Review Article

Metal organic frameworks (MOFs) and their application as photocatalysts: Part I. Structure, synthesis and post-synthetic modifications

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ARTICLE INFORMATION

ABSTRACT

In recent years, metal-organic-frameworks (MOFs) have been considered as a category of new advanced nanomaterials receiving remarkable attention and attaining great importance due to their superior properties such as ultrahigh porosity, remarkable surface-specific area for specific applications like adsorption and gas separation, hydrogen and CO_2 absorption, catalysis, photocatalysis, and biocompatibility. The structure of MOFs plays a key role in their special properties and the employment of an appropriate synthesis technique to achieve the desired properties. Furthermore, the post-synthesis modification (PSM) process is essential for pore modification, forming a functionalized network, and finally improving the pre-formed synthesized structure to achieve desired properties. Finally, the purification, activation, and characterization of MOF are also regarded as essential steps after the synthesis process.

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Graphical Abstract
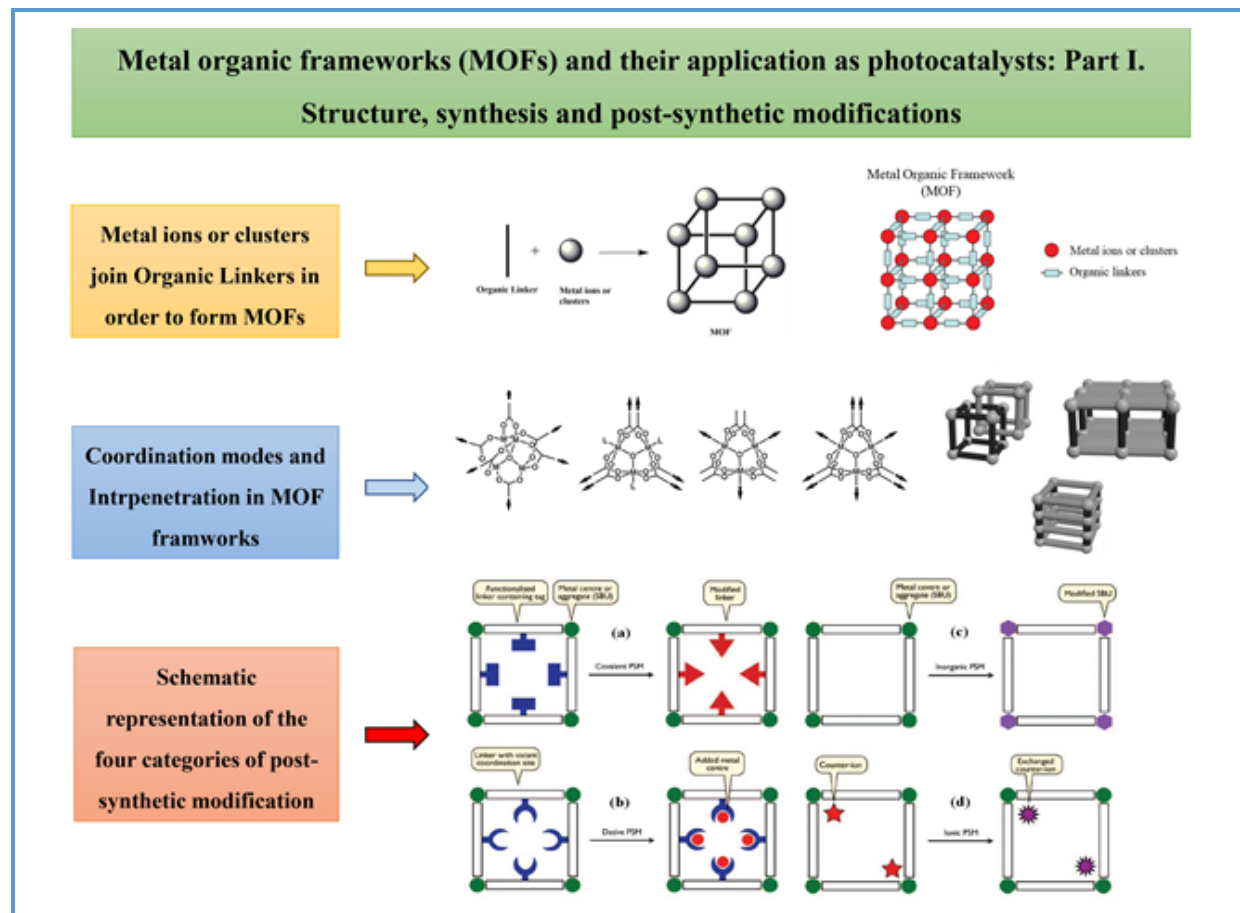
Introduction

A new approach in materials science and solid-state chemistry is a development of new materials with superior properties for specific applications. Several materials like zeolites, phosphites, etc. are conventional porous materials with rigid scaffolds around different structural templates [1]. In recent years, researchers have concentrated on synthesizing and developing new coordination polymers called metal-organic frameworks (MOFs).MOFs are composed of metal ions or clusters acting as joints constrained by multidirectional organic ligands, acting as linkers in the network structure. As also defined by Yaghi *et al*. (Figure 1) MOFs are formed as a result of coordination centers of metal ions joining polyatomic organic bridging ligands [2]. The first reports on coordination polymers started in the late 1950s [3-8], and after that, within a relatively short period, other researchers rapidly rediscovered and continued the MOFs field [9-14].
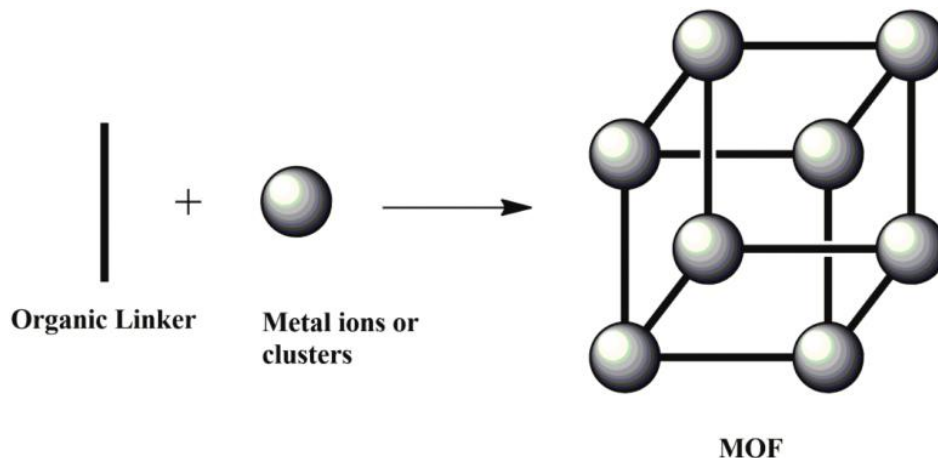
Figure 1. General structure of MOF [15]

MOFs are vastly employed in several industrial and medical applications, such as hydrogen storage, catalysis, and gas separation [16-19], heterogeneous catalysts [20-23], hydrogen and CO_2 absorption [24-26], adsorption and gas separation [27-30], drug delivery [31], Water remediation [32], luminescence [33], chemical production [34], chemical catalyst [35], good chemo-/machinal stability and favorable biocompatibility [36], nanomedicines [37], chemical sensors [38], photocatalysis [39-41], and electrocatalysis [42]. The outstanding properties of MOFs are generally the result of their unique structure and specific surface, making them superior to conventional materials like zeolites and activated carbon [43, 44]. Yet, recent research not only introduced porous MOFs materials as a new class of photocatalysts employable in catalytic degradation of organic pollutants under UV/visible/UV–visible irradiation [45], but also attracted a great interest of researchers in exploring MOF applications as photocatalysts in other aspects [46-49].

