

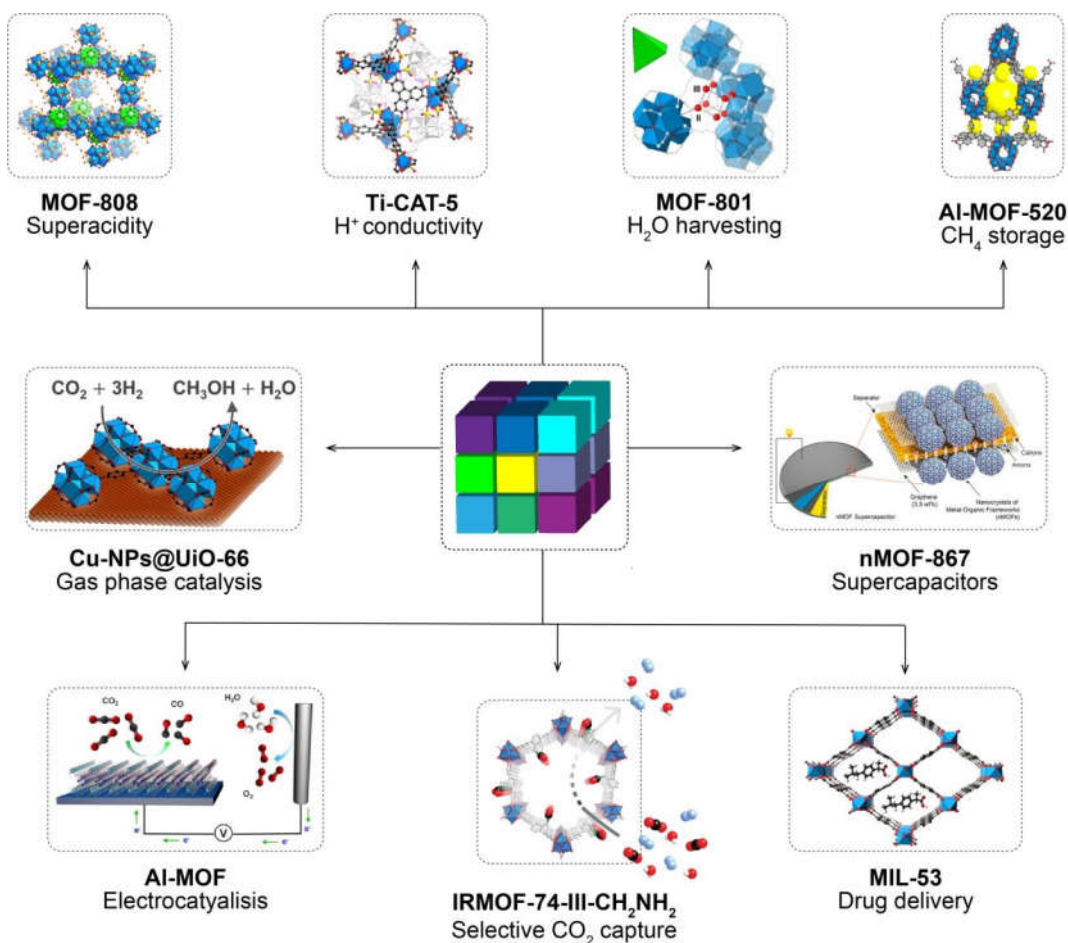


METAL-ORGANIC FRAMEWORKS (MOFS): STRUCTURAL MULTIFUNCTIONALITY AND INTEGRATION INTO DIVERSE PLATFORMS

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Resumen Gráfico - Graphical Abstract



Resumen

Los Entramados Metal-Orgánicos o MOFs (Metal-Organic Frameworks), son una clase relativamente nueva de materiales cristalinos porosos constituidos por la coordinación de nodos metálicos (o clústeres) y conectores orgánicos de variada naturaleza química. Debido a su gran versatilidad estructural y a la posibilidad de incorporar pre- o post-sintéticamente múltiples funcionalidades, los MOFs resultan prometedores en diversas aplicaciones tales como la adsorción y almacenamiento selectivo de gases y toxinas, la construcción de sensores, y el almacenamiento y conversión de energía, entre otras. Este artículo constituye una revisión breve de avances recientes en métodos novedosos de síntesis y modificación post-sintética de MOFs y otros materiales integrando MOFs en su estructura. Los materiales revisados presentan propiedades interesantes tales como súper-acidez, quimioselectividad en catálisis heterogénea, pre-concentración en interfaces electroquímicas, y adsorción selectiva de gases de interés industrial o ambiental.

Abstract

Metal-Organic Frameworks (MOFs) are a relatively new class of porous materials constituted by strong bonds between inorganic clusters (or secondary building units - SBUs) and organic struts forming open crystalline networks. Due to the large variety of inorganic and organic building units possible to be connected, there are more than 10000 MOFs crystallographic structures reported so far in the Cambridge Structural Database (CSD). This structural versatility together with the possibility for their pre- and post-synthetic functionalization, provide with a great number of opportunities in terms of surface chemistry and functionalization for their application in diverse fields such as selective gas adsorption and storage, sensors and actuators, energy storage and conversion, among others. In this article, we briefly survey significant contributions related to synthesis and post-synthetic modification of MOFs and composite materials integrating MOFs. These materials feature interesting properties such as superacidity, high chemoselectivity in heterogeneous catalysis, pre-concentration at electrochemical interfaces, or selective adsorption of industrial and environmentally relevant gases.

