

What Are These Things Called MOFs?

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What are MOFs?

Metal-organic frameworks (MOFs) are crystalline networks of organic ligands held together by nodes comprising metal ions or clusters. The prototype is MOF-5 [$\text{Zn}_4\text{O}(\text{benzene-1,4-dicarboxylate})_3$], which was first reported¹ by Omar Yaghi's group in 1999. The structure of this material, as determined by X-ray crystallography, is presented in Fig. 1. MOF-5 is an infinite cubic framework in which Zn_4O clusters link benzene-1,4-dicarboxylate struts. It is remarkable for its aesthetic beauty, ease of synthesis, thermal stability, and the fact that it is mostly fresh air - about 60% of its volume is accessible to guests. The report of MOF-5 made a significant splash - the original paper has been cited 1400 times in the ten years since its publication - and it can be seen as the genesis of a new field of research. This paper aims to provide an overview of the development of MOF-5 and the direction that the field has taken in the ten years since this landmark publication. It is certainly neither comprehensive nor balanced, being distinctly biased towards MOFs derived from zinc(II) and carboxylate ligands.

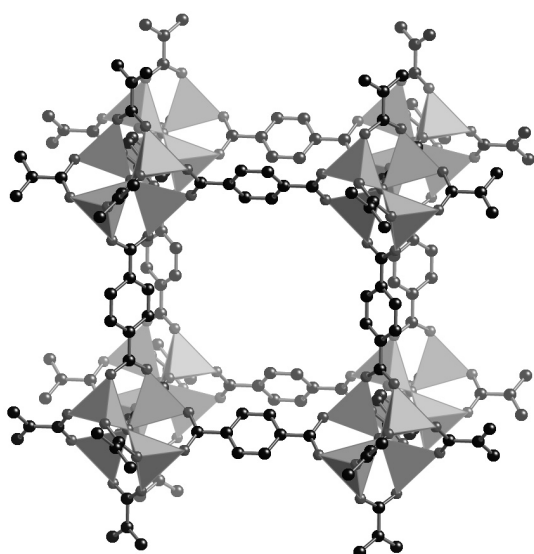


Fig. 1. The structure of MOF-5.

What Came Before MOF-5?

The ability of certain combinations of metal ions and ligands to form polymeric structures was noted by John Bailar Jr. in a 1964 review.² At this time, it was known that many simple inorganic compounds such as palladium(II) chloride and nickel(II) cyanide exist as polymers in the solid state (Fig. 2). The key feature of the ligands of these compounds is their ability to bridge two metal centres, which allows the polymeric structure to propagate. Another example is Prussian blue, a mixed valence iron(II)/iron(III) three-dimensional network with cyanide bridging ligands, which has been used as a pigment since the

early 1700s. Bailar coined the term *co-ordination polymer* to describe this class of compound, although he commented that their properties (plasticity, elasticity *etc.*) do not correlate closely with organic polymers owing to the shortness of the bridging ligands and the rigidity of the co-ordination sphere of the metal ions.

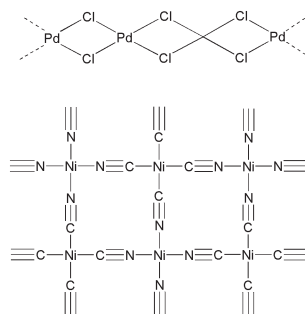


Fig. 2. The solid state structures of palladium(II) chloride and nickel(II) cyanide.

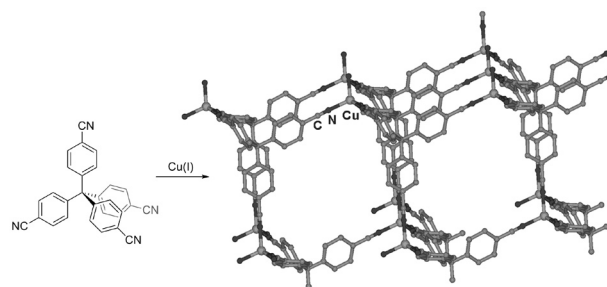


Fig. 3. Formation of a crystalline co-ordination polymer from copper(I) cations and tetracyanotetraphenylmethane. The BF_4^- anions have been omitted for clarity.

