

Synthesis of metal–organic frameworks and their immobilization on surfaces

Síntesi de metal–organic frameworks i la seva immobilització en superfícies

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Abstract: Metal–organic frameworks (MOFs) are porous materials made of metal ions bonded to organic ligands by coordination bonds, resulting in the obtention of structures with two or more dimensions from repeatable units. Lately, research on the use of MOFs in biology has led to the creation of biological MOFs (BioMOFs). In addition, the preparation of MOF films and their growth on functionalized surfaces is required in order to incorporate MOFs into devices and produce surface–coordinated MOFs (SURMOFs). For this reason, SURMOFs' classification, synthesis and applications are presented in this review.

Keywords: Metal–organic framework (MOF), self–assembled monolayer (SAM), surface–coordinated metal–organic framework (SURMOF).

Resum: Els marcs orgànics metàl·lics (MOF, de metal–organic framework) són materials porosos fets d'ions metàl·lics enllaçats a lligands orgànics mitjançant enllaços de coordinació, en què s'obtenen com a resultat estructures amb dues o més dimensions d'unitats repetibles. Últimament, la investigació sobre l'ús de MOF en biologia ha portat a la creació de MOF biològics (BioMOF). A més, la preparació de pel·lícules de MOF i el creixement en superfícies són necessaris per a incorporar MOF en dispositius i produir MOF de superfície coordinada (SURMOF, de surface–coordinated metal–organic framework). En aquest article es presenten la classificació, la síntesi i les aplicacions dels SURMOF.

Paraules clau: marc orgànic metàl·lic (MOF, metal–organic framework), monocapa autoassemblada (SAM, self–assembled monolayer), marc orgànic metàl·lic de superfície coordinada (SURMOF, surface–coordinated metal–organic framework).

Introduction

Metal–organic frameworks (MOFs), also known as porous coordination polymers (PCPs), are synthetic materials composed of metal ions or clusters linked via coordination bonds to organic ligands. These components come together to produce two- or three-dimensional network nanostructures, leading to the obtention of crystalline structures with cavities of different shapes and sizes (figure 1) [1–3].

The modular crystalline structure of MOFs allows the creation of a vast variety of structures with distinct characteristics, topologies, and functionalities [4]. Lanthanides, alkaline metals, and transition metals are employed as metal ions for the synthesis of MOFs, along with additional elements like car-

boxylates, phosphonates, and azolates as organic ligands [1]. Pore size and shape, as well as density and surface area, can vary in MOFs depending on the functionality and the length of the organic linkers [4]. The capability of controlling the porosity, structure, and functionality of MOFs gives rise to a variety of applications, such as catalysis, molecular recognition, gas storage, drug carriers, biomedical applications, and molecular recognition [5, 6].

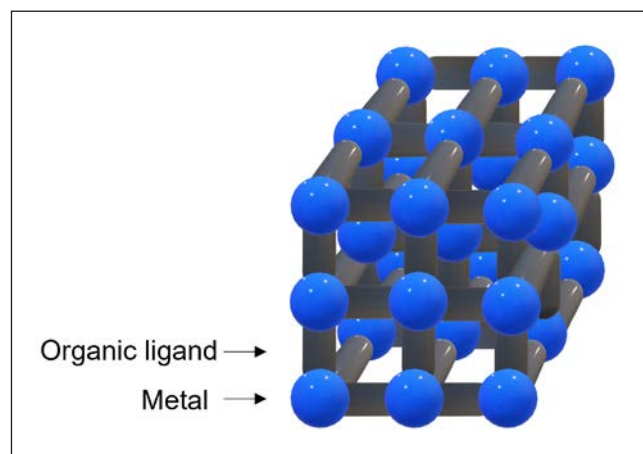


FIGURE 1. Representation of a metal–organic framework structure. Source: Prepared by the authors.

