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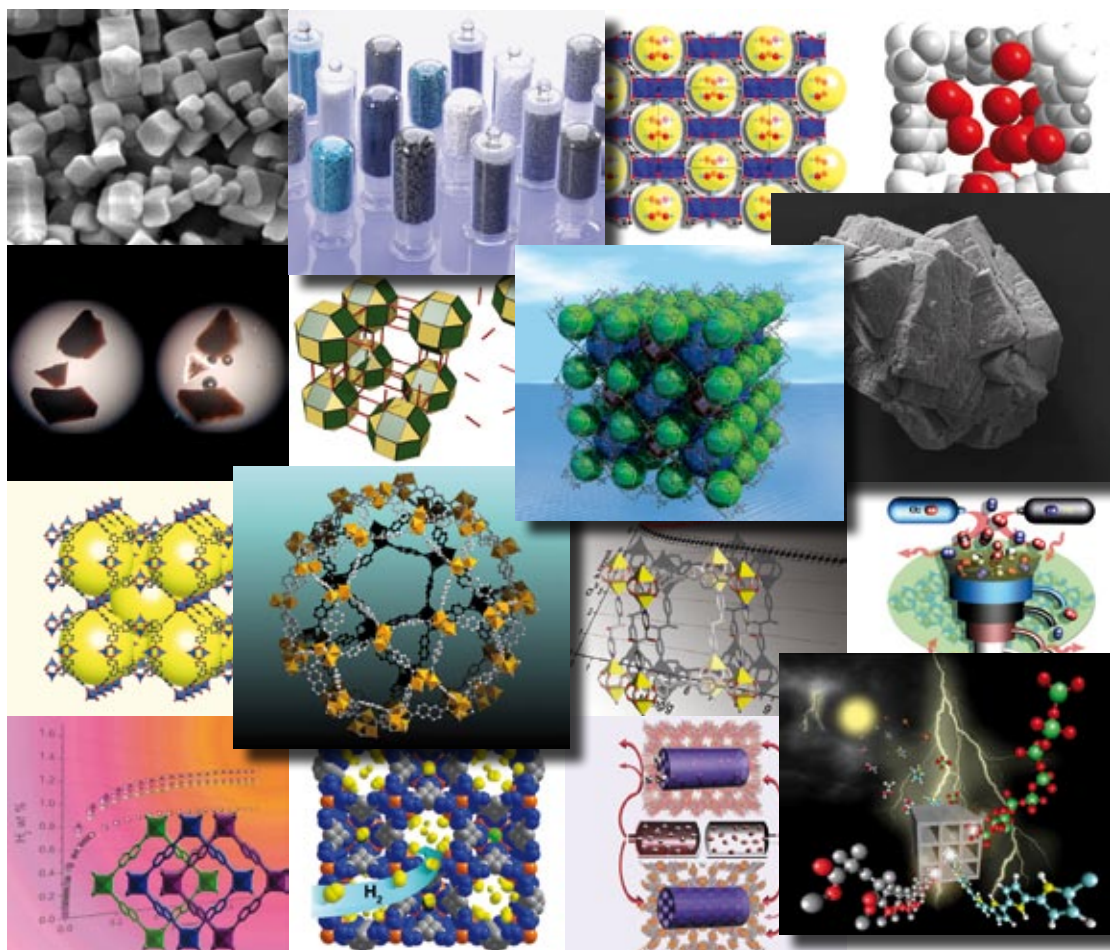
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Reviewing the latest developments across the interdisciplinary area of metal–organic frameworks from an academic and industrial perspective

Guest Editors Jeffrey Long and Omar Yaghi

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Postsynthetic modification of metal–organic frameworks†

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The modification of metal–organic frameworks (MOFs) in a postsynthetic scheme is discussed in this *critical review*. In this approach, the MOF is assembled and then modified with chemical reagents with preservation of the lattice structure. Recent findings show amide couplings, isocyanate condensations, ‘click’ chemistry, and other reactions are suitable for postsynthetic modification (PSM). In addition, a number of MOFs, from IRMOF-3 to ZIF-90, are amenable to PSM. The generality of PSM, in both scope of chemical reactions and range of suitable MOFs, clearly indicates that the approach is broadly applicable. Indeed, the rapid increase in reports on PSM demonstrates this methodology will play an increasingly important role in the development of MOFs for the foreseeable future (117 references).