Although there were subsequent scattered reports of polymers held together by coordinative bonds, these materials tended to be rather ill-defined and poorly characterised. Richard Robson at the University of Melbourne put the field on a firmer footing by elucidating the network topologies that could result from the combination of rigid, divergent ligands with the preferred stereochemistry of various metal ions. In 1990, in collaboration with Bernard Hoskins, Robson reported³ the X-ray crystal structure of $\text{Cu}[\text{tetracyanotetraphenylmethane}]\text{BF}_4$. The combination of tetrahedral copper(I) ions and the tetrahedrally disposed pyridyl donor groups generates a cationic diamondoid network (Fig. 3).

The real breakthrough of this report was the fact that the networks were crystalline and not *miserable, ill-defined, amorphous precipitates, difficult or impossible to characterise*⁴ as had seemed much more likely. This approach overcame the *crystallization problem* that was actually later enunciated by Roald Hoffmann:⁵

Organic chemists are masterful at exercising control in zero dimensions. ... One subculture of organic chemists has learned to exercise control in one dimension.

These are polymer chemists, the chain builders... But in two or three dimensions, it's a synthetic wasteland. The methodology for exercising control so that one can make unstable but persistent extended structures on demand is nearly absent. Or to put it in a positive way—this is a certain growth point of the chemistry of the future.

The early days of this pioneering research were recently given a personal account by Robson.⁴ He recounts that his ideas were seeded by the task of constructing ball-and-stick models of inorganic crystal structures such as sodium chloride, zinc blende, and rutile for classroom demonstrations. Robson pondered whether the simple anions that bridged the metals in these structures could be replaced by rigid molecular units with ligating groups fixed in suitable orientations. This became the guiding principle for the crystal engineering of co-ordination polymers, *i.e.* the pre-meditated rational construction of specific networks.

A surge of papers was published in the early 1990s on the crystal engineering of co-ordination polymers of polytopic pyridyl or nitrile ligands. The popularity of these donor groups stemmed from their simple monodentate nature, that they co-ordinate to a range of metal ions, and the predictability of the orientation of the M–L bond with respect to the ligand backbone (Fig. 4).

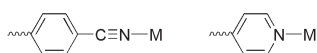


Fig. 4. M–L bond vectors for nitrile and pyridyl donor groups.

Network topologies could often be predicted in advance, or at least rationalised with hindsight, by considering the orientation of the ligating groups and the co-ordination geometry of the metal centre. For example, the reaction of 1,3,5-tris(4-ethynylbenzonitrile)benzene with silver(I) trifluoromethanesulfonate (AgOTf) produces a two-dimensional network composed of ligands and trigonal planar metal ions (Fig. 5).

Conceptually, the above co-ordination polymer can be deconstructed to $\text{Ag}(\text{CN})_3$ units that are linked by an extended trisubstituted benzene core (Fig. 5). It was this insight that led to the design of MOF-5, which can be viewed as an infinite, *polymerized* analogue of well known discrete zinc carboxylate clusters such as $[\text{Zn}_4\text{O}(\text{acetate})_6]$ and $[\text{Zn}_4\text{O}(\text{benzoate})_6]$. The route from the zero-dimensionality of these discrete clusters to the 3-dimensional network is provided by replacing the simple carboxylate ligands by a rigid ligand with two *divergent* carboxylic acid groups (benzene-1,4-dicarboxylic acid). The core Zn_4O cluster is the same in both structures; it is capped by the acetate ligands in $[\text{Zn}_4\text{O}(\text{acetate})_6]$ but *articulated* into a 3-dimensional network by benzene-1,4-dicarboxylate (Fig. 6).

A candid insight into the genesis of MOF-5 was recently published by Michael O’Keeffe.⁶ Initially, many people were sceptical of the ability of these kinds of materials to maintain their integrity upon removal of the solvent, *i.e.* to display permanent porosity. This is true of structures that rely on weak metal–ligand interactions, but the strength of the Zn–O bonds in MOF-5 means that crystallinity is maintained even after heating in air at 300 °C for 24 h. Gas sorp-