MOFs can have both advantages of inorganic and organic materials [50, 51], but lower physical and chemical performance compared to those of carbon materials and zeolites. In the structure of MOFs, metallic ions and bridging

ligands have a major effect on their geometry and behavior. Since the combination of metal ions and bridging ligands are infinite, many applications can be attributed to MOFs like heterogeneous catalysis catalysts, hydrogen and CO_2 absorption, adsorption, separation, and sensors. Specific properties of MOFs are originated from their unique structure and composition, like their high porosity, highly periodical structure, and framework flexibility. By using the X-ray diffraction technique (XRD), it is possible to determine the 3D periodicity or crystallinity benefits of MOFs and correlate their structure-properties relationship. A suitable framework structure and long organic ligands in MOFs can achieve high porosity, making MOFs a suitable candidate for adsorption, storage, and catalysis applications. Subsequently, the pore surface of MOFs with different functional groups of organic ligands leads to application in adsorption, sensing, and separation areas [52].

The most attractive aspect of MOFs is their porosity which permits the diffusion of specific molecules into the bulk structure. This porosity results from long organic linkers, which provides a large storage space and a wide number of sites for adsorption in the structure of MOFs. It is also possible to manipulate their

porous structure [53, 54]. In other words, MOF pores, including their linkers and nodes, regulate reactant and product transport, catalyst sitting, catalyst stability, catalyst accessibility, catalyst activity, co-catalyst proximity, chemical environment composition at and beyond the active catalytic site, chemical intermediate and transition-state conformations, thermodynamic affinity of molecular guests for MOF interior sites, framework charge and density of charge-compensating ions, pore hydrophobicity/hydrophilicity, pore and channel rigidity vs. flexibility, and other features and properties [35].

MOFs are based on organic units (linkers/bridging ligands) and also inorganic units. The organic units include anions like sulfonate and phosphonate. The inorganic units are metallic ions called secondary building units (SBUs). Generally, a bridging ligand reacts with vacant sites of a metal ion. The obtained framework is finally supported by organic and also inorganic linkers. By varying the organic and inorganic linkers, different structures are produced for various applications [54]. MOFs can form interpenetrating structures, which the correct selection of organic linkers should avoid. It is possible to control the porous structure by correctly selecting metals centers/organic ligands and synthesis parameters. Reaching the high porosity leads to critical applications like gas adsorption or separation, sensing, drug delivery, and catalysis. It is also possible to control the pore size in MOFs for the encapsulation of different sizes of molecules. MOFs can be synthesized by relatively simple methods like solvothermal, ionothermal, diffusion, microwave, and ultrasound-assisted, in which the reaction parameters should be controlled for the desired functionalities [53, 54].

Another advance in MOFs is combining them with functional nanoparticles to produce new nanocomposites with improved properties, and the final properties generally depend on composition, size, and morphology [2, 54, 55]. This results from the high compatibility of MOFs with other organic and inorganic materials. Liu *et al*. in 2021 [56], conducted a comprehensive and intensive research on a promising class of porous crystalline materials with various applications dependent on their structures comprising both compositions and architectures. Their results led to an emerging family of MOF-on-MOF hybrid materials constructed by the conjugation of two or more MOFs units on single MOFs, MOFs-based composites via conjugation with non-MOF materials and their derivates. The structural diversity, challenges, and future directions in MOF-on-MOF systems in detail demonstrated how MOF-on-MOF hybrid systems can enable significant progresses in diverse applications. Therefore, as a new class of advanced porous materials, MOFs have become an intense subject of scientific research. As many recent reviews on this field have been published, we will briefly focus on the molecular design, synthetic strategies, and representative properties of MOFs by a series of selected examples.

Structure and design of MOFs

In MOFs, the strength of the bonding and directionality of coordination bonds are in between covalent bonds and supramolecular bonds (like in hydrogen), which reveals that the prediction of MOFs structure is easier than the structure in an organic crystal. There are several methodologies for the design of MOFs structure. The net net-based approach is the most appropriate in these methodologies [17, 57]. Similar to crystalline frameworks, it is

possible to consider the bonds in MOFs as periodic nets. It would be the same in inorganic compounds and also zeolites. These periodic nets can be considered nodes and linkers. In the early works, hypothetical networks were introduced mathematically [58, 59]. This mathematical network exhibits intrinsic bonds. The symbol of this topology is usually named from natural compounds like a honeycomb for graphite (hcb) and diamond (dia) shown in Figure 2.
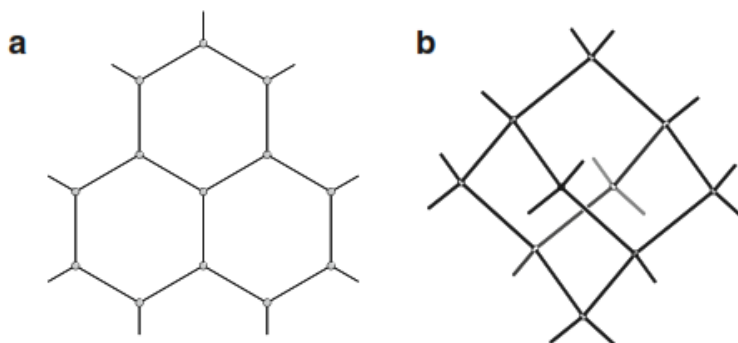

Figure 2. Two simple topologies: (a) hcb, (b) dia [60, 61]

The benefit of this simplified topology is the design of metal-ligand bonds of MOFs. It is possible to choose metal ions/clusters (Figure. 3) or organic ligands (Figure. 4) to emulate the geometry of nodes. Every node geometry can be suitable for building several various topologies [62].
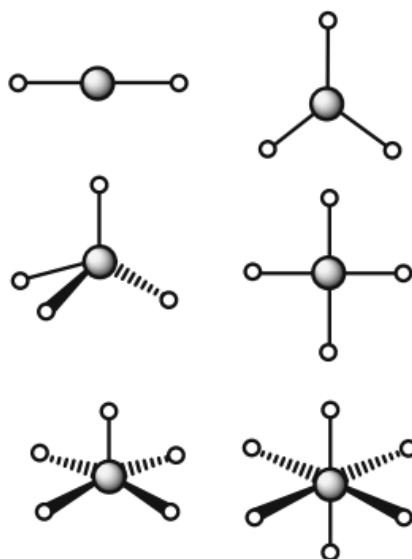