1. Introduction

Metal–organic frameworks (MOFs), a subset of two-dimensional (2D) or three-dimensional (3D) coordination polymers (sometimes referred to as porous coordination polymers, PCPs)^{1,2} that are comprised of metal ions or metal ion clusters and bridging organic ligands, have recently emerged as an important family of porous materials due to their unique structural and functional properties.^{3–18} The 2D and 3D

structures of MOFs can exhibit nano-sized cavities and/or open channels. Among the numerous attractive traits of MOFs are their well-characterized crystalline architectures and record-high surface areas.^{19–22} The modular nature (*via* the combination of inorganic and organic components) of these materials makes them ideally suited for chemical manipulations aimed at fine-tuning structure and function.

The design of MOF materials has been greatly facilitated by the ‘node-and-spacer’^{5,6} and ‘secondary building unit (SBU)’^{7,8} models where molecular precursors, *i.e.*, metal ions and organic ligands or their *in situ* formed intermediates, are conveniently conceptualized as objects such as points, lines, polygons or polyhedra, with MOFs as periodic and complementary assemblies of these geometric entities. Crystals of

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MOFs, often isolated in a form suitable for X-ray diffraction analysis, are typically obtained from 'one-pot' synthesis involving either slow diffusion or direct mixing (generally under solvothermal conditions) of metal ion and organic precursors. Following these simple, yet powerful design principles, a large number of novel MOF structures have been generated over the past decade. Some of these MOFs have already found applications in areas such as magnetism, catalysis, separations, and gas storage,^{9–11} placing them among the most interesting classes of solid-state materials.

A key to accessing advanced MOF materials suitable for more specialized and sophisticated applications is to integrate functionalities of *greater complexity* into these materials. The ability to modify the physical environment of the pores and cavities within MOFs would allow tuning of the interactions with guest species, and serve as a route to tailor the chemical stability and/or reactivity of the framework. In this context, at least three different strategies have been employed to achieve MOF functionalization. The first involves the use of a functionalized ligand as the organic building block. For example, a MOF showing reversible solvent-induced mechanical and magnetic properties can be constructed from an organic radical,²³ whereas a MOF that demonstrates selective anion binding can be prepared using a pyridyl-type ligand decorated with free carboxylic acid groups.²⁴ The second approach exploits functional properties that are associated with metal ions. In one scenario, MOFs can be constructed from metalloligands,^{25–27} where functionality is derived from a coordination compound that serves as the 'organic' building block. More recently, a third approach, which incorporates functional 'cartridge molecules' that are non-covalently bound within MOFs has been demonstrated.²⁸

These three strategies afford several means to modulate the physical and chemical properties of MOF structures, which may increase the use of MOFs as high performance, tailor-made materials. However, the requirement of all three methods to *pre-install* functional groups within the molecular precursors *prior to or during* MOF synthesis does present some limitations that reduce the scope of these schemes. For instance, although some substituents might be highly desirable for material modification due to their unique chemical (*e.g.*, reactivity) or physical (*e.g.*, polarity) properties, incorporating these groups into the MOF can be challenging, either because the groups interfere with the formation of the desired MOF, or because they are not compatible with the MOF synthetic conditions (*e.g.* chemical or thermal instability, insolubility, steric bulk, *etc.*). In addition, as with any MOF synthesis, finding the appropriate reaction conditions for forming a particular MOF with a functionalized molecular precursor can often be time-consuming and highly non-trivial, thus further limiting the use of 'pre-functionalized' precursors for systematic modulation of MOF materials.

An alternative approach that can circumvent these limitations is to chemically modify MOFs *after* the crystalline materials have already been formed (Fig. 1). Assuming that the MOFs are sufficiently robust and porous to allow late-stage transformations without compromising overall framework integrity, a wide variety of chemical reactions should be available for modifying the framework components.

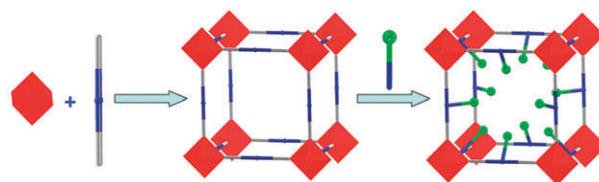


Fig. 1 A general scheme illustrating the concept of postsynthetic modification of porous MOFs.