Palabras Clave: *Entramados Metal-Orgánicos, Materiales Nanoestructurados, Films Microporosos, Adsorción de Gases, Multifuncionalidad Estructural.*

Keywords: *Metal-Organic Frameworks, Nanostructured Materials, Microporous Films, Gas Adsorption, Structural Multifunctionality.*

1. Introduction

Metal Organic Frameworks (MOFs), also known as Porous Coordination Polymers (PCPs), constitute a relatively new class of microporous materials built from organic struts and metal clusters or secondary building units (SBUs) stitched together by strong covalent bonds (Figure

1). Their construction flexibility allow to access great diversity of materials, in terms of pore structure, environment and chemical functionalization.¹⁻⁵

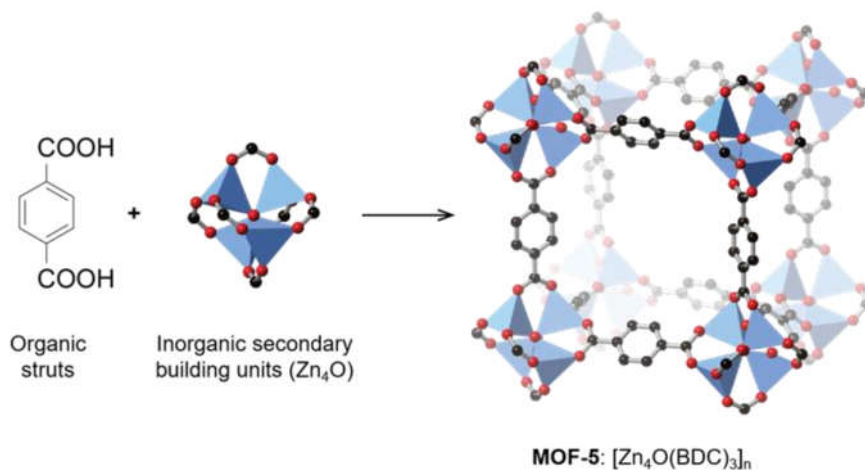


Figure 1. Schematic representation for the construction of MOF-5, in which terephthalic acid organic strut is covalently bound to zinc oxide clusters to form a highly porous 3D structure.

Although several synthetic strategies have been used to prepare MOFs and MOF-containing materials (e.g., compact and defect-free MOF thin films,⁶ solvent-free MOF microcrystals,⁷ or layer-by-layer surface growth of MOF-membranes⁸), the most utilized synthetic method has been the solvothermal reaction of the precursors to yield the crystalline materials. These structures can be separated from the unreacted materials by simple filtration. After the synthesis, the material internal surface (pores) become available through a process known as “activation”, in which the crystals obtained are thoroughly washed with solvent to remove unreacted starting materials and byproducts, and the remaining solvent inside the structure is removed by heat, vacuum, supercritical carbon dioxide, or a combinations of the previous.⁹ Recent years have witnessed an expansion in the number of journal publications and patents featuring specifically designed MOFs constructed to offer alternative solutions to a wide variety of challenges; e.g. capture of greenhouse gases, drug-delivery, biomedicine,¹⁰⁻¹² gas and liquid phase separation technologies,¹³⁻¹⁹ and catalysis among others (Figure 2).²⁰⁻²²

One of the main reasons for the exponential growth in the number of MOFs reported structures, is the great variety of building units that can be combined to create different pore architectures by design, and the ease with which these porous structures can be functionalized by post-synthetic modifications, organic struts mixing (multivariate strategy), and integration with other nanomaterials and polymers. Specifically, designed pores can endow MOFs with “superacidity”, selective carbon dioxide capture in the presence of water, enzyme-like selectivity in catalysis, selective permeation, unique sensing capabilities, etc.²³

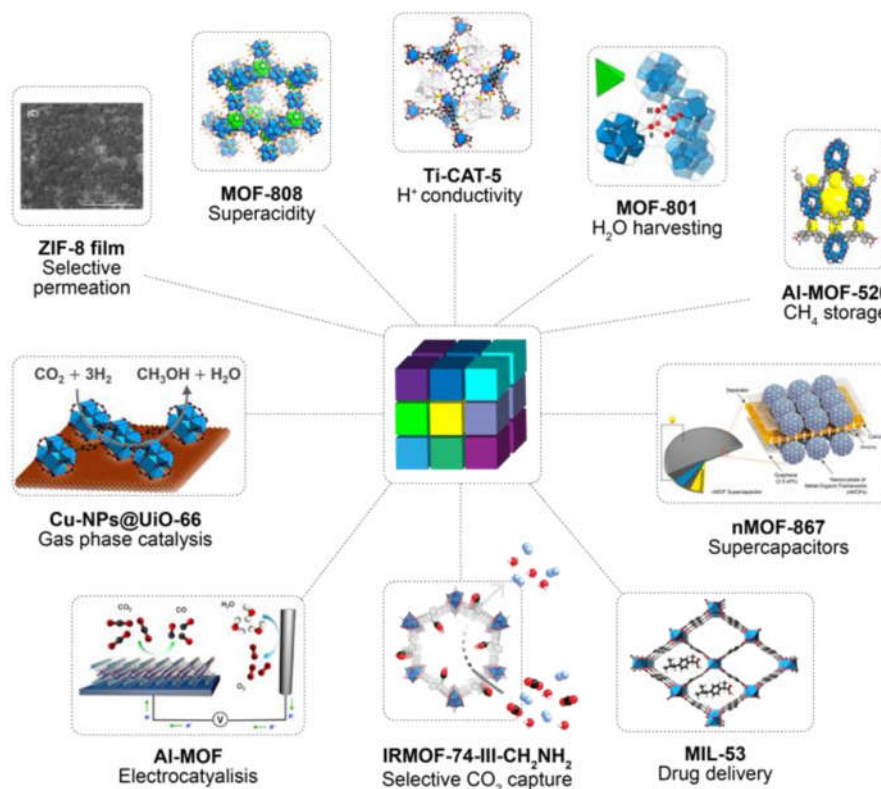


Figure 2. MOFs structural versatility and ease of functionalization which lead to materials suitable for a number of potential applications.