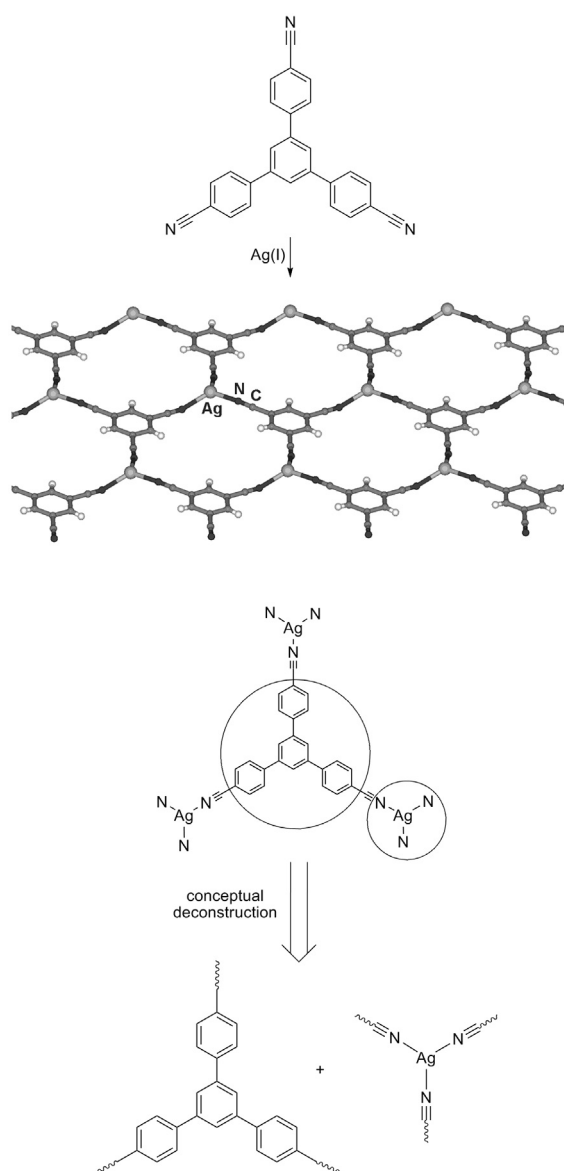


Fig. 5. Formation of a crystalline co-ordination polymer from Ag(I) and 1,3,5-tris(4-ethynylbenzonitrile)benzene. Triflate counter anions have been omitted for clarity.

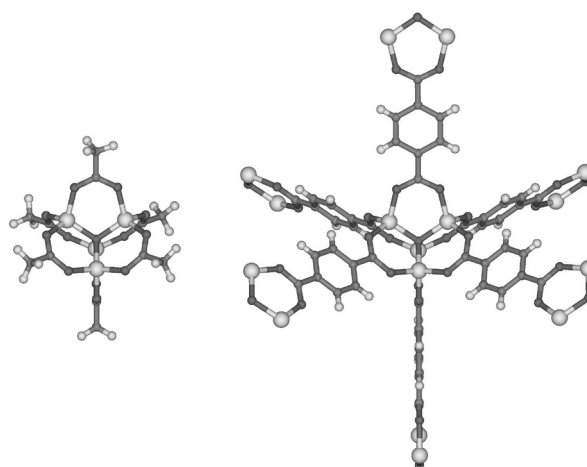


Fig. 6. Replacement of the capping acetate ligands in $[\text{Zn}_4\text{O}(\text{acetate})_6]$ (left) by a ligand with two divergent carboxylic acid groups generates an infinite 3-dimensional network (MOF-5, right).

tion isotherms indicated significant porosity and allowed an estimate of the surface area of 2900 m²/g. These key features of MOF-5 set it apart from previously known co-ordination polymers.

A second prominent milestone in MOF research was a 2002 *Science* report from Yaghi's group,⁷ which has subsequently been cited 1360 times and describes the elaboration of the benzene-1,4-dicarboxylic acid ligand. In all cases, networks with the same cubic topology were observed (Fig. 7).

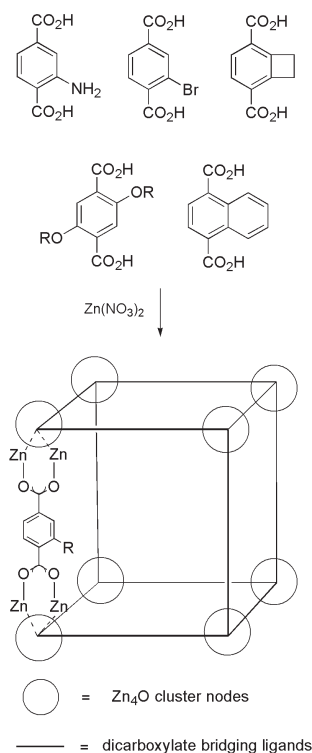


Fig. 7. Replacing benzene-1,4-dicarboxylic acid by more elaborate ligands generates functionalized frameworks with the same cubic topology as MOF-5.