Postsynthetic modification (PSM) of MOFs can thus be broadly defined as chemical derivatization of MOFs after their formation; in a more strict sense, it may refer only to those modifications involving covalent bond formation with the framework. The potential advantages offered by the PSM approach to functionalizing MOFs can be appreciated by the following considerations: (1) it is possible to include a more diverse range of functional groups, freed of the restrictions posed by MOF synthetic conditions; (2) purification and isolation of modified products are facile because the chemical derivatization is performed directly on crystalline solids (*e.g.* heterogeneous); (3) a given MOF structure can be modified with different reagents thereby generating a large number of topologically identical, but functionally diverse MOFs; (4) control over both the type of substituent and the degree of modification allows introduction of multiple functional units into a single framework in a combinatorial manner, enabling an effective way to systematically fine-tune and optimize MOF properties.

The concept of PSM in the context of MOFs is not new, and was contemplated almost two decades ago when development of MOFs was in its infancy. In a seminal paper published in 1990, Hoskins and Robson speculated that "relatively unimpeded migration of species throughout the lattice may allow chemical functionalization of the rods subsequent to construction of the framework."²⁹ It had been well-established since this suggestion that it was feasible to transform MOF structures by the exchange of guest molecules (*e.g.* ion exchange); however, it took MOF chemists more than a decade to demonstrate this concept *via* covalent modification of a porous MOF.³⁰ The past few years have witnessed a substantial increase in the number of studies on the covalent modification of MOFs, which greatly improves our understanding on the scope and fundamental principles of PSM and its broader implications in the manipulation of MOF properties.

The concept of PSM is in no way unique to MOFs. Indeed, the PSM approach is generally more mature in other types of solid-state materials including carbon nanotubes, zeolites and mesoporous silicas, and organosilicas. Even Nature uses this strategy in biopolymers, where post-translational modification (PTM) of proteins is a well-established concept in both naturally occurring and artificial biochemical systems.

This review will briefly survey recent developments in the chemical (or biochemical) modification of proteins, carbon nanotubes, and zeolitic microporous and mesoporous materials. The remainder of the review will be devoted to describing the recent progress made in the PSM of MOF materials. These studies are organized by the nature of chemical interactions invoked in the modification, including non-covalent

interactions, coordination bonds, covalent bonds, and non-stoichiometric doping. Also discussed are the so-called 'tandem modification' approaches, in which serial 'step-by-step' modification of MOFs are performed. Finally, a short summary and remarks on future directions are provided.

2. Postsynthetic modification in proteins, carbon nanotubes, and porous silicates

Nature is, without doubt, the first and the best in terms of exploiting the concept of late-stage functionalization. For example, PTM of proteins, *i.e.*, covalent modifications that occur after translation and synthesis of a polypeptide, represents a common and powerful route to diversification of protein structures and functions within living cells.^{31–33} PTM of cellular proteins usually invokes enzyme-catalyzed reactions that target side chains of 15 of the 20 common proteinogenic amino acids. PTM greatly expands the diversity of proteins by increasing the number of possible functional groups that can be obtained from the 20 amino acids alone. The major types of protein PTM include phosphorylation, acetylation, glycosylation, alkylation, and oxidation. It is believed that PTM is widely used by cells and organisms because starting from one protein scaffold is a more efficient way to create structural and functional diversity than building new protein structures for each desired operation.³⁴ Currently, methods for artificial PTM are also under intensive investigation to elucidate protein function in living systems, which might help the development of protein-based biopharmaceuticals.^{34,35} One major challenge in this area is finding reliable strategies that allow for site-selective functionalization. Recently, a number of these approaches, such as those based on transition metal catalysts³⁶ and 'click' chemistry,³⁷ have been successfully demonstrated.