Recent reviews cover suitable strategies for the synthesis of MOFs with specific properties typically found in other classes of materials (e.g., to introduce macro and mesoporosity into otherwise homogeneous microporous MOF without losing crystalline order).²⁴ However, the above mentioned strategies include the use of metal nanoparticles, functional surfaces, or inorganic nanocrystals among others in the construction of MOF-containing hybrid materials.²⁵ The possibility of manufacturing a porous network nearly at will, with surface areas beyond $7000 \text{ m}^2 \cdot \text{g}^{-1}$,²⁶ is an appealing opportunity to develop highly active heterogeneous catalysts in which the crystallinity of these materials also provide the unique advantage of placing catalytically active centres (e.g.; metal nanoparticles) within this high inner surface.^{27,28}

Chemical and structural flexibility of MOFs find application also as porous supports for the fabrication of microdevices (e.g., through the so-called “nanoarchitectonics” approach, as coined recently by Ariga).^{29–32} Since many of these attractive properties are enhanced by the use of films, a great deal of effort has been devoted to study several growth and anchoring strategies, and to explore suitable characterization techniques.^{33–39} If MOF films are grown on an electrochemically active substrate, and given that MOF film can selectively adsorb the reactants which will be subject of redox reactions at the surface (e.g., CO_2 or O_2), then an interesting

enhancement effect on the electrode reaction can be observed.⁴⁰ In order to achieve this functional composite material, affinity between substrate surface and MOF film must be ensured because this would ultimately provide mechanical stability and thickness control.^{41,42}

Throughout this article, we will briefly describe some examples of the above discussed characteristics and applications of MOFs, with emphasis on the latest developments regarding synthesis strategies oriented to enhance functional properties.

2. Pre- and post-synthetic MOF functionalization.

Architectural versatility and functionality can be achieved in MOFs by the infinite variety and combination of building units. Nevertheless, further introduction of reactive chemical functionalization can be achieved by pre- and post-synthetic transformation of the building units. Different kind of functionalities can be incorporated also by the simple functionalization the organic struts prior to MOF synthesis, strategy named “pre-synthetic functionalization”. However the functional groups thus incorporated must be compatible with the MOFs synthetic conditions. Examples of this procedure can be found in literature, since the report of isorecticular MOFs (IRMOFs) derivatives, where halogens, aromatic amines and other functionalities, were introduced to the cubic MOF-5 structure.⁴³ For instance, the MOF-5 structure is composed of octahedral ZnO clusters linked by terephthalic acid as organic strut, reticulating a primitive cubic structure (see Figure 3a) with exceptional rigidity and surface area. On the other hand, the use of 2-aminoterephthalic acid, instead of terephthalic acid, yield crystals of IRMOF-3 which has the same underlying topology than MOF-5 but features aromatic amine functionalities decorating the MOF surface area (see Figure 3b).

In addition, it was also demonstrated that different functionalities can be incorporated simultaneously to the pores of MOF-5, originating multivariate MOFs (MTV-MOFs, Figure 3c) with different properties compared with their non-functionalized or homogeneously-functionalized versions.⁴⁴

There are, however, some reactive functional groups that cannot be directly introduced to the precursors by pre-synthetic modifications or MTV-approach, as these functionalities might interfere with the formation of the MOFs extended structures. A clear example is

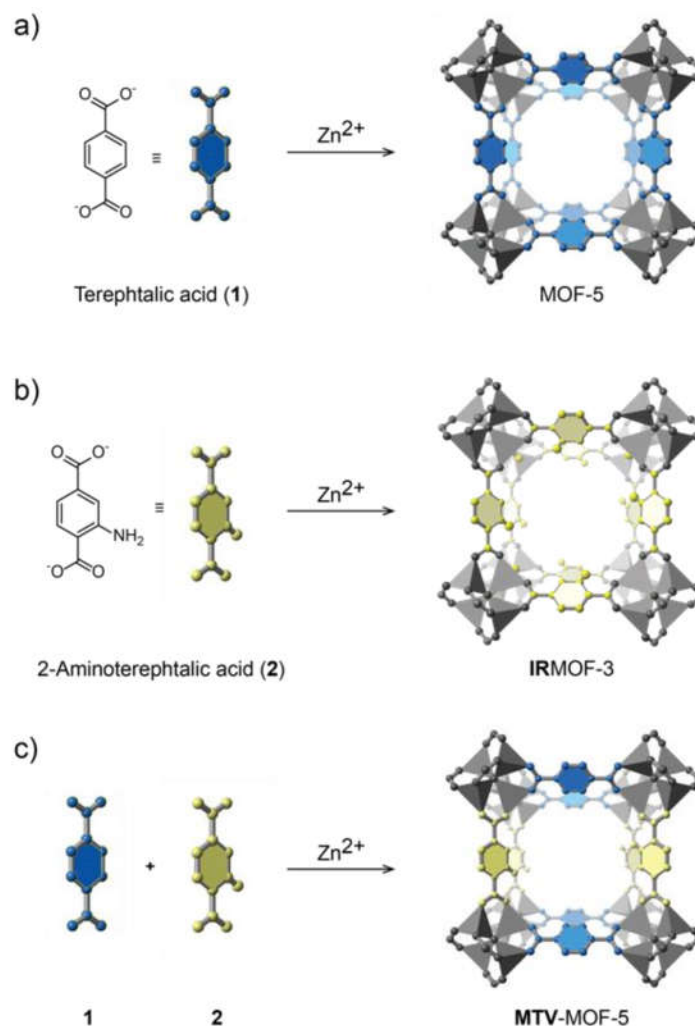


Figure 3. Schematic representation for the pre-synthetic functionalization of MOF-5. a) Synthesis of MOF-5, b) synthesis of IRMOF-3 which features the same underlying topology than MOF-5 but incorporating aromatic amine functionalities in its pores, and c) preparation of MTV-MOF-5, by organic struts mixing.

