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A Mini Overview of Post Synthetic Modification of Synthesized Zeolitic Imidazolate Frameworks

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Abstract: The inorganic metal node and organic linker may be chemically transformed to optimize metal-organic frameworks (MOFs) for various uses. The term zeolitic imidazolate framework (ZIF) refers to MOFs that are topologically isomorphic with zeolites. These can be synthesized in several ways such as hydrothermal, sol gel, solvothermal etc. After the fabrication these can be modified with post synthetic modification (PSM) processes. The idea for PSM was developed in this century. PSM is a procedure that may be used to modify MOFs while still preserving the structural integrity of the framework. PSM makes it possible to functionalize both the metallic and organic components of MOFs. PSM acts as a technique for phase separation, increasing catalytic activity, increased surface area for surface reactions, and improvement of other properties. The purpose of this article is to give a mini overview of the various PSM approaches used for ZIF modification.

Keywords: ZIFs; SALE; Grafting; Covalent Modification; Impregnation composition

1. INTRODUCTION

MOFs have greatly expanded the investigation of porous substances during the past two decades. MOFs are fabricated from metal ions/clusters and coordination bonds formed by utilizing multidentate organic linkers [1]. MOFs of crystalline nature typically have exceptionally high surface areas and tunable pore sizes/characteristics due to the geometry, size, and functionality flexibility of the constituents [2]. As a result of these characteristics, MOFs can be utilized for vast range of purposes, including gas adsorption and separation, catalysis, sensors, drug administration, proton conduction, etc. [3]. ZIFs are a type of MOFs with a zeolite-like structure. These can be produced by interacting organic ligands with metal elements including Zn or Co and imidazole or its derivatives. These structures have some advantages over MOFs, such as good thermal and chemical stability. ZIF-8 can treat water due to its distinctive physical structure and chemical capabilities [4]. The need for modification of MOF materials has been met by the later development of PSMs. PSM has been used a lot on ligands with different functions and different types of frameworks. Nevertheless, the formation of modified linkers within the material is crucial for modifying the characteristics of substances. The modified linkers have an effect on the uses of these materials. Consequently, a more complex objective is not only to endow something with a particular property via PSM, but also to employ the subtle management regarding how deep and where such PSM methods reach [5]. The PSM techniques include solvent-assisted linker exchange (SALE), Impregnation composition, grafting, and covalent modification (see Fig. 1). The SALE technique has been utilized in the solvent-based PSM techniques of ZIFs. The present observation indicates that ZIF possesses exceptional capabilities in tackling various separation obstacles due to its distinct pore size, which allows for accurate molecular sieving, and its elevated porosity. The biggest issue in ZIF modification is unanticipated topologies. The SALE technique works for predictable topologies. SALE controls catenation, produces MOFs with longer

linkers, mixed linkers, and bigger cages, and uses high-energy polymorphs. SALE has been used to generate several daughter MOFs that were previously difficult to make. SALE allows full linker molecule exchange in very durable ZIFs under certain circumstances [6]. By the utilization of a specific impregnation composition, researchers have yielded a novel and beneficial ZIF. Grafting is a remarkable technique for PSM of ZIFs. Grafting may change the reactivity of ZIF pores, improving its catalytic characteristics. Grafted compounds are more effective than their parent molecules [7].

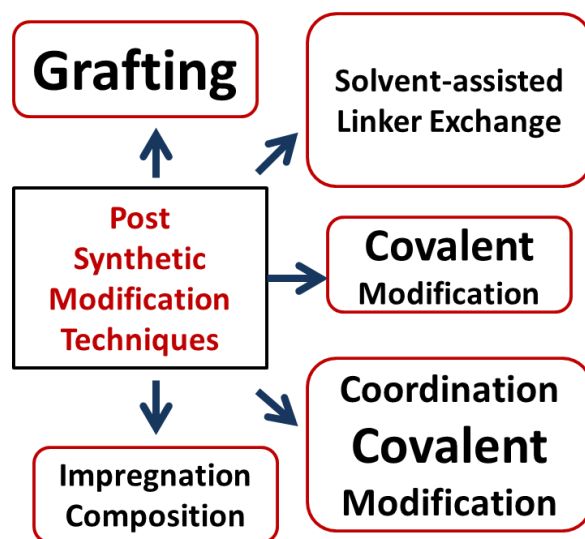


Figure. 1. Various ZIF modification processes with PSM methods.