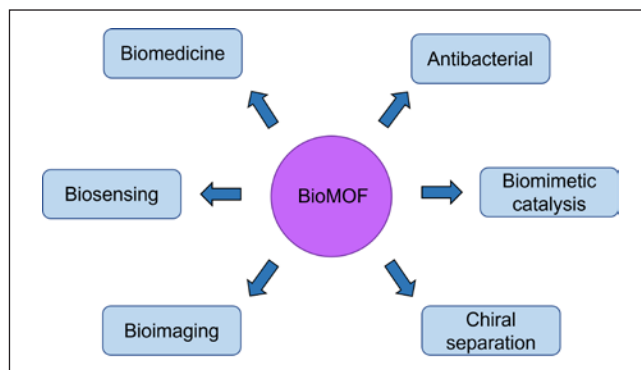
Biological metal-organic frameworks (BioMOFs)

Recent research on MOFs for biological applications has led to the creation of BioMOFs. Both of the following definitions apply to these structures: (1) BioMOFs are porous MOFs that have one or more organic ligands which are biomolecules, or (2) BioMOFs are structures that can be utilized in a variety of biological and medical applications [5].

The interaction between a material and a living organism is what determines biocompatibility, which is the primary prerequisite for bioapplications. As a result, MOFs' potential toxicity must be taken into account. According to reports, morphology, surface charge, and size all affect how well MOFs perform, which means that an improper formulation could result in major hazardous problems and reduced efficacies [1]. Therefore, when entering a living organism, the features of these structures must be stable [7].

To prevent toxicity, BioMOFs employ biomolecules such as proteins and nucleobases, among others, as organic ligands, and Ca^{2+} , Mg^{2+} and Zn^{2+} as non-toxic cations [8]. Another important element to take into account is the solvent employed: using non-toxic solvents makes it possible to create more biologically compatible structures [7]. If Zn^{2+} is employed as the metal ion and curcumin (CCM) as the organic ligand, a BioMOF named Medi-MOF-1 ($[\text{Zn}_3(\text{CCM})_2]$) can be obtained. This porous structure is characterized as acting as a host for the delivery of molecules such as ibuprofen and having a large surface area ($3002 \text{ m}^2/\text{g}$) [9, 10].

In recent years, BioMOFs have been widely used in a vast variety of bioapplications. First of all, BioMOFs can be employed in biomedical applications because they are excellent candidates for drug delivery hosts due to their drug-loading capacity and biocompatibility. Also, BioMOFs are present in the biosensing and bioimaging fields as biosensors due to their range of functionalities and structures. Likewise, they can be employed in antimicrobial applications if they have low-toxic cations such as Zn and Co ions; in biomimetic catalysis if they have hydrophilic and hydrophobic pores that mimic the environment of the enzymes' active sites; and in the separation of chiral molecules if they have chiral ligands. Hence, they are excellent candidates for enantioselective separations when interacting with chiral molecules (scheme 1) [11].



SCHEME 1. Applications of biological metal-organic frameworks. Source: Prepared by the authors.

Surface-coordinated metal-organic frameworks (SURMOFs)

Some reported MOF structures have now demonstrated exceptional performance in terms of environmentally friendly energy. However, their current bulk or powder forms restrict their practical applicability to some extent. For this reason, the precise control of MOFs during their application has gained considerable attention. The ability to attach a MOF to a solid substrate to form MOF thin films opens up possibilities that are not offered by the conventional MOF powders produced by standard bulk synthesis methods. Hence, using uniform substrates or surfaces can lead to the controlled growth of thin films due to an increased exposure of active sites [12].

Nevertheless, it is important to distinguish between polycrystalline films and surface-coordinated metal-organic frameworks (SURMOFs), two different groups of MOF thin films. Polycrystalline films are obtained from the assembly of random-oriented MOF crystals and deposited onto a substrate. The attachment of crystals in a particular direction is enhanced by interactions with the corresponding substrate. In this particular instance, the crystals' size is on the micrometer scale and it affects the thickness of the film. These films can be obtained using a variety of techniques, such as growth at room temperature or slow diffusion reactants.

SURMOFs are ultrathin crystal multilayers and are exceptionally oriented, at least in one direction. These films exhibit low roughness, nearly no defects, and are constructed from large in-plane single crystal domains [3, 13].

SURMOF synthesis

When synthesizing SURMOFs, it is essential to control the size, orientation, and crystallinity of the crystals, for which reason functionalized substrates with ordered molecules or self-assembled monolayers (SAMs) are employed [3, 13]. SAMs are two-dimensional orientated structures of ordered molecules that spontaneously grow as layers on surfaces [14].

Three elements compose the structure of a SAM: the head group, which binds to the substrate; the aliphatic chain, which provides thickness to the layer and orientates it; and the terminal group, which determines the SAM's reactivity as well as its chemical and physical characteristics (figure 2) [14].