introduction of primary or secondary amines to the pores, which cannot be achieved by simple functionalization of the organic struts as these groups will affect the metal coordination and the solution pH, preventing the MOF crystalline structure from forming under the above described solvothermal conditions.⁴⁵ Thus, a wide variety of strategies were recently developed to incorporate these reactive functionalities to the MOF. One successful strategy consists in performing reactions over the already prepared MOF crystals, approach known as *post-synthetic modifications* (PSM). These PSMs can be achieved on both, the inorganic clusters (known as *dative PSM*) or the organic struts present in the MOFs (i.e. *post-synthetic deprotections* and *covalent modifications*). For instance, in order to incorporate the organocatalyst proline (containing a secondary amine) to IRMOF-10 (an expanded version of MOF-5), *tert-*

butyloxycarbonyl (Boc) protecting group was employed. Thus the protected version of the secondary amine did not interfere with the MOF synthesis, and the protecting group was successfully removed with no deterioration of the MOF crystallinity or porosity. This later bond-breaking reaction to release secondary amine functional groups in the MOF pores, represents a successful example of the *post-synthetic deprotection*, mentioned above.⁴⁵

Covalent incorporation of reactive functionalities such as primary and secondary amines have a deep impact in the materials properties and represent an opportunity to fine-tune the pore environments for a particular application.

It was reported that MOF constructed from magnesium oxide rods joined by the linear 2,5-dihydroxyterephthalic acid strut is an exceptional material for taking up carbon dioxide⁴⁶ (8.9 wt. % dynamic capacity), however it losses almost 80% of its capacity in the presence of water, an impurity commonly present in the flue gases. On the other hand, primary amine functionalized IRMOF-74-III showed 3.5 wt. % dynamic CO₂ uptake capacity, but this capacity remains unchanged in the presence of water.¹⁶

Taking advantage of protecting groups and the crystallographic precision with which functional groups can be installed into MOF structures, it is possible to further react functionalized frameworks to achieve high complexity in the pore environment. Recently, it was demonstrated that this primary amino-functionalized IRMOF-74-III can undergo up to seven post-synthetic modifications *in tandem* to install tripeptides in the pore interior. More importantly, these seven reactions performed over the previously synthesized MOF proceed with no loss in the material crystallinity or porosity.⁴⁷ This reported example suggest that enzyme-pocket architectures can be achieved in the MOF pore environments, making possible to carry out examples of catalysis previously known only by enzymes (Figure 4).

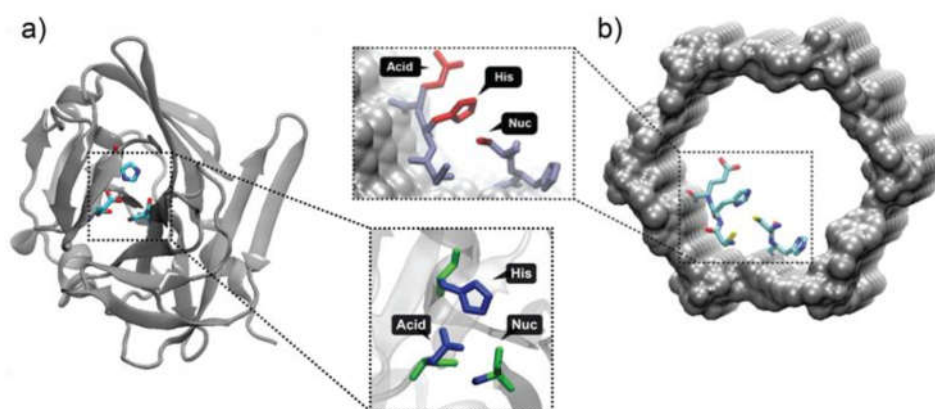


Figure 4. a) Comparative representation of 1D pores of IRMOF-74-III covalently modified with the tripeptide $-\text{CH}_2\text{NH-Asp-His-Cys-NH}_2$, and b) the catalytic triad in the active site of TEV-protease.

Post synthetic modification has proved to be a useful strategy also in the area of MOF film formation, where it can be applied not only to improve film deposition quality, but to modify the properties of the synthesized film. A recent example of this strategy was used in ZIF-8 MOF nanocrystals as recently reported.⁴⁸ In this work, an archetypal member of the Zeolite Imidazolate Frameworks (ZIFs) MOF subclass, constituted by tetrahedrally coordinated Zn^{2+} ions with 2-methylimidazolate linkers, was surface modified without crystallinity lost, using a controlled and simple methodology in order to obtain surface confined thiol moieties that can be used to create self-assembled films on gold substrates. This proof of concept constitutes an interesting example for two main reasons; it represents a general way to confer MOF nanocrystals with specific affinity for a given desired surface, and on the other hand, the modified material features chemisorption of tunable size units resembling to their molecular analogues in a typical thiolate Self Assembled Monolayers (SAMs).