When polyethylene glycols are chemically bonded with ZIFs, the scientific terminology used to describe this process is "grafting." Multiple classifications of polyethylene glycols exist. Through this modification technique, ZIFs undergo enhancements in various aspects such as surface roughness, polarity, and surface area. The implementation of covalent modification represents an additional avenue for the PSM of ZIFs,

thereby augmenting the organic reactivity of the ZIF surface [8]. Being a chemical modification of the linkers existing in a manufactured MOF to generate an objective consequence that was not possible during the process of synthesis [9], PSM of ZIFs can offer new potential sites to enhance gas adsorption capacity, specificity, and production of new working regions for heterogeneous catalytic processes in reactions involving organic compounds [10,11]. Thus PSM has developed as a potent and versatile method for strengthening and improving the physical and chemical characteristics of MOFs [12]. In a PSM of ZIF-90, researchers observed transforming the free -CHO groups to alcohol (see Fig. 2) and the ethanolamine to an imine to generate ZIF-91 and ZIF-92, respectively. Covalent functional group modification of ZIF improves its applicability. The framework may identify the expected group and the intended result [13,14]. In this study, we demonstrate various PSM techniques of ZIFs along with their respective examples and applications. In second section we explain various modification methods such as SALE, Impregnation, grafting, and covalent modification.

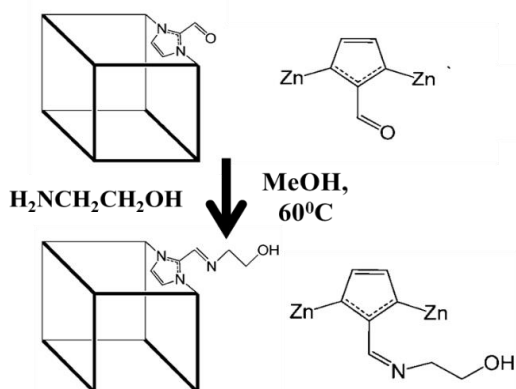


Figure 2. Modification of ZIF-90 by changing organic units with conversion of -CHO groups to -OH groups [14].

2. MODIFICATION OF ZIF

The PSM of ZIFs (see Fig. 3) offers an extensible structure for adjusting their attributes and characteristics to fit specific needs. ZIFs can be made more effective for uses including gas separation, catalysis, drug administration, and sensing through the addition of suitable functional groups, guest molecules, or metal ions [15].

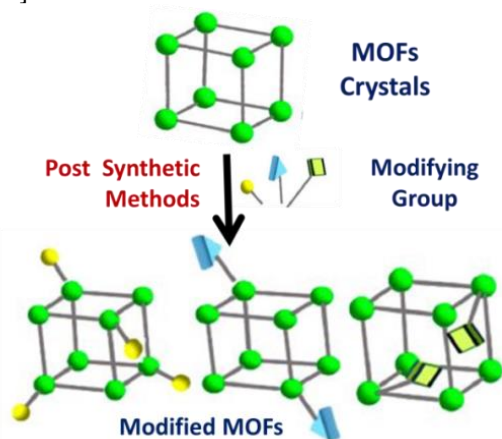


Figure 3. Schematic diagram of the PSM of ZIF by utilizing modifying group [18]

This degree of versatility and regulation offers PSM an appealing approach for developing ZIF-based materials. PSM of ZIFs can be accomplished using a variety of methods. PSM of ZIFs can be achieved through post-synthetic ligand exchange, encapsulation, metal substitution, surface functionalization, and linker modification. These procedures allow for the addition of additional ligands, metal ions, or functional groups, which changes the characteristics of the framework. Contingent upon stimulus intensity, such PSM can prompt structural collapse and solid state amorphization of the system [16][17]. The modification processes along with applications are given below:

2.1 Solvent-assisted linker exchange

SALE is a PSM method used to include novel ligands into ZIFs. SALE enables the substitution of the primary linker compounds in the ZIF with a variety of ligands, allowing the framework characteristics to be adjusted for particular uses [19]. The ZIFs are submerged in a solution with a new linker during the SALE process. The selection of solvent is essential as it enables the exchange technique. The ZIF and new linker compounds will usually dissolve employing a polar solvent. The polar solvent supports in destabilizing the coordination interactions within the initial linkers and the metal ions [20,21]. SALE provides a high level of control in the structure and characteristics of modified ZIFs. Researchers can add particular functionalities and can change the size of pore, surface area, and stability of a framework through the choice of various linker structures [22,23]. The modified ZIFs developed via SALE can enhance the catalytic activity, selectivity, or stability in catalytic reactions of ZIFs. It's possible for the modified ZIFs to show enhanced gas adsorption capabilities, making them useful for gas separation or storage [24]. Dissolution and recrystallization are the main steps of SALE transformation (see Fig. 4). By carefully balancing the creation of new links and the cleavage of existing bonds, researchers have produced a variety of 1D/2D/3D MOF nanostructures [25]. Utilizing more oxophilic, high oxidation state metal ions, or incorporating kinetically inert metal ions, or by modifying both the metals and ligands to obtain a stronger ZIF framework, water-stable ZIFs have been produced by a variety of methods. On the basis of powder X-ray diffraction (PXRD) data, the vast majority of the materials are acquired as microcrystalline granules that are stable in and unaffected by water and other polar solvents [26]. So, SALE becomes important PSM methods. The primary objective of SALE is to replace principal ligands with alternative linkers and it is solvent related process. [27]. As a result of the unique pore size for precise molecular sieving and high porosity for increased flux, the adsorbents in this instance have demonstrated tremendous promise as a solution for various separation difficulties [28]. For the unpredictable nature of the coordination chemistry of ZIFs [29][30], SALE can demonstrate an efficient method for system adjustment and gate-opening management [31]. Recent researches indicate that the further development of SALE in ZIF modification can be employed to improve gas separation efficacy [32][33]. By using a 3-day SALE on

a ZIF-8 membrane, the 2-methylimidazole linker in ZIF-8 crystals was exchanged with 2-imidazolecarboxaldehy. This led to the organization of hybrid shape crystals with larger pore sizes than ZIF-8 in the ZIF-8 membrane's outside. As an outcome, the ZIF-8 modification reduced membrane thickness, increasing the stability of propylene. In order to increase propylene/propane selectivity while minimizing the impact on propylene durability, the ZIF-8 membrane's outer surface is widened using a new SALE method called MSLE. For a different amount of MSLE time, the 2-methylimidazole linker in this instance was substituted out for a thicker 5,6-dimethylbenzimidazole. Thus, with short-duration MSLE modified ZIF-8 membranes; a 40–70% improvement in propylene/propane selectivity was discovered with a minor reduction in propylene persistence losses. This study demonstrates that the use of MSLE can enhance the selectivity of ZIF-8 membranes for propylene/propane mixtures. Short-duration MSLE modification has limited effectiveness in improving gas perm-selectivity. However, it is still utilized due to the inefficiency of long-duration MSLE in enhancing membrane separation characteristics [34]. Unexpected topologies are main challenge in ZIF modification processes. SALE is an easy method which is feasible for predictable topologies. SALE has ability of controlling catenation, accessing polymorphs with comparatively high energy, and producing MOFs with longer linkers, mixed linkers, and larger cages. SALE has been employed to produce numerous daughter MOFs that had been challenging to prepare directly. SALE can even be applied to some of the most robust ZIFs and the linker molecules can be completely exchanged under appropriate conditions [29][30] [31].

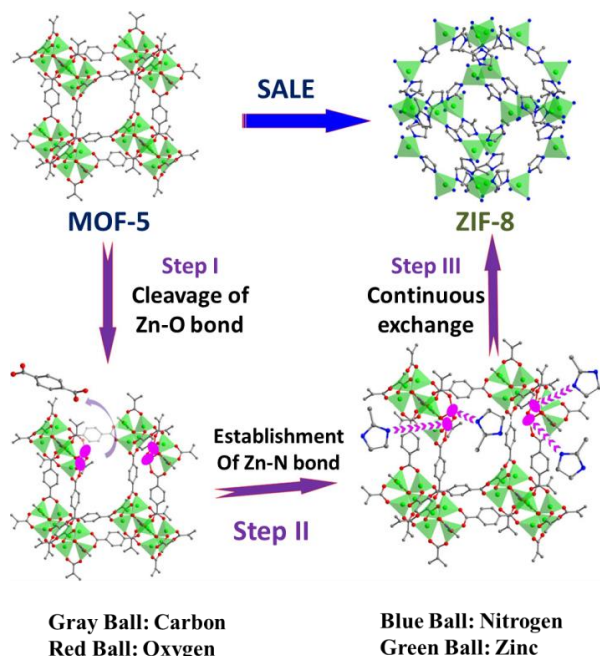


Figure 4. Modifying ZIF-8 for transforming it to MOF-5 with the typical process of SALE with establishment of Zn-N bond [25].