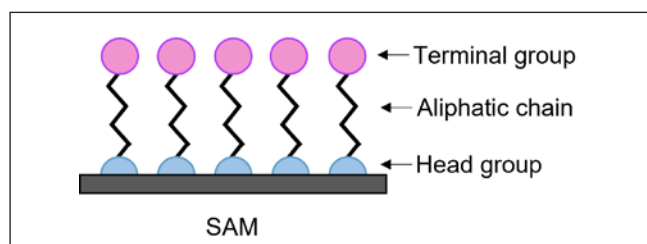


FIGURE 2. A representation of a SAM structure, consisting of the terminal group, the aliphatic chain, and the head group. Source: Prepared by the authors.

Surface functionalization enables the alteration of different properties, the creation of new applications, and better control of a system when it is attached to a substrate. In this case, covalent bonds allow the molecules to be attached

to the substrate. In addition, SAMs are commonly utilized in electronic devices as sensors and film transistors [15, 16].

Two different approaches have been developed for growing MOFs onto a functionalized substrate with control of orientation and thickness: liquid-phase epitaxy (LPE) and Langmuir Blodgett layer-by-layer deposition (LB).

Liquid-phase epitaxy

Liquid-phase epitaxy is a technique that consists in the absorption of the solution components onto the surface by immersing the substrate in a saturated solution of the starting materials to grow crystals, in this case the respective SURMOF (figure 3). In relation to this method, there are several notions that have to be considered. First, the substrate must be functionalized in order to allow the nucleation of the MOF and the subsequent growth of the SURMOF. In addition, this method must be carried out at low temperatures under kinetic control. Also, the thickness and crystal orientation are greatly controllable [17]. LPE was originally created for polyelectrolytes attached via ionic interactions, but this method was subsequently extended to metal complexes and coordination polymers [3].

In 2019, Yu and co-workers employed this method to successfully synthesize twenty-six multivariate SURMOFs (MTV-SURMOFs) by using different dicarboxylate linkers, such as $\text{NO}_2\text{-bdc}$ ($\text{bdc} = 1,4\text{-benzenedicarboxylate}$), $\text{C}_4\text{H}_4\text{-bdc}$, bdc , Br-bdc and $\text{F}_4\text{-bdc}$, and employing Cu^{2+} as the metal ion [18].

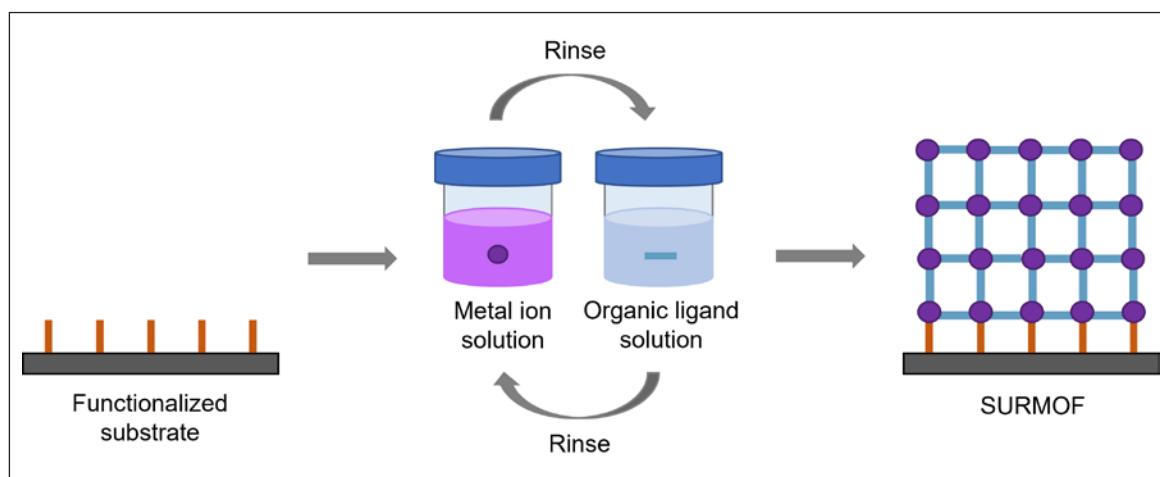


FIGURE 3. Representation of the liquid-phase epitaxy technique. Source: Prepared by the authors.