Carbon nanotubes (CNTs) are another area where methods analogous to PSM have been extensively investigated.^{38–42} As-synthesized CNTs are insoluble in almost all organic solvents and aqueous solutions, which dramatically impedes the manipulation and processing of CNTs as molecular devices and hybrid composites. Chemical modification of CNTs, on the other hand, greatly improves their dispersibility in solutions and makes them more compatible with other materials. PSM of CNTs can be directed toward their end caps, defect-sites, and most importantly, sidewalls. In fact, CNTs can be considered as either sterically bulky π -conjugated systems or electron-deficient alkenes. As a result, a wide variety of chemical reactions, including covalent (*e.g.*, halogenation, cycloaddition, radical addition, electrophilic addition, nucleophilic addition, *etc.*), coordination, and non-covalent modifications, can be applied. Successful utilization of these synthetic techniques has led to many exciting applications, ranging from separation of metallic and semiconducting single-walled CNTs,⁴³ chemical and biochemical sensing,⁴⁴ materials applications,^{45,46} and drug discovery and delivery.^{47,48}

Efforts on the PSM of microporous zeolites (aluminosilicates) and the related zeolitic materials (*e.g.*, aluminophosphates) have been less abundant presumably due to their relatively small pore size and lack of accessible chemical functionality. Modification of as-prepared forms of zeolites is largely limited

to calcination or ion exchange of the organic-cation components of the materials. In contrast, PSM of mesoporous silicas, which possess much larger pores that are lined with reactive silanol (SiOH) groups, have been more extensively investigated. Grafting of organic functionality (R) to these structures is commonly realized by reacting organosilanes ((R'O)₃SiR), chlorosilanes (ClSiR₃), or silazanes (HN(SiR)₃) with the free silanol groups on the pore surfaces.⁴⁹ Immobilization of other species, including coordination-complex based chiral catalysts, can be achieved similarly or by non-covalent means such as ion exchange.⁵⁰ Recently, a new class of hybrid structures, the so-called periodic mesoporous organosilicas (PMOs) that contain organic moieties as framework bridges,^{51,52} offer another unique opportunity for the PSM of mesoporous materials. The presence of organic components and the extremely high chemical and thermal stability of the frameworks allow these materials to be derivatized with very corrosive reagents under harsh reaction conditions.^{53,54}

3. Postsynthetic modification of metal–organic frameworks

Although the idea of PSM was proposed for coordination solids as early as 1990,²⁹ and conceptually similar efforts had already led to impressive results on other related materials, initial progress in PSM of porous MOFs was surprisingly limited. Early studies were essentially restricted to those relying on non-covalent interactions, and synthetic tools based on transforming covalent bonds have not been applied until very recently. The biggest challenge perhaps came from the notion that breaking and reforming *covalent* bonds on *coordination* solids would not be feasible. **However, recent developments suggest that MOF crystals can in fact be treated as chemical substrates^{30,55,56} and the past two years, in particular have seen a tremendous advancement in the covalent modification of porous MOFs.^{57–70} New methodologies based on different forms of chemical modulation, such as transformation with coordination bonds,^{71–77} doping with metals or metal ions,^{78–86} and step-wise tandem modification,^{62,66,87} have also been demonstrated in various systems.** Nevertheless, it is reasonable to state that this is only the beginning of a new era for MOF functionalization and that many more exciting opportunities provided by PSM can be expected in the coming years.

3.1 PSM of MOFs by non-covalent interactions

The most common forms of postsynthetic non-covalent modification of MOFs include guest removal, guest exchange, and ion exchange. Whereas the action of ion exchange is necessarily restricted to charged frameworks, guest removal and guest exchange are more generally applicable. Removing guest species that occupy the free space of the lattice was detrimental to many earlier generation MOFs, and caused collapse of the frameworks;⁴ however, some systems were shown to maintain their crystallinity upon simultaneous exchange with other guests.⁸⁸

Subsequent developments in MOF synthesis led to a generation of more robust materials that allowed for free movement of neutral guest molecules without compromising the