2.2 Impregnation composition

The impregnation composition technique is employed for the incorporation of functional compounds into ZIFs.

This technique enables the inclusion of guest species within the pores of ZIF crystals, leading to the alteration of the properties and broadening potential usages [35]. The impregnation composition method involves immersing ZIF crystals in a solution or suspension containing the specific substance. The selection of a solvent is contingent upon the characteristics of the guest compound and its compatibility with the ZIF framework. Ensuring the facile diffusion of guest species into the pores of ZIF crystals is of utmost importance [36]. ZIFs possess nanoporous pores that can accommodate various guest molecules. During the process of impregnation, ZIFs serve as a host framework, offering a confined environment for the guest compounds. Guest species selection can be determined by particular functions [37]. Impregnation methods vary depending on the characteristics of the guest species and the ZIF framework. In certain instances, the guest species is capable of entering the pores of ZIF crystals via molecular diffusion, facilitated by their small size [38]. Larger guest compounds can be impregnated using a combination of diffusion and physical adsorption. The guests compounds can be adsorbed onto the external surface of ZIF crystals and then penetrate into the pores. The connection between guest compounds and the ZIF framework is impacted due to variables such as surface chemical composition, pore dimensions, and guest-host connections [39]. The impregnation method enhances the productivity of ZIF for different uses. For example, a new catalyst for the manufacture of biodiesel, magnetized ZIF-8 has been impregnated with NaOH [20]. Recently, ionic liquids (IL) have been incorporated into ZIF-8 for the purpose of separating CO₂ and CH₄ from a mixture [40]. Impregnating a material with an IL can result in collapse of the structure. ILs have been employed for PSM of MOFs through infiltration of the crystalline pore-network. Previous studies have demonstrated that the IL atoms confined within the pores of ZIF-8 do not undergo a shift in phase at lower temperatures. This observation suggests that there is no freezing of the ionic liquid taking place. Nanoconfinement can significantly enhance the ionic conductivity of the composite compared to the bulk IL at lower temperatures [41]. In a study, the CO₂ adsorption capacity of ZIF-8 has been enhanced by incorporating amino functional groups through the impregnation method. For example, polyacrylonitrile/ZIF-8 mats have been functionalized by impregnating with polyethyleneimine, which introduces amine functional groups that enhance CO₂ adsorption [42]. The CO₂ adsorption capacity of ZIF-8 has been significantly increased by impregnating it with 30% tetraethylenepentamine (TEPA), surpassing the capacity for adsorption of the original ZIF-8 [43]. The wetness impregnation method has been employed to incorporate TEPA into ZIF-8. This incorporation has potential for CO₂ post combustion capture. It involves physical adsorption onto the microporous channels of the MOF supports and chemical adsorption onto the amino groups. TEPA was selected due to its cost-effectiveness, low toxicity, high amino-content, and linear molecular geometry, which enables its diffusion through the microporous pathways of MOFs [44].

2.3 Grafting

The grafting technique is employed to bind organic compounds onto the outermost part of ZIFs, enabling the alteration of the characteristics and chemical composition of ZIFs [45]. In the process of grafting, the ZIFs are usually exposed to a solution or vapor that contains the needed functional groups or particles. The selection of a grafting agent is based upon the intended features and its suitability with ZIF. Functional groups vary in complexity, ranging from basic organic particles to intricate molecules possessing particular characteristics. Grafting requires an association between the functional groups of the grafting agent and the outer sites of ZIFs. Chemical connections can take place via diverse mechanisms, including covalent attachment, coordination bonding, and electrostatic attraction. The process involved varies depending on the grafting agent and the surface chemistry of the ZIF [46–48]. Grafting can be described as a novel and versatile method for functionalizing MOF involving the covalent attachment of polyethylene glycol to the surface. The “grafting from” polymerization method has been utilized to develop polymer chains from dynamic sites at the surface of MOFs. This strategy involves utilizing an initiator-carrying linker to induce the polymer to be included within the porosity of the MOF. Graft fast is a technique that has been developed to attach organic polymer films of specific thickness onto various surfaces through covalent bonding. In contrast to other functionalization approaches, Graft fast presents various benefits. This process occurs rapidly and is completed within a brief timeframe. The system is highly versatile. The reactions take place under ambient conditions and in aqueous medium, rendering this approach biocompatible, sustainable, and scalable [49]. Through an adaptive coordination-based PSM technique, a novel alpha monomethoxy-omega-amino poly ethylenglycol (PEG-NH₂) functionalized ZIF-8 composite membrane (ZIF-8/PEG-NH₂) has been developed. The ZIF-8/PEG-NH₂ membrane showed an excellent capacity for adsorption with enhanced adsorption specificity for 4-nonylphenol adsorption [50]. By combining the magnetic core in ZIF-8, a composite of a unique multifunctional nanoprobe has been developed. It was named after Fe₃O₄@PDA@mTiO₂@PEI-g-ZIF-8. This material consistently demonstrated the presence of advanced phosphorylated peptides as well as glycosylated peptides [51]. Nano ZIF-8-grafted short carbon fibers(SCF) (ZIF-8@SCFs) has been developed through in situ development of nano ZIF-8 onto the SCFs surface. The grafted nano-ZIF-8 showed upgraded roughness, polarity, and wettability of SCFs surface [52]. Polyethyleneimine (PEI) grafted ZIF-8 (PEI-g-ZIF-8) has been developed by utilizing Zn²⁺, 2-methylimidazole and hyperbranched PEI. Synthesized PEI@ZIF-8 has been demonstrated a significant increment of CO₂ capacity and CO₂/N₂ selectivity compared with ZIF-8 [53]. The H-ZIF polyhedral nanocrystals has been utilized as an inorganic filler for the development of mixed-matrix membranes (MMMs) containing a poly (vinyl chloride)-g-poly (oxyethylene methacrylate) (PVC-g-POEM) graft copolymer matrix. It is reported that the manufacture of mixed-matrix