Layer-by-layer dipping method

Layer-by-layer dipping methodology is an LPE procedure which consists in immersion of the functionalized substrate in the organic ligand solution, followed by immersion in the metal ion solution, or vice versa, rinsing the surface after every immersion and repeating the same steps in a cycle. The layer-by-layer dipping method is suitable for different forms of substrate, including particle and foam substrates. The previously mentioned HKUST-1 SURMOF was synthesized using this method by employing a functionalized Au substrate with COOH-terminated SAM and immersing it in a $\text{Cu}(\text{OAc})_2$ solution, rinsing with ethanol and dipping in a benzene-1,3,5-tricarboxylic acid solution [12, 19].

Layer-by-layer pump method

In this case, the initial objective of the layer-by-layer pump approach to synthesizing SURMOFs was to establish reliable conditions for LPE LBL standardization. This technique involves a pump system in a completely enclosed space in which the precursor solutions are controlled by the pumps in the reaction cell. The pump system consists of four different pumps, three of which are in charge of introducing the organic ligands and metal ions, of rinsing solvent into the reaction cell and, hence, of covering the substrate completely. Lastly, the fourth pump is employed for the extraction of the reactor's waste solution. Consequently, the fabrication of SURMOFs can be precisely controlled while significantly reducing the negative effects of the environment by using the pump method [15]. SURMOFs such as

$[\text{Zn}_2(\text{bdc})_2(\text{H}_2\text{O})_2]$ and $[\text{Cu}_2(\text{bdc})_2(\text{H}_2\text{O})_2]$ were synthesized by Arslan, Shekhah, and coworkers by means of this method [20, 21].

Layer-by-layer spray method

The layer-by-layer spray method uses a minute nozzle system that creates an aerosol by expanding the metal ion and organic ligand solutions in order to spray them onto the substrate-forming layers. The organic ligand and metal ion solutions are sprayed successively, followed by solvent for rinsing after each step (figure 4). The main advantage of this method is that it can quickly prepare SURMOF films while maintaining a high level of orientation and crystallinity. In addition, this is considered an excellent method for producing uniform homogeneous SURMOFs; it takes less time, uses less solution and produces thicker SURMOFs, and it is faster than the dipping and pumping methods [12, 20, 22].

Layer-by-layer spin-coating method

The layer-by-layer spin-coating approach allows the obtention of homogeneous thin films from solutions of starting materials, with shortened preparation time and consumption of lesser amounts of chemicals and solvents. This method is carried out on a spin-coating machine, where the different compound solutions and rinsing solvents are dropped onto a rotating substrate that has been chemically functionalized. By this approach, the droplets can be manually applied, or automated micro syringes can be used, causing the dripping liquid to spread uniformly on the surface due to centrifugal force, which

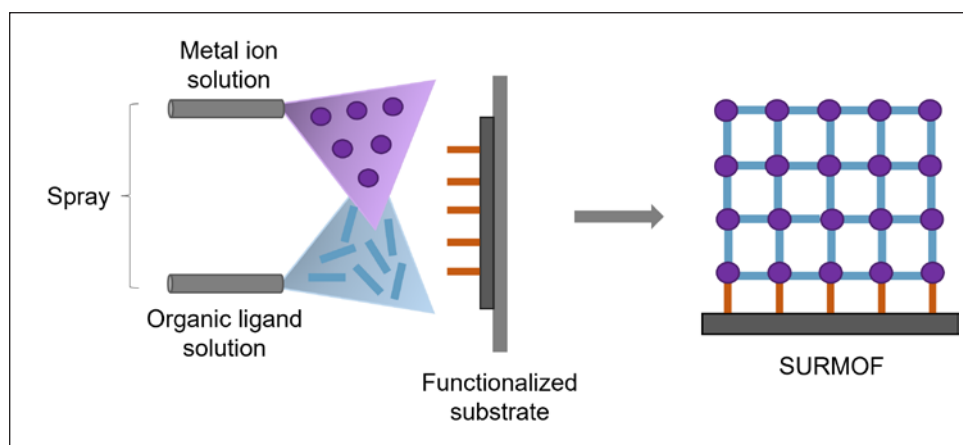


FIGURE 4. Representation of the layer-by-layer spray method. Source: Prepared by the authors.

leads to the formation of the respective SURMOF (figure 5). The rotation speed and time and the drop volume are also key factors for the optimization of SURMOF growth [12, 20]. Using this method, Chernikova and coworkers reported the obtention of zeolitic imidazole framework-8 (ZIF-8 SURMOF), composed of Zn^{2+} ions and imidazole as ligand [23].