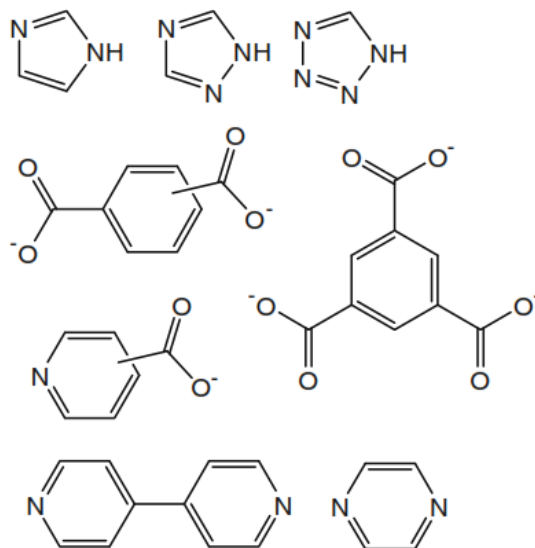**Figure 3.** Common coordination geometries of metal ions [60]

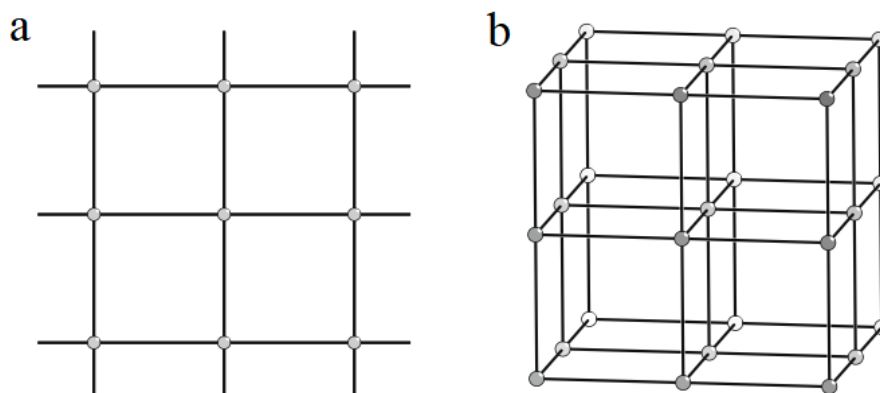**Figure 4.** Examples of simple bridging organic ligands [60]

Figure 5. Topologies of (a) sql and (b) pcu [60]

Therefore, high symmetry and also simpler topologies can be regarded as usable building units of MOFs. For instance, common geometries for divalent transition metal ions are square planar, tetrahedral, and octahedral. These common geometries are appropriate for building sql, dia, and pcu topologies (Figure 5).

The topology of two-dimensional sql can be built by linear bipyridyl-type ligands and Ni (II) or Cu (II) ions [63, 64]. Also pcu networks based on single metal ions, are usually few [65]. It should be noted that dia is the most common topology in MOFs, which is related to high amounts of tetrahedral metal ions and linear ditopic bridging ligands [66].

There are several suitable porous compounds that are based on sql and dia topologies. However, the low dimension and interpenetration can limit the porosity in these topologies. So by keeping the same node, the three-dimensional nbo and lvt topologies have more porosity compared to two-dimensional topologies. It is also possible to mix two-dimensional and three-dimensional topologies. This is due to the point that lower porosity structures are more energetically stable. It

should also be mentioned that nbo and lvt topologies are uncommon. The difference between the three most common topologies is related to the dihedral angle between adjacent square planar nodes. To have higher control on the network topology, it is possible to shorten the bridging ligand [67, 68].

The metal clusters merging into MOFs significantly improves stability and porosity. Although, the metal-containing building units and coordination bonds are typically formed in the original place, almost only via a one-pot process reaction. On the other hand, linkers are predesigned and generally retain their integrity during MOF construction. Although the first MOF researchers are mainly inorganic chemists, MOF research in the past decade has been significantly influenced by organic ligand design

and post-synthetic modification of the linker [69].

Since the importance of the construction of targeted topologies in MOFs, the easy rotation of molecular building parts around individual coordination bonds cannot improve control over node-to-node direction [60]. For example, rigid polynuclear clusters such as $Cu_2(RCOO)_4$ and $Cu_2(Rtz)_2$ can provide more directionality; therefore, they can serve as secondary building units (SBUs) [70]. The $M_2(RCOO)_4L_2$, $M_4(\mu_4\text{-}O)(RCOO)_6$, and $M_3(\mu_3\text{-}O/OH)(RCOO)_6L_3$ are the most frequently used SBUs. L represents a monodentate terminal ligand, and the carboxylate (RCOO) represents a multitopic ligand when these SBUs can be performed as square-planar, octahedral, and trigonal-prismatic nodes, respectively (Figure 6).
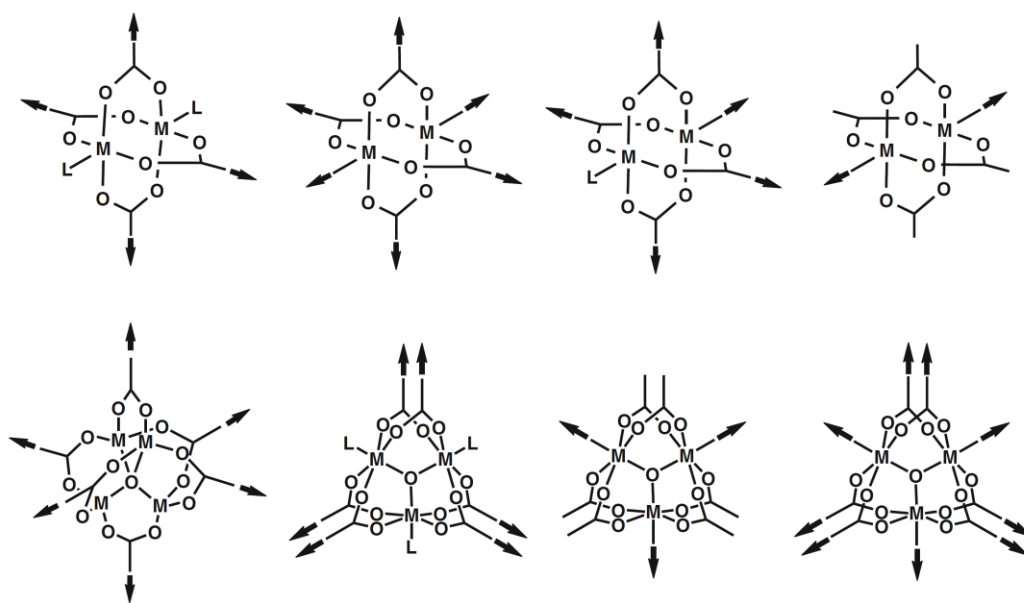

Figure 6. The $M_2(RCOO)_4$, $M_4(\mu_4\text{-}O)(RCOO)_6$, and $M_3(\mu_3\text{-}O/OH)(RCOO)_6$ SBUs and their representative coordination modes [60]

The solvothermal reaction of $Cu(NO_3)_2$ and benzene-1,3,5-tricarboxylic acid (H3btc) provided $[Cu_3(btc)_2(H_2O)_3]$ (HKUST-1) with a highly superior symmetric porous network with a (3,4)-connected **bor** topology, in which $Cu_2(RCOO)_4(H_2O)_2$ cluster and the btc^{3-} ligand

serve as the square-planar and trigonal-planar nodes, respectively (Figure 7a) [71]. To use enlarged tricarboxylate ligands, further porous analogs, sometimes interpenetrated, could have been constructed [72, 73].

