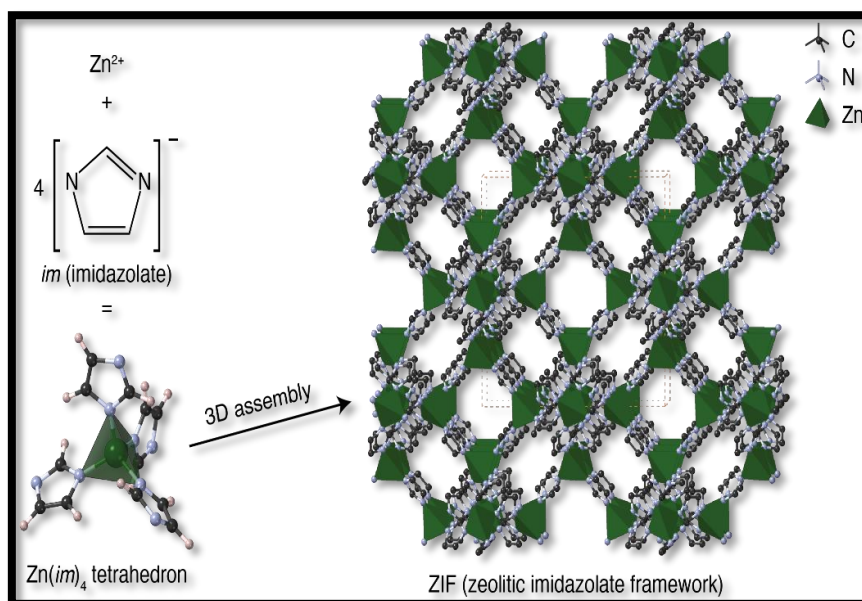
- 2. Zeolite Imidazole Framework (ZIF):** The ZIF series MOFs were constructed by copolymerizing zinc and cobalt ions with imidazole-type linkers, and a particular form of MOF designated as ZIF-8 was created in my most recent survey and subsequently employed in other syntheses. The ZIF structures, which are made up of nets of seven distinct aluminosilicate zeolites, substitute the tetrahedral Si/Al clusters with Zn or Co and the bridge O with bridging imidazolate [15].

Since then, ZIF glass has received substantial interest from researchers as an unearthed form of well-known material. ZIF-4, ZIF-62, ZIF-76, and perhaps ten additional MOF family members have all been successfully converted to their glassy states. Glass can be categorized into three main groups in conventional materials science: inorganic, organic, and metallic. As chemical bonds, the structure is made up of mixed ionic/covalent, covalent, or metallic bonds. MOF glass, a relatively novel organic-inorganic coordinated glass, differs greatly from the three previously described glasses in structure. It is known as the fourth type of glass [16].

In catalysis, zeolites are especially helpful. The Si/Al connecting points and the two-coordinated oxide linkers are continuously coordinated in a tetrahedral arrangement, which restricts the size of zeolites. Only about 200 zeolites have been discovered thus far. MOFs, however, have a wider variety of coordination geometries, polytopic linkers, and auxiliary ligands (F, OH, H<sub>2</sub>O, to name a few). Zeolitic catalysis is limited to relatively tiny organic molecules (often no larger than xylenes) since it is difficult to generate zeolites with pore diameters larger than 1 nm [17].

- 3. Structure and Different Forms of ZIF:** ZIFs have superior thermal and chemical stability when compared to other MOFs. For instance, ZIF-8 maintained its complete crystallinity when suspended for 7 days in boiling water and several chemical solvents. In comparison to MOF-5, which has a porous cubic structure and decomposes at 450° C in N<sub>2</sub>, ZIF-8 can withstand temperatures of up to 550 °C. ZIFs feature persistent porosity similar to zeolites and consistent pore size. For many years, the industry has relied on zeolites due to their durability in harsh environments. As many of the principles may overlap with those of zeolite chemistry, the similarities between zeolites and ZIFs have

made it easier to comprehend the foundations of ZIFs and will ultimately make it easier to utilize ZIFs for commercial uses [18].