framework integrity. Lee *et al.* demonstrated that a 2D MOF based on 3-coordinated Ag(I) and tritopic 1,3,5-tris(3-ethynylbenzonitrile)benzene ligand could undergo a single-crystal-to-single-crystal transformation by partially releasing benzene guests upon heating at 110 °C for 10 min.⁸⁹ This process was reversible and the material could reabsorb the same amount of benzene rather rapidly, indicating a zeolite-like behavior. Similar properties were also observed by Yaghi and co-workers in a 2D Co(II)BTC (BTC = 1,3,5-benzenetricarboxylate) based MOF, which was stable upon loss of pyridine guests.⁹⁰ Quite significantly, the guest-free form of this latter MOF selectively absorbs aromatic molecules such as benzene, nitrobenzene, cyanobenzene, and chlorobenzene, but not acetonitrile, nitromethane, or dichloroethane. The laboratories of both Kitagawa and Yaghi went a step further and independently confirmed the open framework structures of MOFs by using gas sorption isotherms.^{91,92} Their results unambiguously established the true microporosity of MOF materials and were largely responsible for initiating an exponential growth of studies on gas storage in porous MOFs.¹¹ Indeed, guest exchange with more volatile solvents followed by guest removal under vacuum has now been recognized as a standard practice for activation of porous MOF materials.⁹³ In certain cases, release and uptake of guest molecules imposes a profound influence on the structure and functional property of MOFs.¹⁵

Similar to microporous zeolites, MOFs can also be modified by exchanging the ionic species originally present inside the lattice. In contrast to zeolites, where only cation exchange is feasible due to the anionic nature of zeolite frameworks, MOFs can undergo both anion²⁹ and cation^{94,95} exchange depending on their framework charges. An intriguing scenario was demonstrated by Cohen and co-workers in which anion-exchange appears to occur in a single-crystal-to-single-crystal transformation process in a metalloligand-based MOF.²⁷

3.2 PSM of MOFs by coordinative interactions

In principle, there exist at least two different approaches to PSM of MOFs with metal–ligand interactions. The first targets the exposed metal sites of MOFs, whereas the second explores the coordination chemistry of the organic components. Several research groups have recently applied both approaches and demonstrated their utility and versatility in incorporating a variety of complex functionalities into MOFs.

Under appropriate conditions, a number of MOF structures have shown the propensity to release auxiliary ligands from the metal ion nodes, which often leads to generation of coordinatively unsaturated metal centers.^{71,92,96–99} While removing auxiliary ligands is a justified form of PSM in its own right, the subject has been thoroughly discussed in the context of hydrogen storage in a recent review article.¹⁰⁰ More importantly, unsaturated metal centers can provide further modification sites for functionalization of MOFs. In 1999, Williams and co-workers reported the now well-known HKUST-1 compound, which is a highly porous 3D MOF derived from dimeric Cu(II) paddle-wheel SBUs and BTC ligands.⁷¹ Their study indicated that the lability of axial aqua ligands on the paddle-wheel SBUs in HKUST-1 permits their

replacement by other molecules. Treatment of the dehydrated HKUST-1 with dry pyridine, for example, results in a different formulation of the MOF, with pyridine as the new axial ligands, while the 3D lattice remains intact. Interestingly, the authors also suggested that the pyridine-decorated HKUST-1 cannot be obtained directly from a reaction of Cu(II) salts, BTC, and pyridine.

PSM investigations were performed by the Férey laboratory on their materials MIL-100¹⁰¹ and MIL-101,²¹ which are porous 3D MOFs constructed from Cr(III) trimers bridged by BTC and BDC (BDC = 1,4-benzenedicarboxylate) ligands, respectively. In both MOFs, there are potential open metal sites at the Cr(III) trimers, which are occupied by water molecules in their as-synthesized forms. Introduction of excess deuterated methanol to the dehydrated MIL-100 sample at room temperature appears to be sufficient to introduce the new axial ligands.⁷³ An infrared (IR) spectrum obtained on the modified sample previously evacuated at 373 K overnight supports the presence of coordinated methanol. The characteristic bands, including a strong $\nu(\text{OH})$ band at 3625 cm^{-1} and two $\nu(\text{CD}_3)$ bands at 2264 and 2089 cm^{-1} , are red shifted relative to the frequencies of liquid methanol, suggesting that deuterated methanol molecules are indeed located at the open metal sites of Cr(III) trimers. Despite the long evacuation time, the immobilized methanol seems to remain stable, highlighting the utility of this approach to modifying functional properties (e.g., Brønsted acidity and sorption behavior) of MOFs. Following similar strategies, MIL-101 was treated with a number of organic multifunctional amines such as ethylenediamine (ED), diethylenetriamine (DETA), and 3-aminopropyltriethoxysilane (APS).⁷⁵ For example, mixing the dehydrated MIL-101 sample with ED in toluene and heating the solvent to reflux readily generates the ED-functionalized MIL-101. IR spectra, powder X-ray diffraction (PXRD), and nitrogen adsorption isotherms support the successful grafting of amine functionalities onto the open metal sites (*i.e.*, Cr(III) trimers) of the MOF. It was proposed that only one amine group from each ligand is involved in coordination to the metal and the other amine group(s) can serve as immobilized base catalyst. Thus, the modified products, ED-MIL-101, DETA-MIL-101, and APS-MIL-101, were evaluated for their catalytic properties in the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate. As anticipated, the amine-functionalized MOFs all show significantly higher activity for this reaction than the unmodified MIL-101 sample (>96% vs. 31.5% in conversion). Size selectivity on different carbonyl substrates was also observed in the ED-MIL-101 catalyzed reactions, suggesting a heterogeneous mechanism and further corroborating successful grafting of amine functionalities.