Yaghi *et al*. [74] in their research, reported a series of pcu-type MOFs, consisting of $Zn_4(\mu_4 O)(RCOO)_6$ cluster and linear dicarboxylate ligands with various lengths and side groups, which were isoreticular having the prototypical structure $[Zn_4(\mu_4-O)(bdc)_3]$ (MOF-5, H_2bdc = benzene-1,4-dicarboxylic acid) shown in (Figure 7b). Several analogs of this oxo-centered tetranuclear cluster are also recognized. There are a few examples in whichCo(II) ions can entirely or partially replace them, Zn(II) ions. Also, the carboxylate groups can be replaced by pyrazolate groups [75].

In another work by Fe´rey *et al*. various 6-connected porous MOFs consisting of $M_3(\mu_3-O/OH)(RCOO)_6L_3$ clusters were developed. The trigonal-prismatic geometry of $M_3(\mu_3-O/OH)(RCOO)_6L_3$ SBU permits four such clusters to get arranged into a super-tetrahedron, which can further interconnect with each other by sharing their vertexes to form zeolitic networks such as MIL-101, shown in Figure 8 [76].
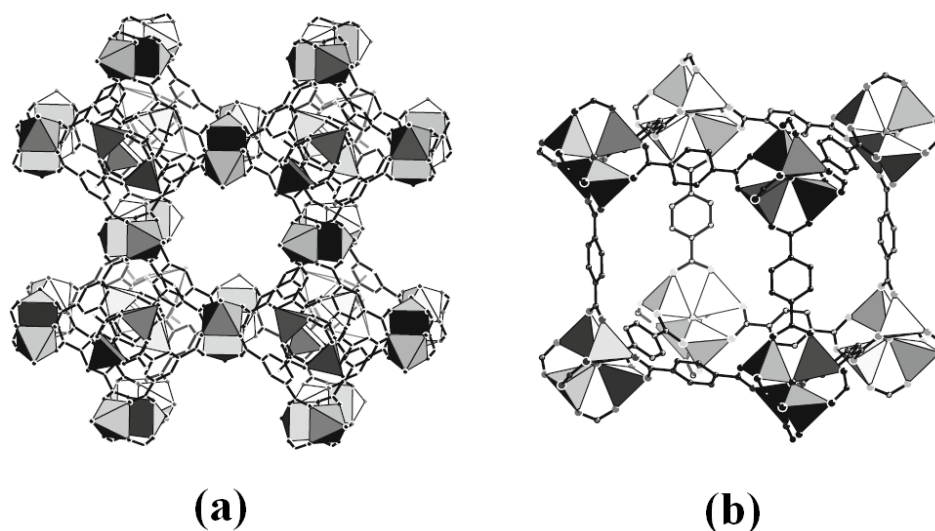

(a) **(b)**

Figure 7. Structures of (a) HfKUST-1, (b) MOF-5 [60]

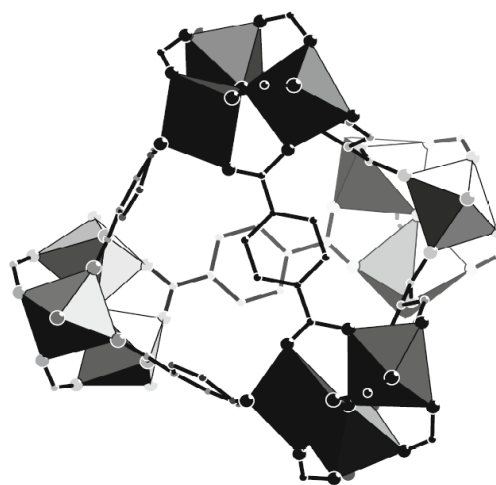**Figure 8.** Structure of MIL-101 [60]

The MOFs, which are based on the $M_2(RCOO)_4L_2$ and $M_3(\mu_3\text{-}O/OH)(RCOO)_6L_3$ SBUs, their monodentate terminal ligand L can be abolished to produce coordinatively unsaturated metal centers, and correspondingly a significant increase in gas sorption affinities. The critical point is that the bonding direction of the carboxylate groups in the $M_3(\mu_3\text{-}O/OH)(RCOO)_6L_3$ can significantly change, leading to the form of highly flexible frameworks structures when the network topology is suitable [77].

The $M_3(\mu_3\text{-}O/OH)(RCOO)_6L_3$ SBUs by possessing three additional links originating from the equatorial plane, are able to be employed as tricapped trigional-prismatic 9-connected nodes. The tritiopic pyridiyldicarboxylate ligands can fully accomplish the 2 to 1 molar ratio required for linking to the carboxylate and pyridyl groups of the trinuclear clusters, which this generates Xmz, as a new type of (3,9) connected topology (Figure 9a) [78, 79].

The breathing behavior of MOFs, which refers to the extraordinary structural flexibility of MOF, is one of the well-studied parameters of MOFs [80, 81]. Breathing occurs due to weak points in the framework at which significant geometrical dimensional reversible changes can occurwithout breaking covalent bonds [81]. Interestingly, the breathing behavior of MOFs is drastically affected by varying the ratio of bridging lengths of the pyridyl and the carboxylate ending parts of the tripodal ligands, which can highly change the binding direction of the carboxylate groups of the clusters [82]. The dicarboxylate and pyridylcarboxylate ligands combination in a 1 to 2 ratio can also meet the desires for coordination requirement of the trinuclear clusters, which causes to generate the ncb topology consisting of unimodal 9-connected networks (Figure 9b). The bridging lengths of the ligands affect the coordination geometries of the clusters in the ncb networks. Therefore, the ncb-type MOFs can only be synthesized by dicarboxylate-pyridylcarboxylate ligand combinations with suitable bridging length ratios, confirmed by geometry calculations and a systematic synthetic trial using a large number of ligand combinations with different bridging lengths [83, 84]. Even when the bridging ligands are very long, no interpenetration for the ncb-type MOFs was observed [60].
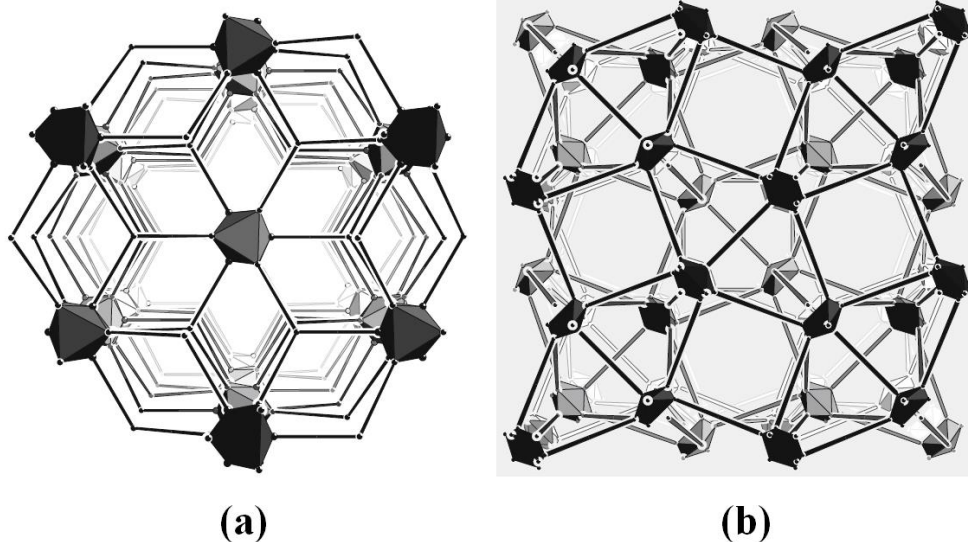