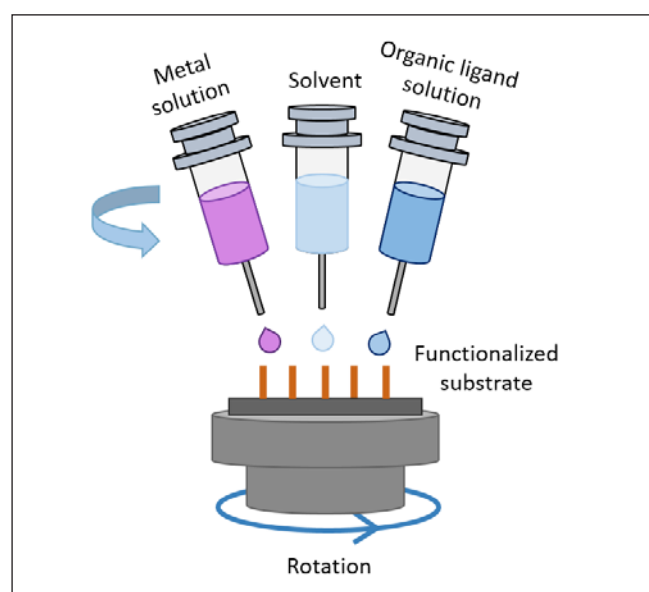


FIGURE 5. Representation of the layer-by-layer spin-coating method. Source: Prepared by the authors.

Langmuir Blodgett layer-by-layer deposition

The second technique for the synthesis of SURMOFs, which was developed by Kitagawa, Makiura, and coworkers, consists in the obtention of MOF layers employing a Langmuir-Blodgett instrument and then transferring them from an air or water medium onto a solid substrate with rinsing steps (figure 6) [3, 24, 25]. The layers obtained are attached to the substrate via weak interactions such as π stacking and the thickness of the respective SURMOF can be determined by the number of deposited organic layers. HKUST-1 MOF ($[Cu_3(BTC)_2(H_2O)_3]_n$) was the first MOF synthesized by the LBL method by Williams *et al.* in 1999 [14] and it is formed by Cu^{2+} clusters linked to benzene-1,3,5-tricarboxylate (BTC^{3-}) ligands. In 2007, HKUST-1 MOF thin films were reported by Shekhah *et al.* and, shortly after, the synthesis of the HKUST-1 SURMOF was reported [20, 26].

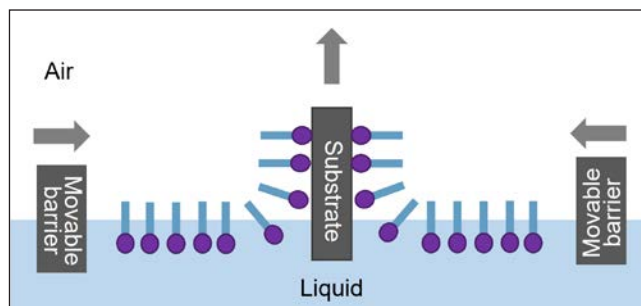


FIGURE 6. Representation of the Langmuir Blodgett layer-by-layer deposition technique. Source: Prepared by the authors.

The approaches previously mentioned allow the controlled obtention of ultrathin MOF films, or SURMOFs, which are characterized as being intriguing from both a conceptual and practical standpoint. Even so, the characterization of these films is challenging from different perspectives, such as porosity, structure identification, and thickness [3, 25].

Classification of SURMOFs

SURMOFs can be categorized into different groups depending on the building blocks chosen. SURMOFs that employ one type of metal ion and organic ligand are pristine SURMOFs, whereas SURMOFs that contain more than one type of metal ion and/or organic ligand are heterostructural SURMOFs.