MOFs and Co-ordination Polymers: What's in a name?

There exists some snobbery on the part of some MOF chemists who pride themselves on pre-designing specific networks using more exotic, customized ligands, and who, as a result, tend to look down upon many co-ordination polymers as the products of blind *shake and bake* experiments using ligands from the Aldrich catalogue. The term *MOF* is certainly a trendier brand name for your newly synthesized (and about-to-be-published) material, but some of those in the MOF camp believe that the term is being used where co-ordination polymer would be more appropriate. This has generated some spirited discussion in the literature (see below). While some researchers are happy to use the terms interchangeably, a consensus on appropriate use of the terms is beginning to emerge.

The term *metal-organic framework* was first introduced by Yaghi in 1995 to describe the newly synthesized compound [Cu(4,4'-bipyridine)_{1.5}](NO₃)₂, which forms a stable and porous 3-D network structure.⁸ Yaghi has since argued that the MOF moniker should be reserved for materials that, in addition to certain structural attributes,

display certain properties such as robustness and linking units that are available for modification by organic synthesis.⁹ More recently, he has proposed that the formal bond valence of the metal-ligand bond is also an important criterion.¹⁰ Bond valence is a concept widely employed by solid state inorganic chemists, and it was proposed that metal-ligand bonds in MOFs should have a formal bond valence of around ½, which corresponds to a high bond energy, *ca.* 350 kJ/mol. In contrast, a typical co-ordination polymer such as [Zn(N,N'-bis(4-pyridyl)urea)₂]ClO₄ contains Zn-N bonds, which have a formal bond valence of around zero and are therefore rather weaker.

There are several pitfalls in these arguments, not the least of which is the fact that they would disqualify the Cu(I)-bipyridine structure reported in the paper where the term was coined! The concept of formal bond valence is used by solid state inorganic chemists but is potentially quite unfamiliar to many of those working in the field of MOFs. Furthermore, there are many MOFs that contain mixtures of ligands with, for example, both pyridyl and carboxylate donors.

The view that MOF-5 and Prussian Blue are categorically different does have validity, however, and a distinction between MOFs and co-ordination polymers is sensible. Biradha *et al.* have recently suggested how this distinction may be made based on structural features alone.¹¹ They propose that *the term MOF is very much appropriate to use for three-dimensional networks, it is inappropriate to use for extended one-dimensional or two-dimensional networks.* This builds on accepted terminology in solid state chemistry where the term framework distinguishes a 3-D from a 2-D network (layer). In addition to having a 3-D structure, MOFs are categorically different from co-ordination polymers in that the framework should have potential porosity, *i.e.* potentially be accessible to incoming guests. The adjective *potential* is important here as it means that the porosity can be inferred from the structure of a material without the need for experimental verification by sorption experiments, which are often problematic from a practical perspective owing to framework collapse upon the removal of occluded solvent, *etc.*

How Are MOFs made?

MOF-5 can be prepared by several different methods. In the original 1999 paper, crystallization was achieved by the diffusion of triethylamine into a solution of zinc(II) nitrate, benzene-1,4-dicarboxylic acid, and hydrogen peroxide in DMF (N,N'-dimethylformamide).¹ The hydrogen peroxide was the source of the O²⁻ of the Zn₄O nodes, while the amine acted as the requisite base for deprotonation of the carboxylic acids. Control of the rate of this latter step by the slow diffusion of vapours of amine limits crystal nucleation and allows large crystals to grow at the expense of microcrystalline or amorphous material. The formation of large (> *ca.* 20 micron), high quality single crystals (Fig. 8) is a key target, as these are generally amenable to structural determination by single crystal X-ray diffraction.