Another example of the above described approach, is the recently reported modification of MOF films with highly charged polyelectrolytes as capping agent.⁴⁹ In this study, it was demonstrated that the hydrophobic/hydrophilic character of MOF films can be modulated by simple dip-coating of the films in PSS (poly-styrene sulfonate) aqueous solutions. More importantly, it was proved that the capping agent modification was not limited to the film surface but also permeates through the mesocavities present, thus changing the transport properties of the entire film. This modification of hydrophilicity constitutes an interesting alternative to important applications in catalysis as it allowed for the synthesis of d-block metal nanoparticles *via* direct aqueous chemical reduction of the precursors in the polyelectrolyte-modified film.

3. MOF films: influence of surface anchoring sites on growth dynamics and structure.

MOF films and membranes can be produced in a straightforward way following several different procedures. Among them one can mention the *seeded-growth method*,⁵⁰ which involves the seeding of solvothermal pre-synthesized units forming a layer (e.g., *via* spin-coating), followed by secondary heterogeneous growth under different conditions aimed to favor certain desired morphology.⁵¹ As in general for nucleation of crystalline solids in presence of interfaces, both homogeneous and heterogeneous nucleation processes are present when synthesizing a MOF film. Depending on supersaturation and temperature conditions used, a critical size nuclei leading to solid formation need an induction time to occur.⁵²

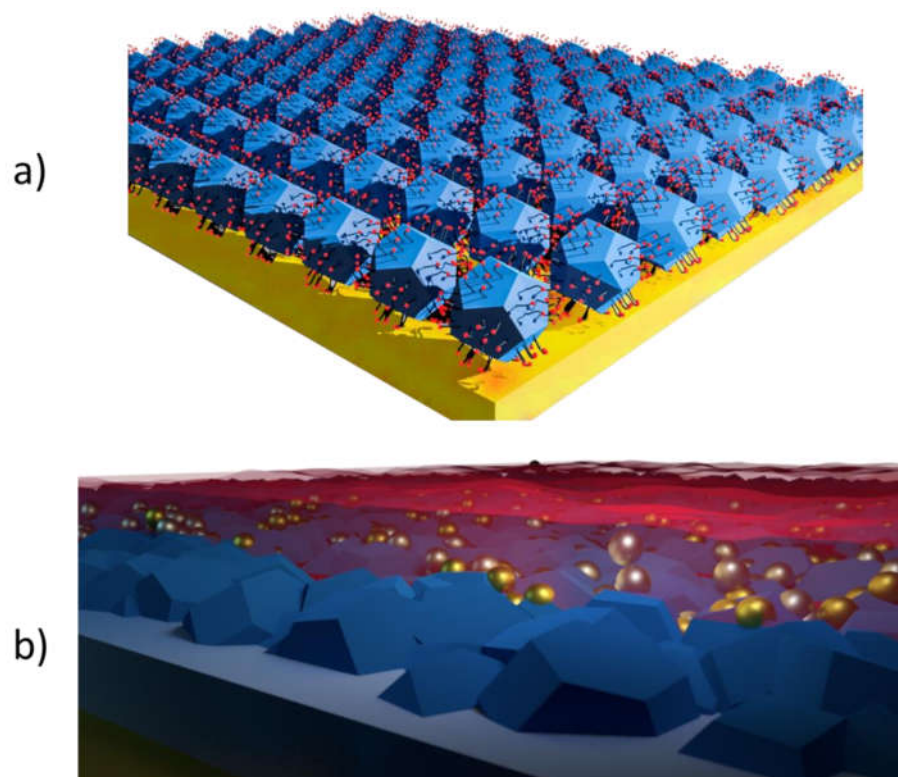


Figure 5. Schematic representation of **a)** film formation of chemical assembled Cys-modified ZIF-8 crystallites, **b)** ZIF-8 film modification with PSS as capping agent and reaction-diffusion synthesized d-block metal nanoparticles throughout film z-direction.

Different from the above discussed examples, *one-pot* MOF film synthesis strategies, offer simpler procedures and extra degree of control on the obtained material. The need of seeded surfaces can be circumvented by using suitable surface modifications of the substrates employed, in this way, the induction time can be drastically reduced. This effect was reported for the synthesis of several MOF films, where surface chemistry compatible with building blocks showed both a strong effect decreasing the induction time, and also promoting preferential growth in a certain crystalline direction.^{42,52,53} Figure 6 shows an example of time evolution and growth extent observed for Zn-based ZIF-8 MOF films synthesized over different chemically-modified Au substrates followed by Quartz Crystal Microbalance (QCM) technique.

Aside from the interesting different induction times observed in Figure 5, self-assembled monolayers (SAMs) featuring $-\text{SO}_3^-$ moieties (MPSA) present an important enhancement of film growth. This was hypothesized to occur due to strong coordinative interactions between sulfonate groups and Zn^{2+} ions, as already reported.⁴² A further example of this enhancement effect was obtained using grafting of tridimensional primers, rather than 2D SAMs, constituted by polymeric brushes of 3-sulfopropylmethacrylate monomers.⁴¹ In this way, preconcentration of metal ions within the macromolecular 3D primer triggers a rapid increase of nucleation sites in