(a) **(b)**

Figure 9. The topologies of (a) xmz and (b) ncb [67]

Interpenetration in MOFs Framework

One of the most prevalent phenomena concerning the coordination of polymers is the interpenetration of frameworks in MOFs, which is often consideredan unfavorable condition for polymers construction of highly porous frameworks. Although in some cases at low pressures condition, interpenetration can increase gas sorption ability and framework stability [85-87]. In the nbo network as an example, network interpenetration is prevented because the network dual net is 8-connected Bcu rather than itself. To express it differently, interpenetration often occurs for self-dual topologies such as dia because crystals tend to consist of repeating identical units [60, 88]. Although, some interpenetrating nbo networks have been observed since 2003 [89,

90]. The more complicated zeolitic topologies, which are also based on tetrahedral nodes, can scarcely show framework interpenetration compared to the dia topology [91].

To perform reasonable construction of non-interpenetrated porous frameworks, there are some practical strategies. In 3D networks, interpenetration can only happen when the porosity is more than 50% for a single network. Therefore, reducing a single network by adding small side groups and increasing the final crystal porosity can be suggested. Indeed, the crystal porosity acquired by this procedure has a noticeable upper value. By considering that interpenetration must happen in all three dimensions in 3D networks, partial blocking of the coordination network can stop interpenetration and keep possession of high porosity (Figure 10).
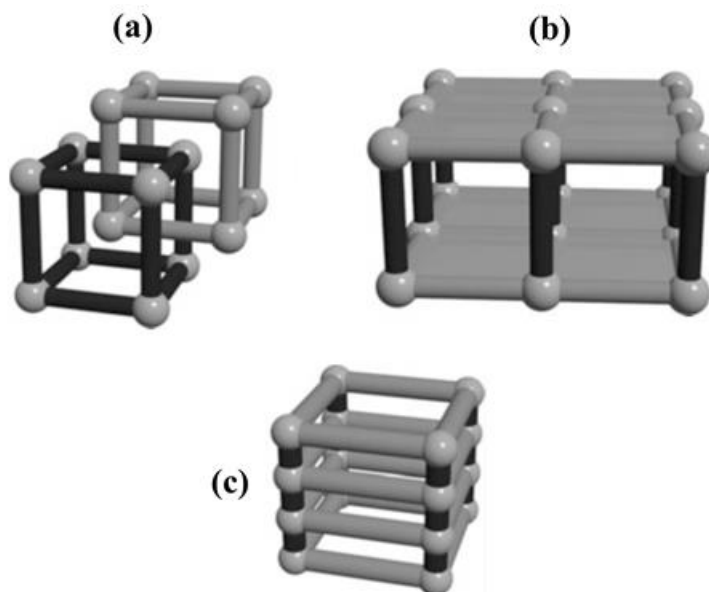

Figure 10. Control of interpenetration of pcu-type structures. (a) Normal interpenetration, (b) a formal pillared-layer structure consisting of dense layers and long pillars, and (c) a non-interpenetrating pcu net consisting of porous layers and short pillars [67]

The MOFs, consisting of pillared-layer structures, due to their comparatively dense layers, which inducesblocking of one of the three dimensions, show no interpenetration in

their framework. For the construction of a suitable layer structure containing coordinatively unsaturated sites, changing the pillar ligand causes to obtain MOFs with

different pore sizes, porosity, and surface [60]. Therefore, it is that no framework interpenetration occurs due to the suitable arrangement of pillar ligands employing controlled and determined distribution of coordinatively unsaturated metal ions.

The 3D structure of a pillared-layer structure is generated due to the forming of the layer first, and the pillar connects later, but this can hardly be perceived directly since the crystallization and self-assembly of MOFs are generally done in a one-pot synthesis reaction. Nevertheless, the individual single-layer structure can sometimes be synthesized by using suitable non-bridging ligands instead of pillar ligands. Occasionally, the hypothetic monolayer and pillared double layer have been isolated during synthesizing a pillared-layer MOF [92].

During the synthesis process of MOFs, one of the main concerns is that real condition is always more complicated than theoretical expectation. Various factors usually influence the molecular assembly processes , such as parameters that significantly influence the reaction and minor dissimilarities in the structures and properties of the ligands and the metal ions or clusters [93]. Thus, there still exist many compounds which produced more unintendedly than predesigned. However, many compounds have been successfully generated by the net-based method or reticular chemistry strategy with either single metal ions or metal clusters as nodes, as well as the pillar-layered strategy. Therefore, MOFs constructed by these techniques will have different pore sizes, shapes, and surface properties by using similar bridging ligands with different lengths and side groups. Also, mixed ligands with the same coordination mode and length but different side groups or cores can be used to design and construct solid-solution-type frameworks (periodic lattice with non-periodic metal/ligand distribution), which are becoming

an effective strategy for pore surface improvement to avoid interpenetration [94-96].

Synthesis methods and post-synthetic modification of MOFs

Up to now, various procedures and methods have been reported due to the understanding of the MOF formation process and its basic mechanisms [93]. A wide variety of analytical techniques and chemical parameters are being assessed through the perception of these mechanisms and processes and reaction conditions. Nevertheless, the designed synthesis of a new material is still considered almost impossible, especially since the diversity of possible inorganic building units and topologies prevents the prediction of the reaction product structure.

Being aware of the crystallization principles assists in understanding reaction conditions and chemical parameters, which permits the synthesis of new MOFs [97]. Synthesis is the primary technique for constructing MOFs, and its importance on the final properties of MOFs is highly verified. Solution-based methods are mostly synthesis techniques employed to construct MOFs under different conditions. Crystallization is considered one of the main steps during the synthesis process. MOFs, in general, are crystallized from the primary synthesis solution. MOF crystals automatically grow in a solution containing the metal salt and organic ligand. In some cases, there are solubility problems for the reactants and products; other methods, such as diffusion and hydrothermal/solvothermal reactions, may be functional, particularly for the growth of high-quality and large-sized crystals for single crystal diffraction. The reaction method and condition are crucial for constructing some types of MOFs,

especially for MOFs containing polynuclear SBUs [60].