Most recently, Hupp *et al.* prepared a new 3D porous MOF with a tetracarboxylate ligand (4,4',4'',4'''-benzene-1,2,4,5-tetracarboxylate) and *in situ* formed dimeric Zn(II) paddle-wheel SBU.⁷⁶ They subsequently removed the axial ligand DMF (DMF = dimethylformamide) from the MOF by heating the crystalline material under vacuum at 150 °C. Several pyridine ligands (py-R, where R represents various functional groups on the pyridine ring) were introduced to the DMF-free MOF samples by immersion in a CH_2Cl_2 solution.

The samples were extensively washed, soaked, and dried. ^1H NMR measurements on the digested MOFs confirm the presence of pyridine ligands in the original solid materials. CO_2 sorption experiments performed on the py-R functionalized MOFs reveal decreases in surface areas and pore volumes, consistent with an expected PSM result. Initial results indicate that the hydrogen sorption properties of the MOF have also been accordingly modified.

Compared to the above metal-based PSM strategy, it is perhaps somewhat more challenging to incorporate unbound, and thereby available, ligands into the organic components of the MOF. As has been emphasized above, ligands with potential coordinative capability tend to interfere with the formation of desired MOFs in the initial synthesis. Nevertheless, recent studies suggest that the ligand-based coordination approach can still afford unique opportunities for PSM of MOFs.

Lin *et al.* designed a 3D homochiral porous MOF from $\text{Cd}(\text{II})$ and a BINOL (BINOL = 1,1'-bi-2-naphthol) type chiral bridging ligand that contains pyridyl and orthogonal dihydroxy functionalities.⁷² While the pyridyl groups coordinate to the

$\text{Cd}(\text{II})$ centers as part of the framework backbone, the dihydroxy substituents are not involved in coordinative interactions and are therefore accessible for further chemical functionalization. The MOF was treated with $\text{Ti}(\text{O}^i\text{Pr})_4$, a complex known to coordinate to BINOL and its derivatives to produce Lewis-acid catalysts (Fig. 2). Unfortunately, no structural or spectroscopic characterizations were provided to confirm the successful grafting of $\text{Ti}(\text{O}^i\text{Pr})_4$ species. However, data subsequently obtained reveal that the $\text{Ti}(\text{O}^i\text{Pr})_4$ -treated MOF indeed catalyzes the addition of ZnEt_2 to 1-naphthaldehyde, which affords (*R*)-1-(1-naphthyl)propanol with complete conversion and 93% enantiomeric excess (ee). Further studies showed that the modified homochiral MOF also catalyzes addition of ZnEt_2 to a range of other aromatic aldehydes with complete conversion and ee values similar to a comparable homogenous catalyst. Most importantly, the MOF shows remarkable size selectivity in catalyzing these reactions. Substrate conversion was found to decrease as the size of the aldehydes increased, indicating a true heterogeneous catalytic process.