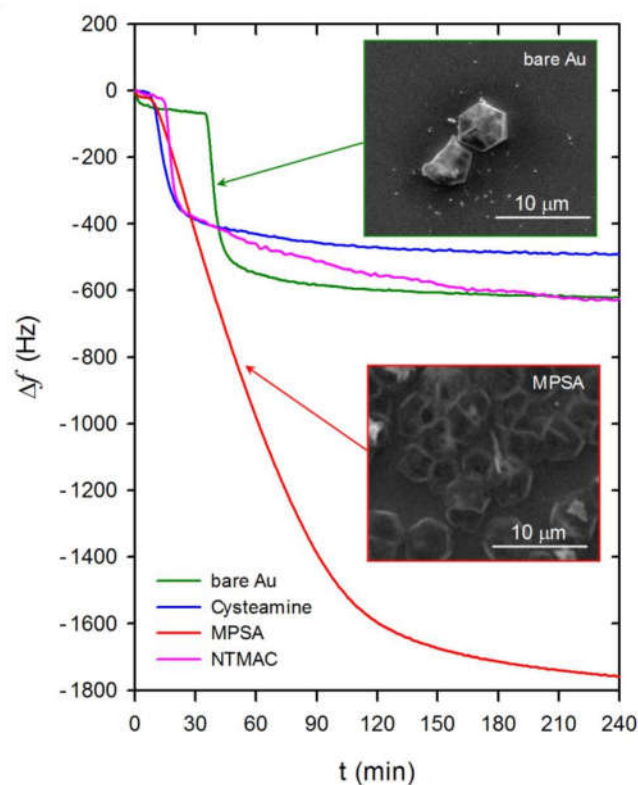


Figure 6. Time evolution of ZIF-8 film growth over Au and three different chemically modified Au substrates. Bare Au, and Self-Assembled Monolayers (SAMs) of the following thiol-bearing molecules: cysteamine exposing primary amine moieties, MPSA (3-mercaptopropionic acid) exposing sulfonate moieties, and NTMAC (N,N,N-trimethyl(3-mercaptopropyl)-ammonium chloride) exposing quaternary amine terminal groups.

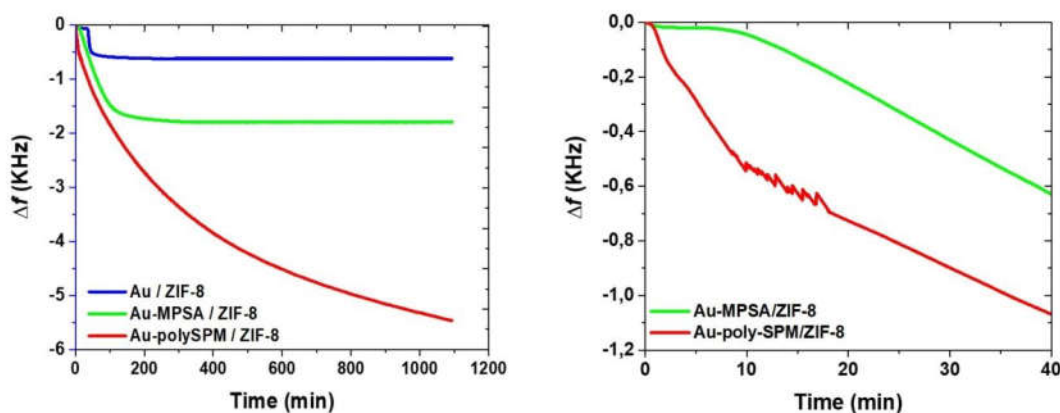


Figure 7. *Left*, deposition of ZIF-8 films on different surfaces, as detected by QCM: (blue) bare gold, (green) MPSA modified-gold, and (red) polymer brush. MOF film growth is directly proportional to the frequency change. *Right*, early stages of time in the film growth evolution.

the primer. Figure 7 shows the obtained increase in both growth speed and extent when polymeric brushes with sulfonate pendant groups are present. Figure 8 shows the 3D primer surface as observed *via* Atomic Force Microcopy, together with schematics of synthesis procedure.