Organic solvents and water generate highly porous materials containing pores filled with guest molecules such as solvents, structure-directing agents, or unreacted linker molecules. However, due to the energetic point of view and thermodynamically, dense structures are more stable. Therefore, the integration of guest molecules and especially the kinetics of the formation of inorganic building units play a pivotal role in forming MOF structures. The source reason for crystallization is consideredan equilibrium reaction between the dissolved predecessors and the new solid compound (MOF). According to the thermodynamic reaction at constant pressure, which is described below with the Gibbs-Helmholtz equation (Eq. 1) [97]:

$$\Delta G = \Delta H - T\Delta S \qquad (1)$$

The entropy of a solid compound is too lower than that of a solution or liquid because of the fewer stable microstates of the solid.

Crystallization is affected by the temperature and concentration of the solution. As seen in (Figure 11. left), the equilibrium shifts to the dissolved compound solution stable region by temperature increasing. It also shifts stable precipitation region by increasing the concentration, which is caused due to the finite solubility of the reactants. The recrystallization process for the purification of a substance is an excellent simple example in which increases in temperature and amount of solvent causes the dissolution of the substance and the recrystallization can be caused by evaporating the solvent and decreasing the temperature [97].

A crystal formation is a two-step process; nucleation and growth. Nucleation occurs as a result of the assembling of ions or molecules to form a cluster. If the cluster size is below a specific critical size which is named r_c (in the nm-range), is not stable and re-dissolves. Once the cluster size becomes equal to or greater than r_c, then it is thermodynamically stable and is called a nucleus. The Gibbs free energy of crystallization (ΔG_N) is constituted of two terms, the surface energy term (ΔG_S) and the volume energy term, which scales are r^2 and r^3, respectively (Figure 11, center). The following equation (Eq. 2), is applied for a spherical body:

$$\Delta G_N = \frac{4}{3}\pi r^3 \, \Delta G_V + \, 4\pi r^2 \gamma \qquad (2)$$

Since ΔG_V is a negative and ΔG_S a positive term if the cluster size becomes equal or greater than r_c, ΔG_N quickly decreases, and the crystal grows.

However, the crystallization is also highly dependent on kinetic parameters. The La Mer-diagram can describe the time-dependent growth of a crystal from a solution (Figure 11 center, right). At t = 0, the reactants are combined and react with each other. Then the reaction leads to forming precursors, such as inorganic building units and deprotonated organic linker molecules, and the concentration (c) increases. The concentration surpasses the thermodynamical solubility c_s, forming a supersaturated solution. In this heterogeneous nucleation, nucleation on surfaces such as a glass wall, an impurity, a seed crystal, and bubbles can happen. Homogeneous nucleation occurs without preferential nucleation sites above the critical nucleation concentration c^*_{min}. After the nucleation period, these seeds form larger crystals until the concentration is lowered to c_S [97].
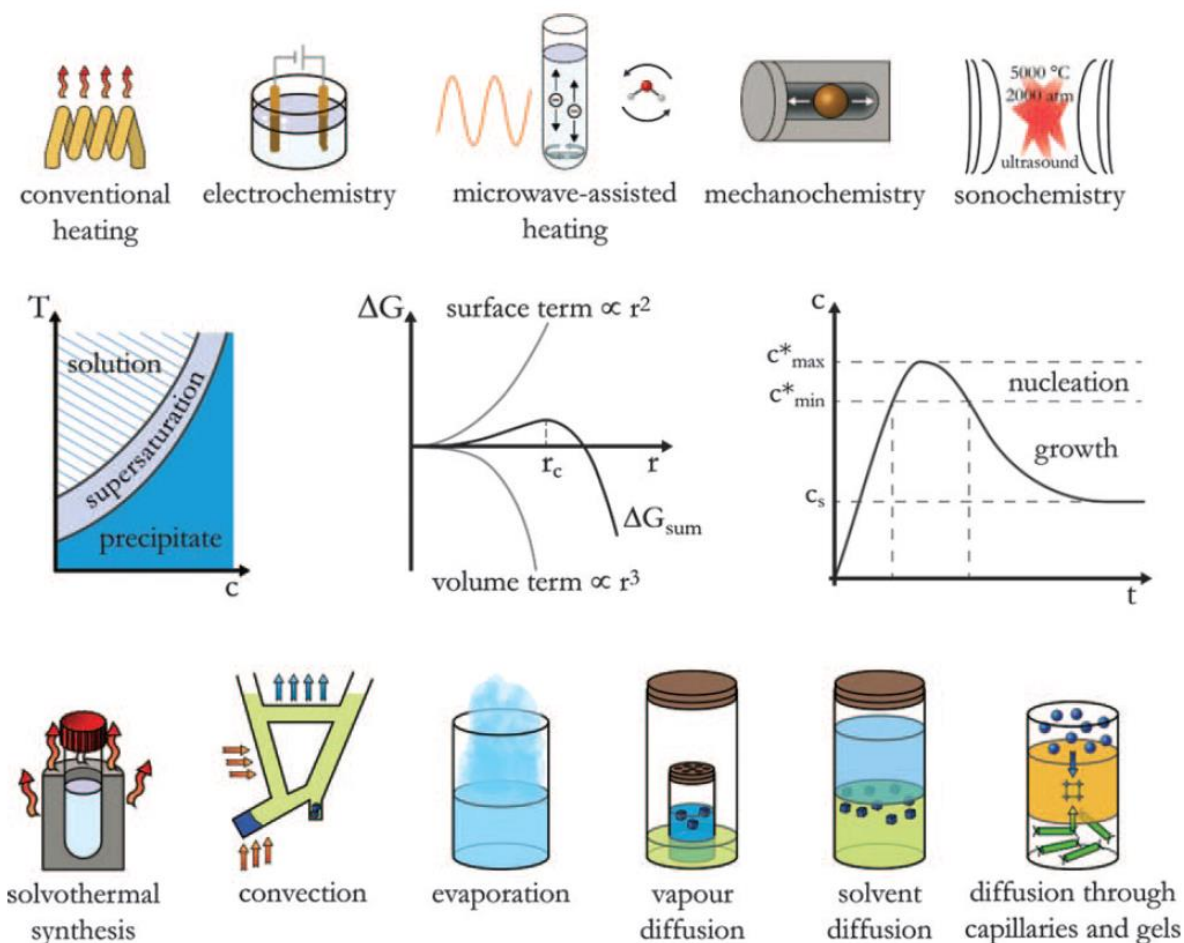
Figure 11. Aspects of crystallization in the synthesis of solid compounds [97]

In situ characterization methods in the reactor can investigate the crystallization procedure while the reaction occurs [98]. Since the particles and clusters are too small and their atomic assemble arrangement cannot be obtained effortlessly. For example, the size of particles can be measured by dynamic or static light scattering (DLS and SLS). Phase identification during the crystallization process and crystal growth can be monitored by *in situ* energy dispersive X-ray diffraction (EDXRD). Various studies on forming MOFs have been recently reported, such as CAU-1-NH$_2$, HKUST-1, and Al-MIL-101-NH$_2$ [97]. Different experimental setups and various methods for the synthesis of MOFs are also shown in Figure 11. Some of these synthesis methods are described in the following. The reaction time of MOF synthesis can be significantly accelerated by increasing reactant concentration, rapid mixing of reactants, heating, and microwave irradiation [99]. Although progressive achievements have been reached in the field of MOFs synthesis, the potential of using machine learning (ML) methods to predict MOF synthesis parameters is an interesting approach used for rationalization and acceleration of the MOF discovery process through directly anticipating the MOF synthesis conditions based on its crystal structure. For instance, Lue *et al.* [100] in 2022, established the first MOF synthesis database via automatic extraction of synthesis parameters from the literature, then trained and optimized ML models by the

employed MOF database, and finally predicted the synthesis conditions for new MOF structures, in which the results of automated synthesis prediction indicated a good prediction performance of ML models, even at an initial stage, outperforming human expert predictions.