membranes (MMMs) involving nanocage-like H-ZIF polyhedral nanocrystals embedded in PVC-g-POEM. It is utilized for utilization in CO₂/CH₄ separation [54]. In another study, ZIF-8 was developed by utilizing surface modification with {Mo132}. After fabrication of ZIF-8, {Mo132}, it served as a nano-structure catalyst for the efficient oxidative desulfurization of dibenzothiophene (DBT) in a model fuel when tert-butyl hydroperoxide (TBHP) was present as an oxidant [55]. A unique PPS@ZIF-8 reverse demulsifier was developed by researchers by grafting with polyether polysiloxane (PPS) compounds onto the ZIF-8 crystal using the epoxy ring-opening method. [46]. A group of researchers created a powerful antibacterial adsorbent by grafting an abundant number of amidoxime groups (AO) onto ZIF-90. In this investigation, the researchers inserted cyanide groups by performing a Knoevenagel condensation reaction of ZIF-90 with aldehyde groups and malononitrile. After this, they were able to successfully construct a porous material ZIF-90-AO. In order to create an effective U(VI) adsorbent, ZIF-90 was first grafted with malononitrile using the Knoevenagel reaction. The high maximum uranium adsorption capacity of ZIF-90-AO was made possible due to the strong chelation power of amidoxime groups with uranium and the mesoporous structure of ZIF-90. ZIF-90-AO also shown strong antibacterial activity against both *Escherichia coli* and *Staphylococcus aureus* [48]. Grafting is a viable technique for modifying pores' reactivity of ZIF, which is beneficial for catalysis. Grafted molecules are more effective in the application than the parent form of molecule.

2.4 Covalent Modification

Covalent modification is employed to attach functional groups onto the ZIF by establishing robust covalent bonds (see Fig. 5). This technique enables precise manipulation of organic moieties incorporation onto the ZIF structure, leading to modified properties and improved functionalities. Covalent modification involves treating ZIF crystals with a reactive compound or solution containing the desired functional groups. The reactive compound must exhibit suitable reactivity with the ZIF surface and the capacity to establish stable covalent bonds. The covalent modification process entails chemical reactions between a reactive compound and the surface of the ZIF material. This can be achieved through various reactions, including nucleophilic substitution, condensation, Michael addition, or click chemistry. The reaction mechanism varies based on the properties of the reactive compound and the functional groups on the surface of the ZIF. Covalent modification has multiple advantages when used as a post-synthetic technique for ZIFs. This process enables precise control over functionalization, facilitating the introduction of specific functional groups at defined positions on the ZIF structure. Customization offers opportunities to improve properties such as selectivity, catalytic activity, stability, and affinity for target molecules [56–58]. Recent study has shown that aldehyde groups of ZIF-90 enable for the covalent functionalization with amine groups via an imine condensation process. Imine functionalization

can decrease the pore size of ZIF-90, which inhibits bigger molecules from entering the pores. Covalent PSM reduced non-selective transport through invisible intercrystalline flaws, which increased separation selectivity. Imine functionalization can constrict the pore aperture of ZIF-90. The ZIF-90 membrane demonstrated a significant degree of resistance to hydrothermal change. In contrast, the imine-functionalized ZIF-90 membranes demonstrated a high degree of resistance to deformation when exposed to steam. The inclusion of the imine functionality in ZIF-90 caused the pore aperture to become more constricted, which improved the molecular sieving capabilities of the material for the separation of H₂ from CO₂ and other big gases. Through the use of covalent PSM, the H₂/CO₂ selectivity was raised from its starting point of 7.3 to 62.5 [59].