A more general and convenient route to zinc(II)-carboxylate MOFs has since been developed. This involves the

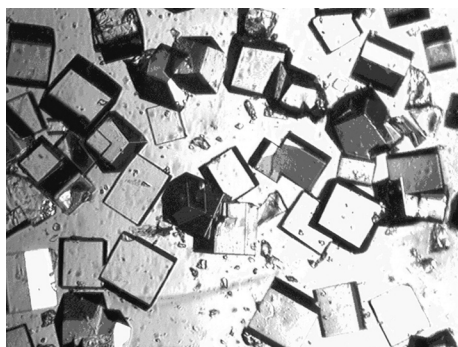


Fig. 8. A photograph of MOF crystals (size *ca.* 0.2 x 0.2 x 0.2 mm) prepared in our laboratory.

reaction of hydrated zinc(II) nitrate with aromatic carboxylic acids in DEF (N,N'-diethylformamide) under solvothermal conditions.¹² This procedure reliably produces large single crystals of MOFs involving a wide variety of ligands.⁷ Under these conditions, the base required to deprotonate the carboxylic acids is generated by the slow hydrolysis of the solvent. Initially this produces diethylamine and formic acid, although the latter is thought subsequently to decompose to hydrogen and carbon dioxide.¹³ The source of the central O²⁻ ion in this case is probably water. It has been shown that the nitrate anion *can* serve as the source of this oxide,¹⁴ although it is not clear to what extent this occurs under standard conditions. Furthermore, MOFs can be synthesized at room temperature by replacing the zinc(II) nitrate by zinc(II) acetate. Zinc(II) oxide can also be used as a precursor, which parallels the synthesis of discrete complexes such as [Zn₄O(OAc)₆],¹⁵ in which case the origin of the O²⁻ ion is obviously beyond doubt.

In light of the potential applications outlined below, BASF has recently started the production of MOFs on an industrial scale.¹⁶ Several interesting challenges had to be met regarding their bulk synthesis and processing. For example, although Zn(NO₃)₂ is typically used as a precursor to Zn-based MOFs, this generates high nitrate concentrations, which pose a safety hazard. An electrochemical method was therefore developed, which relies on bulk sacrificial metal electrodes which are oxidised in the presence of dissolved ligands. Owing to the high amount of occluded solvent in these materials, filtration and activation of the materials is a tedious operation even on a laboratory scale.

What Are MOFs Good For?

Upon guest removal, MOFs can often support a vacuum owing to the strength of the bonding interactions that hold them together. MOFs with pore sizes of up to 30 Å and surface areas of 5000 m²/g have been reported.¹⁷ They are stable in dry air up to temperatures at which ligand combustion occurs (~400 °C). As they comprise mostly fresh air by volume, they can have densities lower than 0.21 g/cm³, the lowest yet known for crystalline materials. This combination of key properties is not seen in any other class of molecular materials. It is noteworthy that the application of co-ordination polymers as molecular sieves and heterogeneous catalysts was anticipated by Robson in his 1990 paper.³

The performance and utility of MOFs in the applications outlined below can be compared with their zeolite cousins. Zeolites have higher thermal stabilities and are generally less susceptible to hydrolysis than MOFs, which means they are more suited to high temperature applications such as the cracking of hydrocarbons. Advantages of MOFs include:

- MOFs do not have walls to impede the diffusion of guest molecules, unlike zeolites.
- Most MOFs are neutral, negating the need for charge-balancing counterions in the pores.
- The solvent itself acts as the main template in MOF synthesis, obviating the requirement for added templates such as amines and quaternary ammonium salts.
- Functional groups can be introduced into the structure via the ligands. These often line the MOF channels and are accessible to incoming guests.
- MOF pores are lined with both hydrophobic (ligand backbone) and hydrophilic (metal cluster) constituents which may enhance their sorption properties.
- MOFs can have greater surface areas (1000-4000 m²/g) than zeolites (typically ~700 m²/g).

Undoubtedly, the most sought-after technological application of MOFs, which draws on these properties, is gas storage.¹⁸ Relatively non-polar gases such as hydrogen, carbon dioxide and methane can be absorbed by MOFs in significant quantities. Vessels that are pre-filled with MOFs can thus enhance gas storage capacity in a given volume or store an equivalent amount of gas at a lower pressure.¹⁹ This is highlighted in Fig. 9 for the storage of hydrogen in various MOFs. Efforts to further improve the hydrogen storage capacity of MOFs are motivated by the US Department of Energy which has set targets for its on-board storage on hydrogen-powered vehicles of 6.0 wt% (45 g/L) for 2010 and 9.0 wt% (81 g/L) for 2015 under ambient conditions. In practice, the latter target is anticipated to allow vehicles to store around 10 kg of hydrogen, which will allow them to travel about 500 km. The best MOFs are approaching these targets at 77 K, however significant sorption has not yet been observed at room temperature.