A unique organometallic approach was recently adopted by the Long laboratory in an effort to functionalize a known

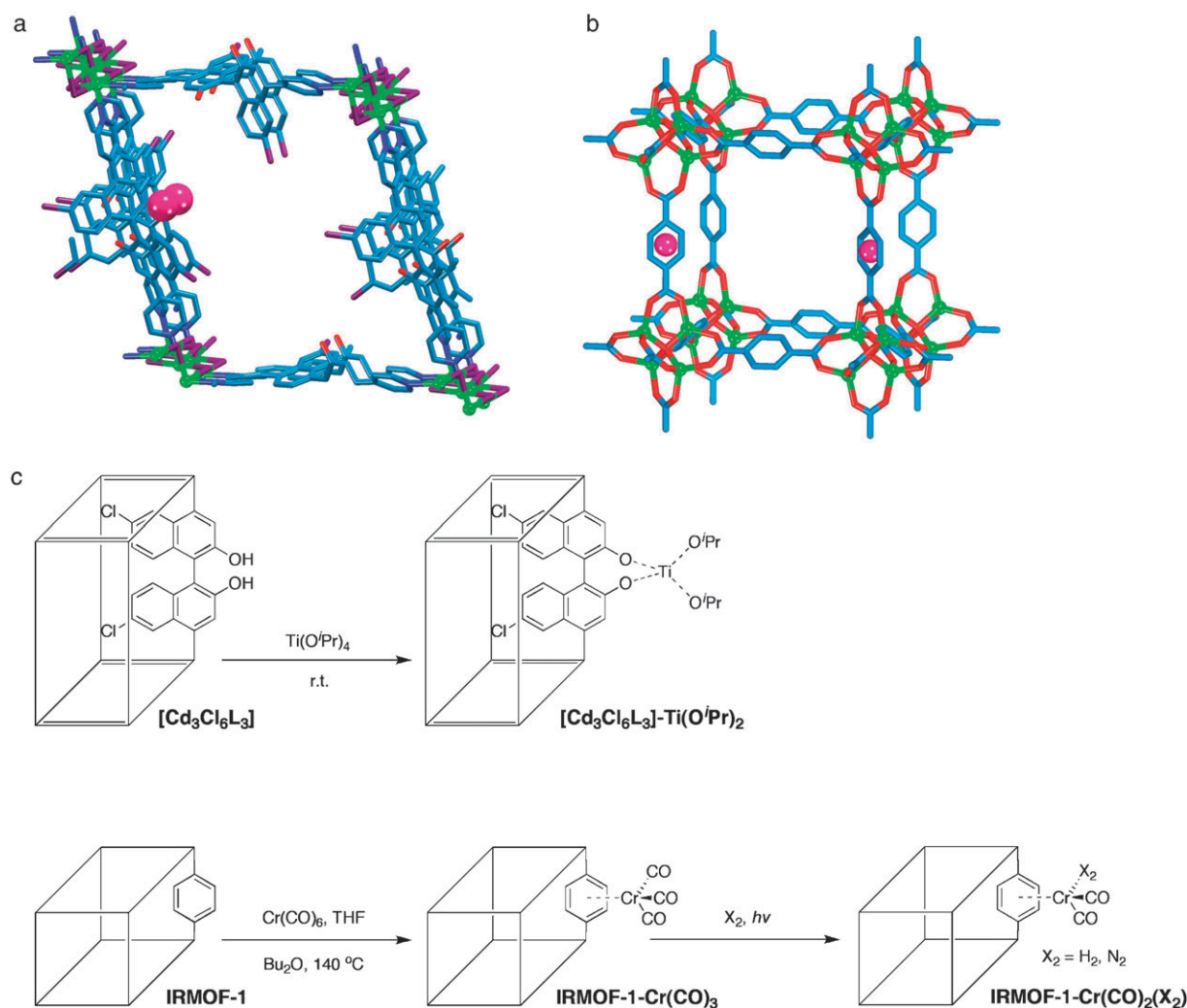


Fig. 2 Structural representations of $[\text{Cd}_3\text{Cl}_6\text{L}_3]$ MOF (top left) and IRMOF-1 (top right); some sites of postsynthetic modification are highlighted with magenta spheres. Scheme of the postsynthetic modification of each of these MOFs with metal ion complexes (bottom).