Pristine SURMOFs

The MOF compounds directly produced using the LPE LBL methodology, with no postprocessing, are pristine SURMOFs. It is potentially feasible to convert thousands of MOF materials into SURMOFs using the proper substrates, solution, and precursors. Pristine SURMOFs can be categorized into four different classes depending on the building blocks chosen: transition metal, lanthanide, porphyrinic and chiral SURMOFs.

Representative transition metal SURMOF

The first SURMOF to be obtained was synthesized by using a transition metal node. These types of metals are characterized as having several coordination units, which are crucial to the connection of organic ligands when forming the SURMOF.

Ions of transition metals such as Fe, Co and Ni provide various coordination numbers when coordinating organic ligands, therefore different combinations can lead to the synthesis of a vast variety of SURMOFs with different structures and properties. As previously mentioned, the first-ever MOF to be investigated and synthesized for the obtention of the respective SURMOF by the LBL technique was the HKUST-1 MOF, which is made up of Cu^{2+} nodes and 1,3,5-benzenetricarboxylic acid as the organic ligand [12].

Lanthanide SURMOF

Lanthanide-based MOF thin films, also known as Ln-SURMOFs, have a great deal of potential for energy conversion devices on account of their distinctive photophysical features. In addition, they are employed in the fields of optics, lasers, and biomedicine. Thus, lanthanide-based SURMOFs are important for many different applications. Specifically, lanthanides are widely employed in photonics due to their optical properties, for example, for narrow bandwidth signal. Generally, lanthanides with an oxidation state of Ln^{3+} are used for the synthesis of the respective MOFs and SURMOFs, such as Eu^{3+} and Tb^{3+} . In 2019, Chen and coworkers reported two different Ln-SURMOFs using the layer-by-layer method: Eu-SURMOF, which is made from Eu^{3+} as the metal ion ($\text{Eu}(\text{NO}_3)_3$) and BTC as the organic ligand, and Tb-SURMOF, constructed from Tb^{3+} and BTC [12, 27, 28].

Porphyritic SURMOF

The SURMOFs of this type are characterized as presenting potential photoelectric properties and combine functional and synthetic versatility in a defined single porous structure. As a result, these structures are extremely promising for fields such as catalysis, sensing, and optoelectronics due to their outstanding combination of features. In 2018, Meshkov and coworkers reported several SURMOFs based on porphyrins. The layer-by-layer technique was employed to grow SURMOFs built from Zn^{2+} and substituted tetracarboxyphenyl porphyrins on monolayers of graphene oxide. Accordingly, four different porphyrins were used: [5,10,15,20-tetra(3-carboxyphenyl)porphyrinato]zinc(II) (*m*-ZnTCPP); [5,10,15,20-tetra(4-carboxyphenyl)porphyrinato]zinc(II) (*p*-ZnTCPP); [5,15-di(4-carboxyphenyl)-10,20-di(4-pyridyl)porphyrinato]zinc(II) (ZnDPyDCPP); and [5,10,15,20-tetra(4-pyridyl)-porphyrinato]zinc(II) (ZnTPyP) [12, 29].

Chiral SURMOF

Chirality plays a crucial role in nature since many organic molecules are chiral. When it comes to synthesizing SURMOFs, if chiral molecules coordinate with metal ions, the cavities of the initial MOF will acquire the property of having chiral resolution. In addition, chiral SURMOF thin films can be applied in fields such as enantioselective adsorption and sensors, functions that achiral SURMOFs cannot provide. Cu^{2+} is usually employed in the synthesis of chiral SURMOFs alongside different chiral organic ligands to obtain crystalline structures with different pore sizes, for example, $\text{Cu}_2(\text{Dcam})_2(\text{BiPyB})$ (BiPyB = 1,4-bis(4-pyridyl)benzene; Dcam = (1*R*,3*S*)-(+)-camphoric acid) and $\text{Cu}_2(\text{Dcam})_2(\text{BiPy})$ (BiPy = 4,4'-bipyridine) [12, 30].