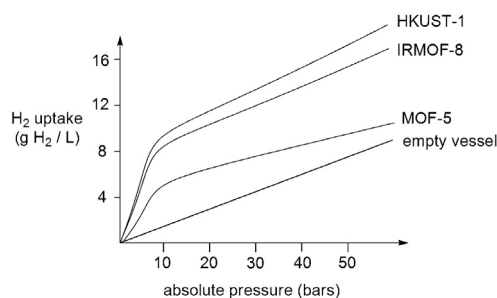


Fig. 9. Comparison of the hydrogen storage capacity of empty and MOF-filled vessels. IRMOF-8 and HKUST-1 are other MOF materials.

A derivative of MOF-5, which has a cyclobutyl group appended to the benzene ring (IRMOF-6), was found to have an exceptionally high affinity for methane.⁷ The

amount of methane contained in a volume of 155 cm³ at standard temperature and pressure can be taken up by 1 cm³ of this material at a pressure of 36 atm (3.6 MPa). This is 70 % of the amount stored in the same volume in liquefied methane, which requires a much higher pressure (>200 atm). The reduction in the pressure required to store methane makes MOF-filled cylinders potentially both safer and more cost-effective. Although some carbon adsorbents have a similar capacity, it can be anticipated that even higher gas uptake can be achieved by optimization of the MOF structure.

One notable feature of MOFs is that the organic struts bear various functional groups, which can be tailored using the toolbox of synthetic organic chemistry prior to incorporation in the MOF. These often line the pores and channels in the resultant frameworks and thus are accessible to incoming guests. Additionally, vacant co-ordination sites on the framework metal atoms may also bind and activate substrates. Applications of MOFs as sensors and heterogeneous catalysts can thus be envisaged, and this aspect of MOF chemistry is witnessing a flurry of activity.

Representative examples of MOF catalysis include the finding that HKUST-1,²⁰ a MOF derived from copper(II) and benzene-1,3,5-tricarboxylic acid, is capable of catalyzing the cyanosilylation of carbonyl compounds such as benzaldehyde and acetone. The catalysis mechanism relies on the Lewis acid activation of the carbonyl group by open copper co-ordination sites.²¹ In a departure from carboxylic acid ligands, Volkmer's group have reported that a cobalt(II)-BPB MOF [BPB = 1,4-bis(4'-pyrazolyl)benzene] can be oxidised by *t*-butyl hydroperoxide to give the corresponding cobalt(III) framework. This material can subsequently catalyze the conversion of cyclohexene to *t*-butyl-2-cyclohexenyl peroxide.²² Researchers at BASF have carried out MOF-catalysed reaction on bulk scales to determine their suitability for industrial processes. For example, the conversion of propyne to methoxypropene at 250 °C was achieved using a copper(II)-benzene-1,4-dicarboxylate MOF (MOF-2) catalyst.¹⁹

What's Hot in MOF Research?

One aspect of MOF chemistry that has surged recently is their post-synthetic modification.²³ The potential feasibility of modifying open co-ordination polymers by reactions with external reagents was first identified by Robson as a method of tailoring the chemical and physical properties of these structures. This approach also allows the incorporation of functional groups that would otherwise perturb formation of the solid state network, *e.g.* by binding to the metal ions in preference to the designated donor groups. However, it is only in the past couple of years that the investigation of this phenomenon has moved on from simple guest exchange processes to the covalent derivatization of organic MOF components. The major impetus has come from Seth Cohen's group who, in 2007, reported on the derivatization of IRMOF-3, [Zn₄O(2-aminobenzene-1,4-dicarboxylate)] with various anhydrides (Fig. 10a).²⁴ Reactions with isocyanates have also been pursued. These produce urea groups that are of interest for their potential

anion binding and organocatalytic properties. Other creative post-synthetic modification reactions on MOFs have included the reaction of MOF-5 with M(CO)₆ complexes to generate *piano stool* complexes in which the aromatic MOF strut functions as an η₆ π-donor ligand (Fig. 10b),²⁵ and the low temperature reaction of acetaldehyde with the amino group of 1-aminotriphenylene encapsulated in co-ordination polymer composed of zinc(II) iodide and 2,4,6-tris(4-pyridyl)-1,3,5-triazine.²⁶ This latter reaction allowed the structure of the carbinolamine intermediate of a classic Schiff base condensation reaction to be observed by X-ray crystallography for the first time (Fig. 10c).