**Figure 1: Structure of Zeolitic Imidazolate Framework (ZIF)**

Additionally, ZIF materials would make excellent templates and precursors to generate porous carbon materials under the right synthesis circumstances because of the highly organized porous structures with rich organic species. Additionally, carbon composites containing nanostructured metal/metal oxide species are more likely to occur during the in situ carbonization process because of the regular arrangement of metal species in ZIF precursors. Under specific controlled synthesis conditions, the pure metal or metal oxide could likewise be produced from ZIF precursors. Future nanomaterial preparation and application will be made easier by these simple synthetic methods [19]. Due to structural variances, ZIF was categorized into numerous categories. ZIFs include ZIF-70, ZIF-69, ZIF-9, ZIF-14, ZIF-68, ZIF-90, ZIF-64, ZIF-11, ZIF-8, ZIF-L, ZIF-7, and ZIF-67. ZIF-8, ZIF-L, and ZIF-7 contain  $Zn^{2+}$ , but ZIF-67 contains  $Co^{2+}$ . Unlike the others, ZIF-7 was produced in dimethyl formamide rather than water. The organic linker used for ZIF-8, ZIF-L, and ZIF-67 was 2-methyl imidazole, but ZIF-7 was benzimidazole [20].

**4. Synthesis Methods of ZIF – 8:** This chapter investigates and presents the most recent breakthroughs in ZIF material synthesis, applications, and ZIF derivatives.

- **ZIF Powder Synthesis:** Most ZIF materials, particularly in the early stages of ZIF research, were created as powders that were isolated from reaction mixtures after solvents or other contaminants were removed. For the time being, powder-based ZIF materials can be synthesized using both solvent-based and non-solvent-based methods [21].

- **Solvent-Based Synthesis:**

**Solvothermal Method:** ZIF-1 to ZIF-12 crystals were formed using organic solvent systems such as N, N-dimethylformamide (DMF), N, N-diethyl formamide (DEF), and N-methyl pyrrolidine (NMP). 55 DMF/DEF/NMP were also utilized as solvents in the synthesis of various ZIF materials, including ZIF-60 to ZIF-77, 56 ZIF-78 to ZIF-82, 66 ZIF90, 25 ZIF-95, and ZIF-100. Later, several researchers synthesized ZIFs with DMF or DEF to examine the method of production and relative characteristics. Recently, modified recipes based on Yaghi's methodology were developed. Deprotonating compounds like pyridine and triethylamine (TEA) were added to the DMF or DEF solvent to accelerate the formation of the material. For example, ZIF-78, a micron-sized hexagonal rod-shaped crystal, was produced using TEA, whereas ZIF-90 was produced by adding pyridine to DMF at ambient temperature [22].

- **Hydrothermal Synthesis:** Organic solvents are undoubtedly costly, volatile, and hostile to the environment, in contrast to the straightforward hydrothermal synthesis method that was prevalent in the early phases of ZIF research. Recently, significant effort has been made to produce ZIFs in an eco-friendly and straightforward manner by using fewer or, ultimately, no organic solvents at all. The 2-methylimidazole (MIm) solution and the zinc nitrate solution were mixed and stirred together for about 5 minutes before the products were combined and centrifuged to recover them. The synthesis of ZIF-8 in an aqueous solution at room temperature was demonstrated first by Pan et al. employing this disciplined approach. Although the stoichiometric molar ratio of the zinc ions and MIm in ZIF-8 is  $Zn^{2+}: MIm=1:2$ , it is clear that too much MIm was discarded in this approach (molar ratio of  $Zn^{2+}: MIm=1:70$ ). There has been a lot of work put towards creating ZIFs using stoichiometric molar ratios of metal ions and MIm derivatives in alkaline solutions. Pure ZIF-8 crystals were successfully grown by Miyake et al. at room temperature in an aqueous solution, and the crystalline ZIF-8 was produced from a molar ratio of  $Zn^{2+}:MIm =1:20$ . The formation of ZIF-67 nanocrystals in aqueous solutions at room temperature also was demonstrated by Qian's group using the molar ratio of  $Co^{2+}: MIm: H_2O =1:58:1100$  [23].

The addition of chemicals to water-based systems for ZIF manufacture also changed them. To restrict the use of the ligand MIm and begin the creation of ZIFs, deprotonation agents TEA 26 and ammonium hydroxide 83 were both used. The ability of Gross and colleagues to produce ZIF-8 and ZIF-67 in an aqueous solution with the addition of TEA at room temperature without the generation of by-products may permit the metal ion: MIm molar ratio to be decreased to 1:4. Yao et al. also

noted that the molar ratios of  $Zn^{2+}$ , MIm,  $NH_4^+$ , and  $H_2O$  could be used to manufacture ZIF-8 in the presence of ammonium hydroxide. With further additives such as triblock copolymers poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) (PEO-PPO-PEO) 83 and polyvinyl pyrrolidone (PVP) 84, ZIFs may be produced from stoichiometric metal ions and MIm ratio in an aqueous environment. For instance, when ZIF-8 and ZIF-67 were both produced from stoichiometric metal ions and MIm in aqueous ammonia systems, it was anticipated that the electrostatic attraction of the metal ions to the triblock copolymer surfactant would encourage the growth of porous ZIF-8 and ZIF-67. According to Shieh et al., PVP can cause micro-sized ZIF-90 crystals to form in an aqueous solution (with a molecular weight of 4000). To maintain crystal form and avoid seed crystal aggregation, PVP was suggested [24, 25].