Synthesis methods

Solvothermal synthesis is a thermo-dynamically closed-system method in which the reactants are completely sealed in an autoclave and heated to a temperature above the solvent's boiling point at standard pressure. The solvothermal synthesis process can be performed in various temperature ranges, which depends on the reaction requirements [101]. The hydrothermal method has been used successfully to synthesize an enormous number of inorganic compounds and inorganic-organic hybrid materials [101].

Conventionally electric heating has been used for synthesis methods. Nevertheless, other new ways of more novel energy input have recently been employed. Microwave-assisted heating synthesis or microwave irradiation is a quick method for producing MOFs and can be applied to minimize reaction times. It is reported that these methods have been largely used to generate nanosized metal oxides [102]. Such processes due to heating the solution with microwaves within about an hour can construct nanosized crystals [101]. In contrast to conventional heating, where the heat is conducted through the vessel's walls, the interaction of the reaction mixture with microwave radiation rapidly heats the entire reaction volume. Often an increase in the nucleation rate is observed that leading to smaller product particles [97].

In the sonochemistry method, the intensive ultrasonic oscillation causes the solvent to move, leading to areas of rarefaction and compression on a microscopic scale and causing chemical changes. Due to this, bubbles are formed and then collapse under their own instability, causing extremely high temperatures and pressures (up to 5000 °C and 2000 atm). The cavitation due to collapsing bubbles creates highly localized mechanical or thermal energy, which can be used to significantly accelerate nucleation and crystallization in some cases by increasing the dissolution rate of reactantsthat are hard to dissolve. Sonochemical methods can produce homogeneous nucleation centers and significantly reduce crystallization time compared to conventional hydrothermal methods [101].

Mechanochemistry is a method in which a ball mill or mortar and pestle introduces mechanical energy. This method has only rarely been used in the synthesis of MOFs but it has some advantages such as its simplicity, non or only small amounts of solvents required, and reduced waste amount [97]. Some MOFs can also be quickly synthesized by mechanochemical reaction of the corresponding metal salt and organic ligand in the presence of a minimal amount or even without solvent. Nevertheless, soluble metal salts are generally necessary for mechanochemical reactions [103].

The Electrochemistry method has been used to synthesize Cu- and Zn-based MOFs. The metal ions are formed in situ via redox processes on electrode surfaces. Since the precursor solution is formed near the electrodes, even thin films of the MOF can be grown on the electrode [97]. The electrochemical synthesis process does not require metal salts. It can generate continuous production of MOF crystals, and this method is employed under milder conditions than typical solvothermal or microwave synthesis, which is a great advantage of this method. Furthermore,

the required time is reduced for synthesis within minutes or hours, whereas solvothermal synthesis may take several hours or days [104].

In contrast to solvothermal reactions, reactions under mild conditions can be conducted in less complicated reactor systems, such as simple beakers or specially constructed glass vessels. The temperature difference induces the concentration gradients along the reactor, leading to convection and crystallization in a colder part of the reactor. Moreover, by applying gels or capillaries, the reactants have to diffuse from opposite directions, slow evaporation of the solvent, or apply an anti-solvent. The vapor diffusion through the gas phase into a clear solution or by liquid/liquid diffusion by cautiously layering a low low-density anti-solvent on top of the reaction solution [97]. Thus, according to difficulty of finding a new MOF structure due to the possibility of different inorganic building units, topologies, and organic linker molecules makes the prediction of a new reaction product structure is almost impossible. Nevertheless, there are many techniques and strategies which have become functional to find new or iso-reticular (same structural topology) compounds and for the optimization of synthesis processes.

According to recent advances in the synthesis field of MOFs, Molecular imprinting technology is employed to construct molecularly imprinted polymers (MIPs). The recent progress regarding synthesizing and sensing applications for metal-organic framework-molecularly imprinted polymer (MOF-MIP) composites in hybrid MOF-MIPs possessing increased sensing properties indicate the high performance for various types of targets such as high sensitivity and selectivity to detect pesticides, mycotoxins, and proteins [105].

Post-synthetic modification of MOFs

Since the importance of using functionalized organic linkers in synthesis, lots of desired functionalities are incompatiblewith the real conditions applied for MOFs synthesis. Therefore, it induces some changes in the desired structure. Thus, an alternative strategy method has been suggested and employed for forming functionalized MOFs, which is a post-synthetic modification (PSM). PSM is applied after the synthesis process. During PSM, the pore's shape is altered, then the coordinative and sensitive functional groups will be permitted to get inside the pre-formed (during the synthesis) network structure pores (106). In general scope, one can say that post-synthetic modification can promote any changes in the synthesized structure to pore modification, forming functionalized network and finally improving and modifying the pre-formed synthesized structure to achieve desired properties and structure network.

Hoskin and Robson in 1990 [10] proposed the general scope of the PSM process to modify network pores. The later reports continued the field development more and more by Williams [71], Kim [107], and Lee [108] in 1999 and 2000. Wang and Cohen in 2007 [109], first directly referred to 'post-synthetic modification' by comparison of posttranslational modification of proteins. The post-synthetic modification is not only contributed to MOFs, but also it has been applied to mesoporous silicas [110], hydrogels [111], organic network structures [112], and biomolecules [113].

According to a review book carried out by Burrows in 2013 [106], the PSM process was divided into four main categories, Covalent PSM, Dative PSM, Inorganic PSM, and Ionic PSM, which are described schematically in Figure 12.

In covalent PSM, which is the most high-developed type of PSM in MOF chemistry, covalent modification of a linker ligand occurs during the process. In dative PSM, a metal center coordinates to a linker. In the inorganic PSM, a modification of the secondary building units (SBUs) occurs, which causes to the formation of the nodes in the MOF network. And in Ionic PSM, a counter-ion exchange occurs in an anionic or cationic MOF.