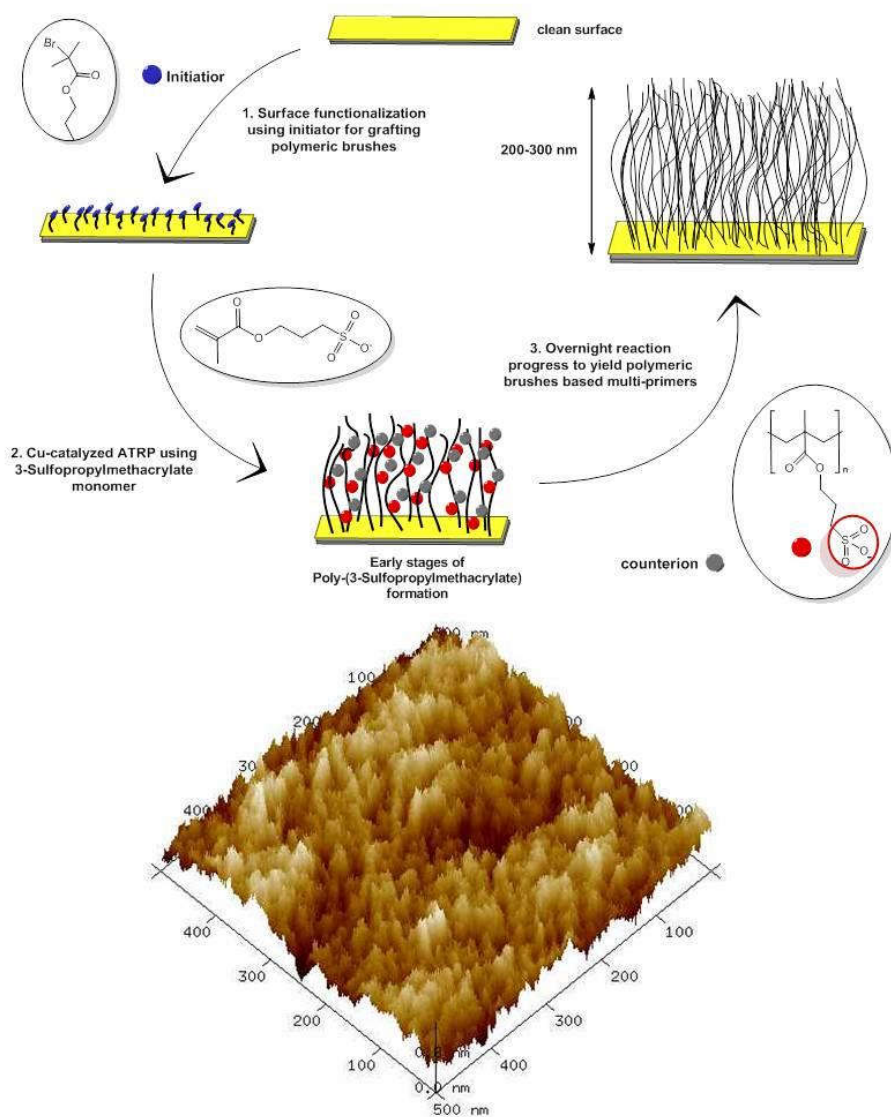


Figure 8. *Top*, schematic representation of the fabrication of polymeric brushes.

Bottom, surface of modified Au substrate as obtained *via* AFM

4. Applications.

4.1 Enhancement of the Oxygen Reduction Reaction (ORR).

As discussed above, high porosity and the versatility of the pore identity are crucial characteristics allowing MOF to be applicable in wide range of fields. Integrating MOFs to *functional composites*, it was proved that ZIF-8 can be assembled on electroactive conductive polymers based on aniline and *p*-amino benzoic acid (PANI-PABA), and synergically by an easy, mild and low cost process, to obtain stable composites, that can improve electrocatalytic oxygen reduction reaction (ORR) via selective oxygen adsorption from neutral pH aqueous solutions, as shown in Figure 9.⁴⁰

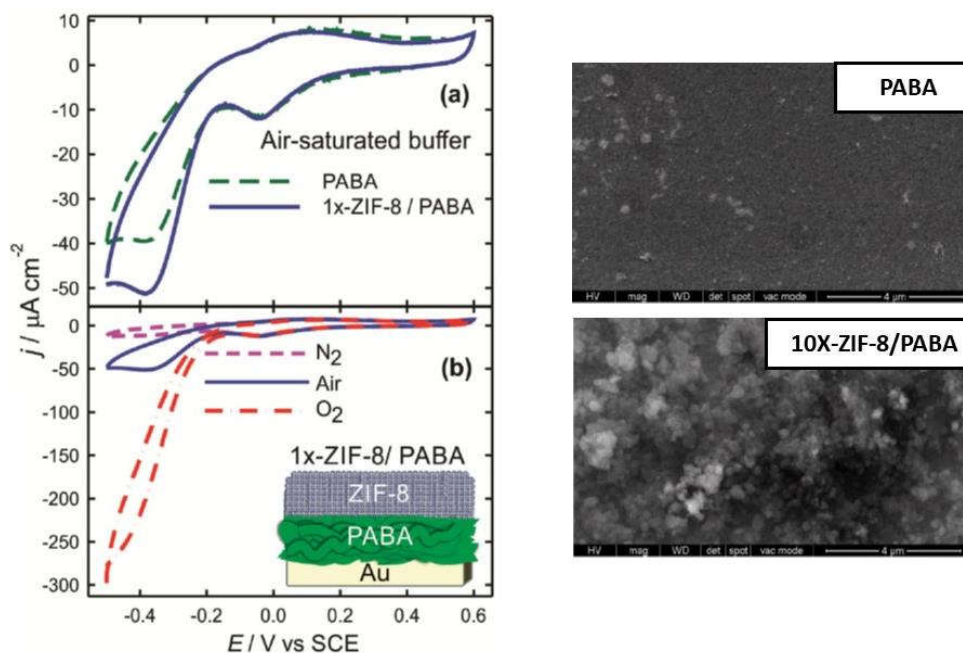


Figure 9. *Left, a)* Voltammetric response of PABA and 1x-ZIF-8/PABA modified electrodes in air saturated buffer. *b)* Comparison of the CV response of a 1x-ZIF-8/PABA-modified electrode at different concentrations of dissolved O_2 . *Right,* SEM images of PABA top surface and 10x-ZIF-8/PABA modified electrodes top surface.

The incorporation of ZIF-8 to the composite material helps preventing contamination of the electroactive film (antifouling), whilst the intergrain mesoporosity gained by MOF inclusion helps to enhance diffusion properties of the conductive polymer.

4.2 Carbon capture and storage.

Anthropogenic carbon dioxide (CO_2) emissions have been identified as a significant cause of global warming and climate change. In order to improve this situation, carbon capture and