We and other groups have recently effectively synthesized ZIFs from stoichiometric precursors using aqueous ammonia modulation. According to Wang's team, ZIF-8 may be produced at room temperature from stoichiometric precursors ( $Zn^{2+}$ : MIm =1:2) in concentrated ammonium hydroxide aqueous solutions. Ammonium hydroxide was shown to be critical for the deprotonation and coordination activities that result in the formation and growth of ZIF-8 crystals. It was also shown that ZIF-8 could be easily manufactured from stoichiometric precursors in an aqueous ammonia solution at room temperature without the need for any further additions. The resulting ZIF-8 materials' structures, particle sizes, and textural properties may be easily changed by varying the amount of aqueous ammonia in the synthesis mixture. Without a doubt, these ZIFs' cost-effective synthesis techniques will significantly encourage their mass manufacture for useful applications [26].

- **Ionothermal synthesis:** Recently, ionothermal synthesis, which creates ZIFs using eco-friendly solvents including ionic liquids and eutectic combinations, has been established. Ionic liquids can operate as solvents and templates at the same time, avoiding the competing interactions between the solvent and template frameworks seen in hydrothermal preparations. They also have low vapor pressure, are non-flammable, and can function as both at the same time. This makes it possible to conduct the synthesis in an open system. Ionic liquids can also be reused again and again. Morris and colleagues were the ones who initially employed the ionic liquid to make ZIFs [27].
- **Synthesis by sonochemistry:** ZIFs can also be produced by procedures called sonocrystallization. In contrast to conventional oven heating for ZIF preparations, sonochemical synthesis can not only encourage nucleation generation but also aid in its uniform dispersion. When bubbles are created and then burst in solutions during the sonochemical synthesis, high local temperatures, pressures, and unusual heating and cooling rates follow. In Seoane's study, pure ZIF-7, ZIF-8, ZIF-11, and ZIF-20 crystals were produced using ultrasonic irradiation with 110 W of power at a frequency of 47 kHz for a shorter time (6–9 h) than was achievable with traditional solvothermal synthesis [28].

- **Solvent-Free Synthesis:**

**Solvent-minimisation method:** Although the water-based system is more cost- and environmentally friendly than the organic solvent-based system, the aqueous synthesis method is ineffective due to several factors, including the overuse of imidazole sources and extensive solvent washing. As a result, solvent minimization techniques have recently been created. Shi et al., for example, used a steam-assisted conversion process to create porous ZIF-8 and ZIF-67. The solid phase containing excess ligands and metal salts was put in a small Teflon cup and immersed in water vapor (or the organic solvent DMF) for 24 hours at 120°C, which is contrary to the typical hydrothermal synthesis process. Because of this, it's possible that a little quantity of water served as a structure-directing agent during synthesis. A vapor-assisted conversion method in the nonpolar solvent n-heptane was also used to create ZIF-8 samples. In contrast to methanol or DMF, the rate of conversion from the solid reagents to ZIF-8 was faster in this process. The technique is straightforward: an evenly ground mixture of ZnO and MIm with a molar ratio of 1:2 was heated at 180°C for 12 hours, and ZIF-8 was recovered. The resulting ZIF-8 sample doesn't require any additional processing and may be used for adsorptive processes. Beobide et al. also achieved the solvent-free synthesis of ZIFs, in which ZIFs were generated in a closed jar at temperatures ranging from 100 to 160°C via an acid-base reaction between ZnO/CoO/Co(OH)<sub>2</sub> and imidazole ligands [29-30].

- **Mechanochemical synthesis:** Mechanochemistry has demonstrated great potential as an eco-friendly and effective method of material development. Consequently, a process for making ZIFs using mechanochemical synthesis (using ball milling) has been developed. By manually grinding ZnO with a large excess of imidazole, the first partial manufacture of nonporous Zn(IM)<sub>2</sub> was accomplished in 2006. Adams et al. used the same nonporous Zn(IM)<sub>2</sub> products via a two-step mechanochemical procedure that began with ZnCl<sub>2</sub>. Frii et al. created the liquid-assisted grinding (LAG) or ion-and liquid-assisted grinding (ILAG) modified mechanochemical method to produce ZIFs at room temperature from a stoichiometric molar ratio (1:2) of ZnO and ligand such as imidazole, 2-methylimidazole, and 2-methyl imidazole [31-32]. This was done because oxide-based precursors for ZIF