In covalent or dative PSM, the MOF structure commonly requires a reactive group existing on a linker. This group, called a 'tag', is a stable, functional group and innocent (which means non-structure-defined) during MOF formation, but can be transformed through post-synthetic modification. Occasionally, following-in-order PSM reactions are carried out, referred to as *tandem* PSM reactions, and typically include two or more continuous covalent modifications or a covalent modification followed by a dative modification. However, other combinations of PSM reactions are also possible [114].
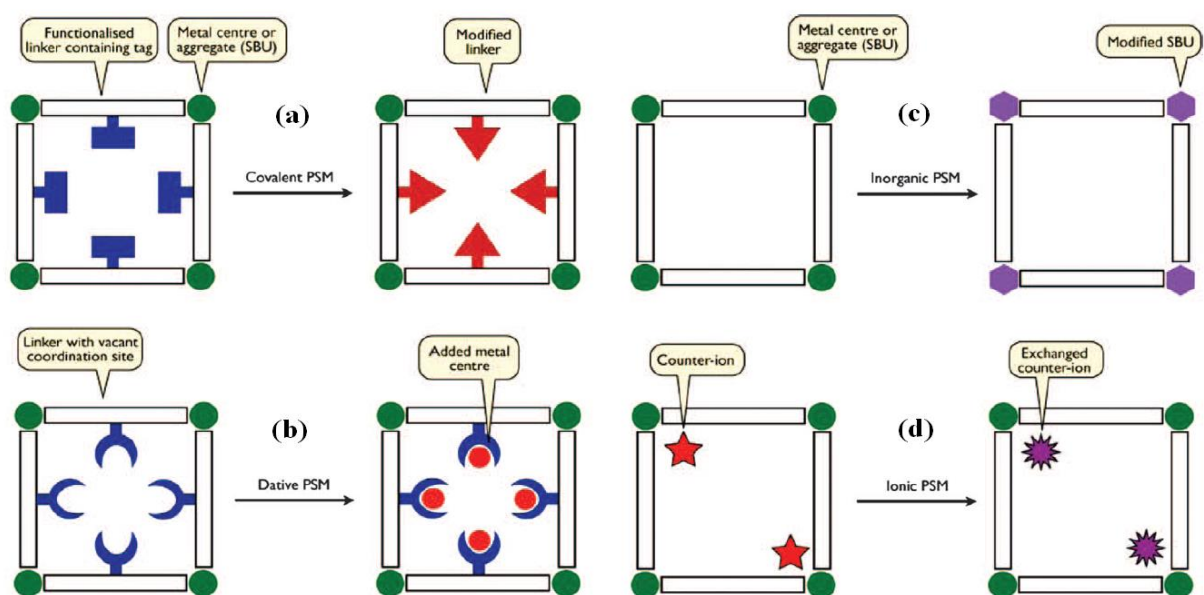

Figure 12. Schematic representation of the four categories of post-synthetic modification [106]

One essential and well-investigated area is the exchange or removal of guest molecules from the pores. For most porous MOFs, activation by removing included solvent molecules from the pores is crucial for activity. Guest removal can occur with changes in pore shape, as observed in flexible MOFs such as [M(OH)(bdc)] (MIL-53, M=Al, Cr; bdc=1,4-benzenedicarboxylate) [115], and occasionally with more considerable changes in the network [116].

Kawamichi *et al.*, in 2009 [117] showed that the reactions of guest molecules within the pores can lead to the isolation and characterization of very reactive species, which are stabilized by confinement within the network of MOF.

Despite outstanding progress made in the synthesis of polycrystalline MOF membranes over the last decade, only a limited number of MOFs have been employed in this field due to the lack of a clear solution for intercrystalline defects, non-selective diffusion pathways in polycrystalline membranes. PSMs are regarded as newly emerging strategies for introducing polycrystalline MOF membrane diversity by

utilizing existing membranes as a platform and enhancing their separation functions through physical and chemical treatments. Thus, there is no need for designing new MOFs and customizing membrane synthesis techniques for targeted MOFs. In the minireview conducted by Kwon *et al.* [118], eight subclasses, covalent tethering, intercrystalline defect plugging, intercrystalline defect healing, the inclusion of functional materials in pores, stiffening, [6] ligand exchange, amorphization, and MOF to MOF transformation of PSM strategies were challenged and discussed.

Finally, it is concluded that during the past few years, the extensive development in the respective research field shows its growing importance and variety in chemistry, structure, synthesis, and post-synthesis modification of MOFs.

MOF Purification

One of the essential steps after the synthesis process is the purification and activation of MOFs. Actually, the purity of a MOF structure has high importance as one of the aspects catalysis, since the by-product's existence can influencecatalytic activity and reduce the sorption capacity of the substance [119]. Impurities are by-products that are not obstructed inside the pores. Crystalline impurities can be observed by powder X-ray diffraction (PXRD), and amorphous impurities compounds can be detected using thermal gravimetry (TG). The removal of these impurities is considered a difficult process. Most observed impurities are eliminated by solvent treatment at high temperatures [97]. Some of the observed by-products have been reported, such as metal oxides in different conditions [120], dense hybrid compounds [121], and recrystallized linker molecules [76, 122]. MOFs are inherently insoluble, making it

impossible for MOFs purification via the conventional procedures usually applied by chemists (distillation, chromatography, recrystallization, and sublimation,). Thus, Farha *et al.* in 2010 (123) reported an approach via their study results to rapid purification. Differences in the density of desired and undesired products would have been a useful alternative method compared to conventional methods.

Characterization of MOFs

From the general scope, the study and investigation of the MOFs characterization becomes essential in carrying out analysis and discussion of important reactions and events occurred in MOFs such as synthesis, post-synthetic modification, de-solvation, sorption and adsorption of gases, photocatalysis and other prevalent processes. Therefore, various spectroscopy analysis methods such as vibrational and rotational techniques including IR, Raman and INS and electronic techniques including UV-Vis, Luminescence, XPS, XANES and XESX-ray, neutron scattering and photoelectron backscattering-based can assist to apply basic steps due to understand different structures of MOFs [124].

The vibrational and electronic spectroscopies combination provides information on the investigated MOF materials properties that cannot be obtained by the structural refinement of XRPD data, BET and TG analyses [125]. Laboratories working in the characterization and synthesis of MOFs should be provided with a FTIR and a DRS-UV-Vis instrument. Raman and XPS due their high cost and INS, XANES and RIXS due to their less easily available spectroscopies should be employed in specific cases. Besides the unavoidable standard laboratory XRPD investigation, the possibility of extending the structural

characterization to less common techniques, such as neutron powder diffraction, metal K-or L-edge EXAFS and neutron or X-ray PDF, will permit better characterization of complex materials such as MOFs [124].

Conclusion and Remarks

In this review article, the authors tried to cover several critical conclusions emphasizing the importance of providing MOFs as a new approach to noble materials due to their outstanding well-ordered porous structure, high specific surface area, and adjustable organic linkers- metal clusters connections. The MOFs structure plays a key role in their special properties and the employment of an appropriate synthesis techniqueto achieve the desired properties. The post-synthesis modification (PSM) process after synthesis is essential to pore modification, forming a functionalized network, and improving and modify the pre-formed synthesized structure to achieve desired properties.

Acknowledgments

Disclosure Statement

No potential conflict of interest was reported by the author.

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