storage (CCS), has been developed and is becoming increasingly commercially viable. Currently employed technologies such as monoethanolamine scrubbing present important drawbacks in terms of energy consumption, adsorbent regeneration, and pipeline corrosion.⁵⁴ These challenges motivated the development of porous solids as CO₂ sorbents including mesoporous carbons, mesoporous silica, porous polymers, zeolites and recently, metal-organic frameworks (MOFs). Porous solids are attractive due to their high surface areas, improved gas-solid mass transfer, and lower regeneration energies due to smaller heat capacities in comparison with aqueous amine solutions.⁵⁵ However, very often the capacity of these porous adsorbents drop when they are exposed to common flue gas contaminants from which carbon dioxide must be separated, especially water. The possibility of carefully and covalently bind functionalities to MOFs in precise positions throughout the material surface area, has given to these porous materials an advantage compared to the other listed above. In this sense, several successful examples of post-synthetically modified MOFs have been reported for the selective capture of CO₂. Among the chosen strategies to enhance MOF selectivity and uptake capacity for CO₂, perhaps the most explored one is the incorporation of amine functionalities to the pores of MOFs. In order to bind active amines to the MOF surface we can clearly distinguish two different approaches: **a**) dative post/synthetic binding of alkylamines to the MOF SBUs^{56,57}, and **b**) pre-synthetic incorporation of alkylamines followed by post-synthetic deprotection (Figure 9).^{16,17,58} In the first approach developed by the Long group (**a**), already prepared by immersion of the already prepared MOF into an alkyldiamine solution. Due to its affinity for the coordinatively unsaturated metal at the MOF SBUs, one of the amines anchors to the metal, leaving the second hanging in the MOF pore. The product of the dative post-synthetic modification on Mg₂(dobpdc), where H₄dobpdc = 4,4'-dihydroxy-(1,1'-biphenyl)-3,3'-dicarboxylic acid] with N,N'-dimethylethylenediamine, showed high affinity for CO₂ at low partial pressures (8.1 wt % at 0.39 mbar) demonstrating the efficiency of this approach to enhance the material as CO₂ sorbent. The second approach developed by Yaghi group (**b**), reactive alkyl amines are incorporated through pre-synthetic functionalization of the organic struts with protected derivatives of these amines. Those amines, are later thermally deprotected in a complete post-synthetic step leaving the free amines in the pores of MOF. The compound prepared by this strategy (IRMOF-74-III-CH₂NH₂), showed a CO₂ uptake capacity of 3.5 wt % under humid and *dynamic conditions*.^a Although the **b** approach involves a larger number of synthetic steps, the amines are covalently bound to the MOF pores, providing the material with an enhanced stability of this active sites against the conditions under which very often this CO₂ capture takes place.

^a Uptake capacity determined by break-through experiments in which a column is packing with the adsorbent material and the time that takes a gas in a mixture of gases to break through this column is measured.

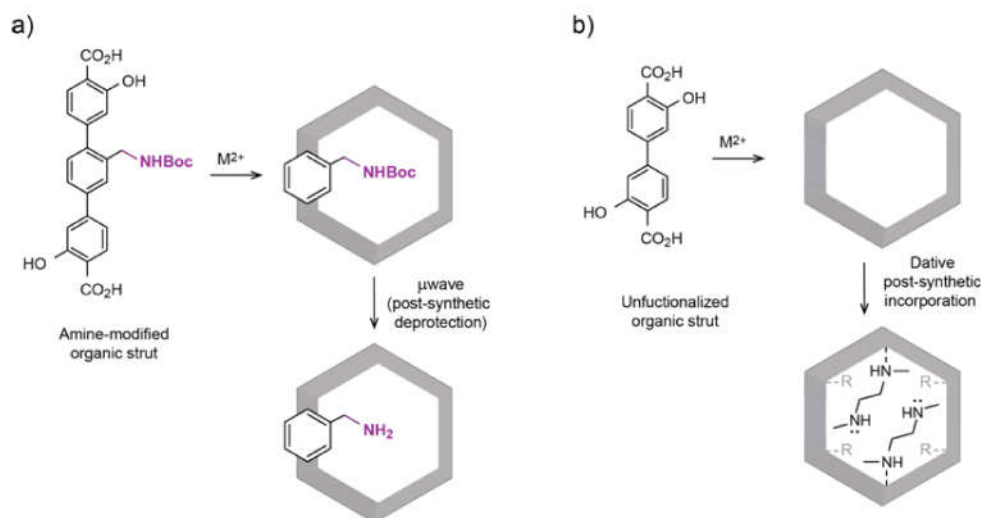


Figure 10. Schematic representation of two different strategies for the amine-functionalization of a MOF featuring hexagonal 1D pores.

Other interesting strategies were employed in order to modify MOFs to enhance CO₂ selectivity in the capture process. Hydrophobic pores, adjustment of pore size, covalent incorporation of other functionalities like OH groups,^{59–63} are some of them, however we do not describe those strategies in deep in this article.

4.3 Enzyme-inspired catalysis.

The efficiency and selectivity with which enzymes perform in catalytic processes is rarely achieved by artificial systems. Therefore, preparing synthetic materials that can function in a similar way than enzymes but in a wider range of conditions has been a long standing goal. The crystallinity, pore-geometry control and ease of functionalization achieved in MOFs allowed several examples of careful tuning of pore properties to enhance the materials catalytic activity.^{64,65} Recently, and taking advantage of sequential post-synthetic modifications without losing crystallinity or pore access, it was demonstrated that MOF pores can function in a way that was previously only known for enzyme pockets (see ref. 47 and Figure 4). The crystalline precision with which atoms are located in the pores of MOFs, the opportunity of tuning the pore geometry and size, and the ease of functionalization by either pre- or post-synthetic modifications allow to design catalytic nanocavities that resemble enzyme pockets.^{66–68}

3. Conclusions

In this minireview, we have introduced fundamental aspects of the *state of the art* in MOF and MOFs membranes focusing on their synthesis, functionalization and applications. Being a relatively new class of porous material and due to their remarkable versatility (both chemical and

structural), the number of reported possible applications are continuously increasing, and thus difficult to cover in detail. This is why in terms of the materials applications, we have restricted our description to some key aspects that will have the stronger impact in the next few decades, namely: *i) CO₂ capture* related applications (both carbon capture and sequestration, and conversion technologies); *ii) MOF composite film synthesis and its application to sensor and energy conversion/storage technologies*; *iii) different aspects of applications in heterogeneous catalysis*. Although the seminal work included here constitute starting points for future research directions, they also represent a clear evidence of the impact of recently developed MOFs in the field of material science, both in fundamental and applied research.

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