**5. Secondary growth crystallisation:** Secondary growth crystallization is typically used to make membranes in two phases. The crystal seeds are initially deposited on the bare or chemically altered substrate using a variety of methods, including rubbing, dip-coating, thermal seeding, reactive seeding by repeated growth, and more. A continuous polycrystalline layer forms under hydrothermal or solvothermal conditions in the second stage. Internal spaces between seeds can be bridged by seed development, resulting in the formation of a continuous membrane. The seeded growth approach has the distinct advantage of allowing for systematic control of membrane orientation. Additionally, this method may modify the grain boundary structure and other membrane properties, which can enhance the performance of the membrane [33].

**6. In-situ crystallisation:** The polycrystalline layer is formed on a plain or chemically modified substrate in a one-step or one-pot solvothermal or hydrothermal synthesis without any seeded growth strategy when using in situ crystallization procedures to create ZIF films or membranes. Many scientists have looked at in situ crystallization processes for making ZIF membranes. In a microwave-assisted solvothermal process, Bux et al. produced a ZIF-8 membrane using an in situ crystallization technique. Finally, by placing

the solution and support in an autoclave and heating them in a microwave, a compact ZIF-8 layer was created on the porous titania support [34].

**7. Applications of ZIF material:** ZIF materials are currently gaining use because of their high porosity, flexible compositions, and programmable topologies. Pure ZIFs and ZIF-based films/membranes have been established as multifunctional materials with remarkable performances that may potentially promote the development of sensing and electrical technology as well as drug delivery, in addition to their more typical applications as adsorbent materials and catalysts. The uses of ZIF materials that are both traditional and new are emphasized and discussed in this section [35].

- **Photo Catalysis Behaviour:** The steps outlined below are typical ones for a photocatalytic reaction: Once the photocatalyst transitions into a charge-separated state, generating a mobile electron ( $e^-$ ) and a hole ( $h^+$ ), pollutants can then be eliminated by interacting with the transportable electron or hole. Photo-generated electron-hole pairs can only happen when the energy of the incoming photons is higher than the energy of the photocatalysts' bandgap. Because ZIF-8 has a high conversion efficiency to light energy when degrading pollutants, it is a promising co-catalyst for heterogeneous photocatalysis. The metal-oxygen cluster can acquire the absorbed light from the organic connection fast thanks to ZIF-8. Later, the valence band's electrons will go to the conduction band and change into conduction  $e^-$ , leaving an  $h^+$  behind. Pollutant oxidation by active molecules produced by photocatalysts is the basic definition of photocatalytic degradation of pollutants [36–37].
- **Antibacterial Responses:** Antibacterial zinc metal oxide is generally implemented in biomedical applications. The metal is biocompatible and environmentally benign.  $Zn^{2+}$  derived from zinc metal oxide has been shown to enhance keratinocyte mobility and aid in wound healing. Metal-organic frameworks (MOFs) having a similar appearance to inorganic porous zeolites have recently been reported as zeolitic imidazolate frameworks (ZIF-8). The zeolite structure is made up of  $Zn^{2+}$  metal ions linked by an imidazolate linker. ZIF-8 is used in biomedical applications. However, a few ZIFs were microporous, causing pre-mature drug release. Various procedures have been used in recent years to prepare the composite incorporating ZIF-8 and mesostructured materials. Such composites were particularly effective because they combined the benefits of micropore ZIF-8 and mesoporous materials [38].
- **Gas Sensing Performance:** The change in energy band bending brought on by the interaction of oxygen ions with CO when the micro-reaction is transformed into macro-signals would lead to the adjustment in the overall resistance/conductivity of the sensitive layer. When  $NO_2$  gas is tested using a polyhedral ZIF-8 nanomaterial gas sensor, the gas molecules capture free electrons from the oxygen adsorbed on the sensor's surface, leading to the formation of a substantial charge depletion layer on the ZIF materials' surface. Rapid  $NO_2$  molecule adsorption causes the surface to become negatively charged, increasing the potential barrier. ZIF materials are porous, allowing them to detect released gas molecules with ease [39–40].



## II. CONCLUSION

The building blocks of ZIFs, a new and distinct class of metal-organic frameworks with structures like those of traditional aluminosilicate zeolites, are metal ions and imidazolate linkers. Numerous prospective uses for diverse ZIF materials have been made possible by their inherent porous characteristics, strong functions, and outstanding thermal and chemical stabilities. In the past several years, many research initiatives have appeared in this quickly developing field, spanning from synthetic methods to alluring ZIF applications.

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