Heterostructural SURMOFs

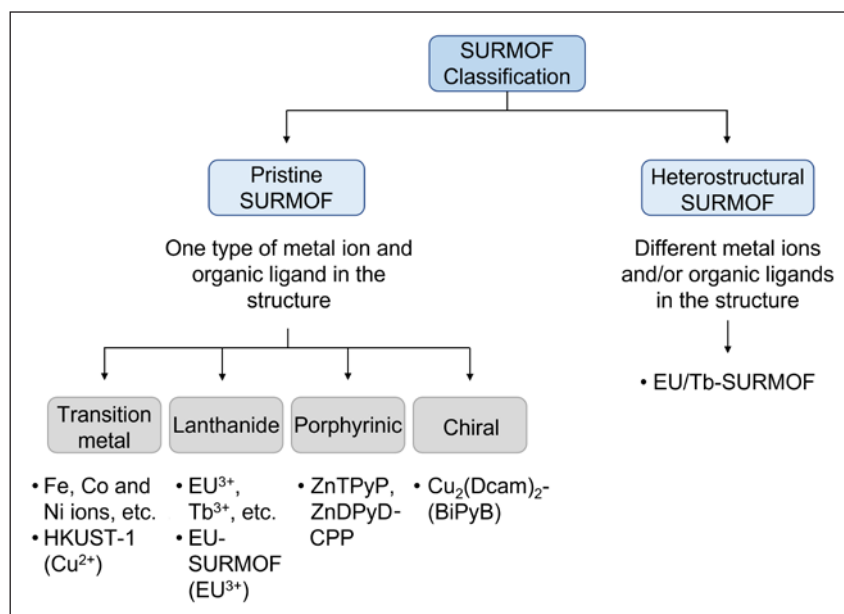
Heterostructural SURMOFs have recently gained attention due to their hybrid properties, using different elements in one structure. The ligands and metal ion solutions can be changed during the fabrication process when the LPE LBL method is employed, allowing hetero ligand- and metal-based SURMOFs structures to be obtained [12]. In 2019, Chen and coworkers reported a hetero metal-based SURMOF, known as Eu/Tb-SURMOF, which was synthesized by the layer-by-layer method, immersing the substrate in a solution of $\text{Tb}(\text{NO}_3)_3$ followed by its immersion in a BTC solution and rinsing between steps. Then, after 44 cycles of this process, the same steps were performed using an $\text{Eu}(\text{NO}_3)_3$ solution as the metal source, executing this method for 55 cycles (scheme 2) [12, 28].

Application of SURMOFs

Nowadays, SURMOFs can be employed in a wide range of areas due to their flexible characteristics and diverse topological structures, which make them convenient for electrocatalysis, photovoltaics, water splitting, and membranes.

Electrocatalysis

SURMOFs offer great potential in the electrocatalytic field and serve as excellent candidates due to their high



SCHEME 2. Classification of SURMOFs. Source: Prepared by the authors.

orientation, manageable growth thickness and accessible active sites [20]. SURMOFs can be employed in different electrocatalytic applications, such as electrocatalytic HER, which is an efficient and promising method for hydrogen production; electrocatalytic OER, which differs from the previous application in being a four proton-coupled electron transfer instead of two-coupled electron one and which consists in water splitting for the obtention of renewable energy; and CO_2 reduction, in which the SURMOF offers an electrocatalytic surface area and is in charge of CO_2 adsorption [12, 20]. Examples of SURMOFs employed for each application are, respectively, NiFe-PBA film, which was prepared by immersing a Ni foam into a $\text{Ni}(\text{OAc})_2$ solution, followed by a $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution, using the LPE LBL method [12]; Co/Ni(BDC)₂TED (TED = triethylenediamine; BDC = 1,4-benzenedicarboxylate), which presents an efficient OER performance and was obtained by the LBL dipping method [31]; and Re-SURMOF, reported in 2016 by Liu, Sun, and coworkers, who prepared it by using $\text{Zn}(\text{OAc})_2$ and $\text{ReL}(\text{CO})_3\text{Cl}$ (L = 2,2'-bipyridine-5,5'-dicarboxylic acid) as the organic ligand [32].