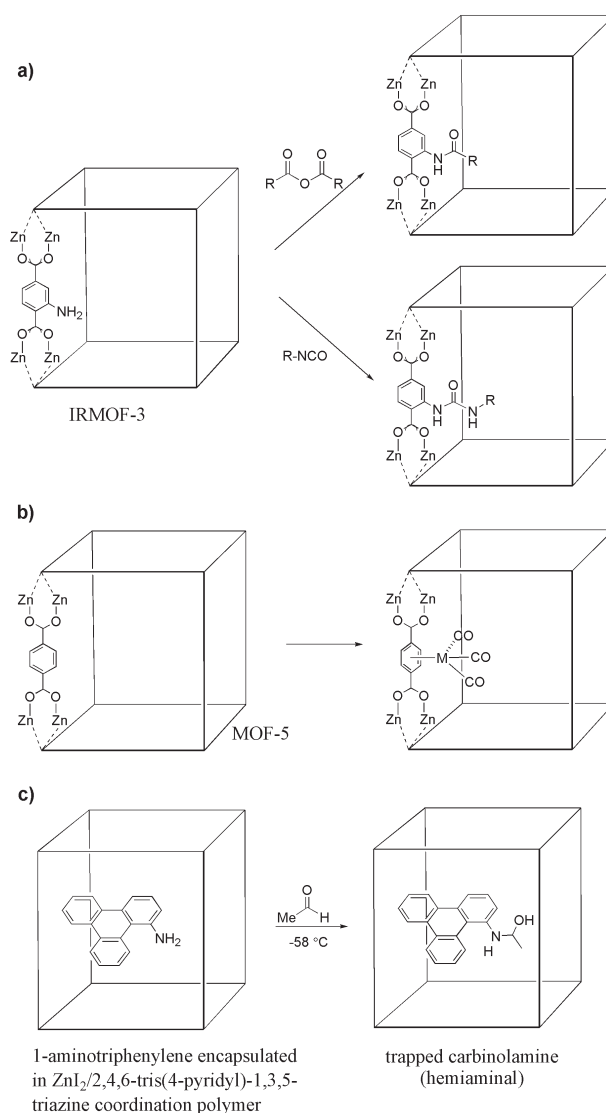


Fig. 10. Examples of the post-synthetic modification of MOFs.

Another area that has recently flourished is the growth of thin films of MOFs on surfaces.²⁷ The fabrication of porous MOF films on solid supports is a pressing challenge, as this MOF morphology is most likely to find application in devices such as sensors and selective membranes. Ideally, the resulting films should be continuous, defect-free, and crystalline, with a well-defined orientation of their pores with respect to the surface. The production of free-standing MOF membranes by the subsequent detachment of the film from the surface can also be envisaged. Research to date has mainly focussed on the growth of MOF-5 and HKUST-1 ([Cu₃(1,3,5-benzenetricarboxyl-

ate)₂) on supports such as alumina, silica, and self-assembled monolayers (SAMs) on gold.²⁸ Although this field is in its infancy, notable progress has already been made. For example, Lai *et al.* have prepared a continuous membrane of intergrown MOF-5 crystals on α -alumina by immersing the substrate in a solution containing the precursor components at elevated temperatures.²⁹

In an intriguing recent development that draws on the high porosity of MOFs, Matzger *et al.* have discovered that microporous co-ordination polymers can remove organosulfur compounds from diesel fuel.³⁰ The process is efficient and highly selective and the high loading capacity of certain MOFs means that practical applications are realistic. The same group has also taken advantage of the porosity of MOF-5 and HKUST-1 in exploring their use as stationary phases in liquid chromatography and gel permeation chromatography.³¹ A combination of molecular sieving and adsorption effects operate to efficiently separate variously substituted aromatic hydrocarbons.

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