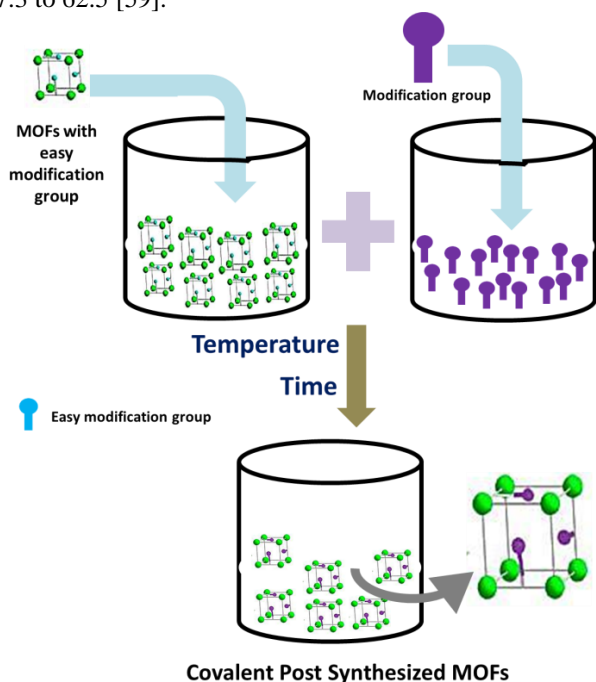


Figure 5. Schematic diagram of obtaining covalent post synthesized MOFs by changing easy modification group [18].

Covalent modification is mainly the chemical modification of the organic linker component of the MOF [60]. Recently, the molecular sieve ZIF-90 membranes have been prepared by utilizing 3-aminopropyltriethoxysilane (APTES) as covalent linker between the ZIF-90 layer and the Al₂O₃ support by an imine condensation reaction [61]. Recent investigations have led to the discovery of free aldehyde groups in the ZIF-90. In general, the accomplishment of achieving typical organic reactions in crystals of developed structures like ZIFs provides the concept of utilizing the "crystal as a molecule" a reality and opens many possibilities for using the available repertoire of organic reactions in the covalent functionalization of developed structures. This is because the idea of using the "crystal as a molecule" becomes a reality when the concept of accomplishing usual organic reactions in crystals of developed structures is accomplished [13]. The covalent organic frameworks (COFs) may serve as a naming inspiration for the hybrid materials known as MOFs. The composite membrane [COF-300]/[ZIF-8] has

excellent results in terms of gas separation for H₂ and CO₂. In this context, covalent modification techniques are utilized to develop this hybrid material. It has been established that COFs and MOFs can be connected to one another through the use of chemically covalent amide bonds. A connection of this kind has the potential to enhance both the stability of the catalyst and the photocatalytic activity of the system by increasing the efficiency with which photo-induced charges can be separated [62]. As covalent modification modify ZIF by modifying functional group of ZIF, the modified ZIF can be more feasible in more applications. Here the expected group can be come in the structure and the expected outcome can be found.

3. Conclusion:

In conclusion, the study of PSM has substantially expanded our understanding of ZIFs and increased the range of disciplines in which they may be used. Researchers have been able to accurately modify ZIF properties including porosity, functionality, and reactivity to meet certain needs via PSM approaches. This innovation has opened up new possibilities in a number of industries, including catalysis, gas separation, sensing, medication delivery, and more. Through smart chemical reactions and novel techniques, PSM has permitted the insertion of functional groups, guest molecules, and structural alterations into ZIF frameworks. By making these changes, ZIFs have become more stable and effective. They have also made it possible to create hybrid materials with complementary features. Today's researchers are more equipped to take on a variety of complicated problems, such as environmental cleanup and renewable energy conversion. We could foresee an emergence of new PSM approaches, better characterization techniques, and a variety of applications leveraging the improved ZIF characteristics as this area of study develops.

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