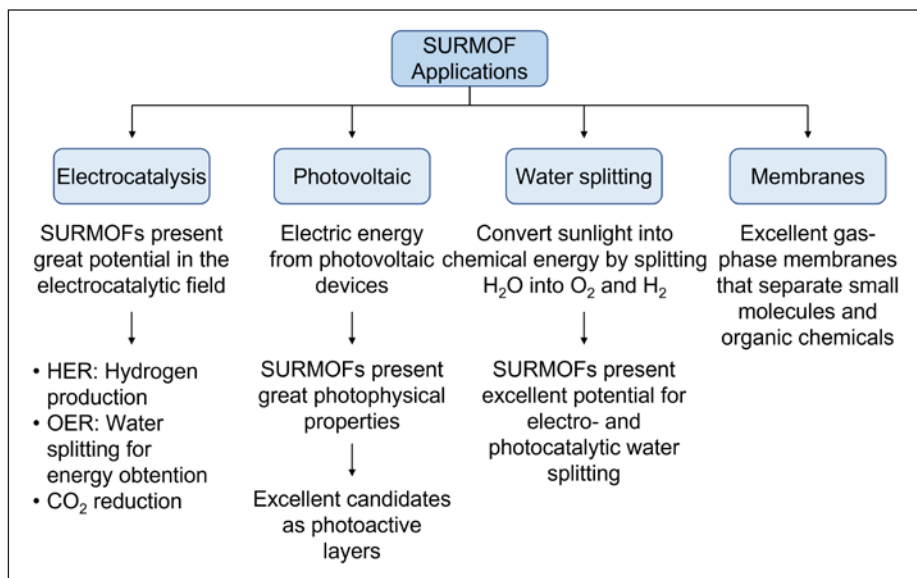
Photovoltaics

In past years, silicon or semiconductor materials have been used for photovoltaic devices in order to obtain electric energy. Indeed, SURMOFs are excellent candidates as photoactive

layers, as was already demonstrated by a wide range of MOF structures including Ru-BTC, $\text{Al}_2(\text{BDC})_3$ and Cu-BTC, and they can be grown on conductive substrates such as FTO or TiO_2/FTO , therefore providing greater photophysical properties for a better outcome [12, 13].

Water splitting

There are numerous possibilities for converting sunlight into chemical energy if water, an abundant source of hydrogen, can be divided into O_2 and H_2 . Water splitting consists of two reactions: first, the oxidation of water (OER) and, second, water reduction (HER). However, H-H and O=O bond formation in and from water is either naturally slow or demands large electrochemical potentials. Wang and coworkers reported a NiCo bimetal-organic framework (NiCo-UMOFNs) built from Ni^{2+} and Co^{2+} as the metal nodes and benzenedicarboxylic acid as the linker, which presented high electrocatalytic activity for OER. In addition, Farha and coworkers reported a MOF material (NU-1000), obtained from $\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{OH})_4(\text{OH}_2)_4$ nodes and BAPy⁺ as the ligand (H_4TBAPy = 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene), which can grow onto an FTO electrode and accelerate the hydrogen evolution reaction (HER). Therefore, it has been shown that SURMOFs can offer excellent potential for electro- and photocatalytic water splitting [13, 33, 34].



SCHEME 3. Applications of SURMOFs. Source: Prepared by the authors.

Membranes

According to recent studies, MOF thin films have a remarkable potential for application as gas-phase membranes for separating small molecules such as CH_4 , CO_2 , H_2 , or CO , as well as volatile organic chemicals like hydrocarbons and alcohols. This may be possible since they provide qualities such as pore size tunability and structural flexibility. $\text{Cu}_2(\text{AzoBPDC})_2(\text{Azo-BiPyB})$, which is a photoswitchable MOF membrane, can be employed for this application and was obtained using the LPE method and $\alpha\text{-Al}_2\text{O}_3$ as the substrate (scheme 3) [13].

Conclusions

This paper makes a review of metal-organic frameworks, including their properties and capabilities, the characteristics of BioMOFs and their applications, and the classification of SURMOFs, the methodologies employed for their synthesis, and the applications for which SURMOFs are suited. Techniques such as liquid-phase epitaxy and Langmuir Blodgett layer-by-layer deposition can lead to the obtention of thin films which present a homogeneous surface, low roughness, almost no defects, and thickness tunability. In addition, depending on the building blocks chosen, different SURMOFs can be synthesized, leading to the obtention of structures with different properties and, therefore, different applications, including electrocatalysis, photovoltaics, water splitting, and membranes.

However, even though SURMOFs show excellent performance in several applications, it is still necessary to continue studying their synthesis, properties, and capabilities so that they can be further employed in a wider range of applications and extended to new fields.

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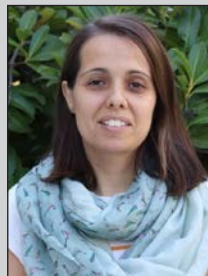
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