MOF, isorecticular metal–organic framework-1 (IRMOF-1, also known as MOF-5), which is a cubic lattice composed of octahedral $\text{Zn}_4\text{O}(\text{RCOO})_6$ nodes bridged by linear BDC ligands.^{19,102} $\text{M}(\text{CO})_3$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) fragments are known to bind to benzene rings in an η^6 fashion to generate classic arene organometallic ‘piano stool’ complexes (Fig. 2). The possibility of attaching these complexes to the BDC moieties of IRMOF-1 was thus tested (Fig. 2).⁷⁴ IRMOF-1 was mixed with $\text{Cr}(\text{CO})_6$, dibutyl ether, and THF (THF = tetrahydrofuran) under a nitrogen atmosphere. Heating the mixture in a sealed tube at 140 °C for 5 days turned the colorless starting MOF a dark red color. IR and ^1H NMR spectra support attachment of the $\text{Cr}(\text{CO})_3$ species to the BDC rings and formation of the desired piano stool complexes within the MOF matrix. PXRD and gas sorption measurements on the modified IRMOF-1 reportedly confirmed the crystallinity and microporosity of the product. Open coordination sites on the chromium center were generated by heating the IRMOF-1– $\text{Cr}(\text{CO})_3$ sample to evolve CO gas. IR spectroscopy of the decarbonylated product confirmed the absence of CO ligands; however, low-pressure sorption measurements performed at 298 K show insignificant uptake of N_2 and H_2 , possibly due to mobilization and aggregation of the chromium atoms upon heating. A milder photolysis of IRMOF-1– $\text{Cr}(\text{CO})_3$ in an atmosphere of nitrogen or hydrogen was thus pursued, which resulted in facile substitution of a single CO ligand per metal site by N_2 or H_2 . Interestingly, the N_2 - and H_2 -substituted complexes immobilized in IRMOF-1 display remarkable stability when compared to the corresponding molecular species.

Edaoudi *et al.* investigated the postsynthetic metalation of a free-base porphyrin encapsulated within a zeolite-like MOF (ZMOF).⁷⁷ The 3D ZMOF was prepared from $\text{In}(\text{III})$, ImDC, and H_2RTMPyP (ImDC = 4,5-imidazoledicarboxylate; H_2RTMPyP = 5,10,15,20-tetrakis(1-methyl-4-pyridinio)-porphyrin tetra(*p*-toluenesulfonate)). The porphyrin H_2RTMPyP could be isolated within the ZMOF as guest molecules. Incubation of the porphyrin-containing ZMOF in a 0.1 M methanol solution of metal nitrate salts at room temperature for up to 24 h readily resulted in coordination of metal cations into the porphyrin ligand within the MOF, as indicated by the solid-state UV-Vis spectra obtained on the modified ZMOFs. The catalytic activity of the $\text{Mn}(\text{II})$ -metallated product was evaluated for cyclohexane oxidation. It was found that 24 h incubation generated cyclohexanol and cyclohexanone as the only products, with a total yield of 91.5%, noticeably higher than other systems of supported metalloporphyrins. A similar transmetalation reaction, in MOF nanoparticles containing a salen-like ligand, was reported by Oh and Mirkin.⁹⁵ In this case, the MOF nanoparticles were prepared with a $\text{Zn}(\text{II})$ metallated metalloligand, whereby the $\text{Zn}(\text{II})$ ion could be readily displaced by exposure of the MOF nanoparticles to $\text{Cu}(\text{II})$, $\text{Mn}(\text{II})$, or $\text{Pb}(\text{II})$.

3.3 PSM of MOFs by covalent bonds

Synthetic methods that facilitate breaking and reforming covalent bonds represent the most powerful tool in modern synthetic chemistry. The covalent approach to the PSM of

MOFs may seem more challenging, when comparing the strength of covalent bonds relative to generally weaker coordinative interactions that sustain the MOF structure. However, the comparison of bonding strength may be true on an individual basis, but the periodic architectures of MOFs can in fact afford remarkable thermal and chemical stability.¹⁰³ Indeed, the explosive growth in reports on the covalent modification of MOFs indicates that this approach is extremely viable and promising in MOF functionalization. Various types of covalent transformations, including amide coupling,^{56,58,63,64,70,87} imine condensation,^{60,62,64,67,68} urea formation,^{59,64} *N*-alkylation,³⁰ bromination,⁸⁷ reduction,⁶⁷ click reactions,^{66,69} and protonation,^{57,61} have been successfully applied to postsynthetic MOF modifications by a number of research groups.

The first example of covalent PSM of MOFs appeared in 2000 when Kim *et al.* reported a 2D homochiral MOF (POST-1) for enantioselective separation and catalysis.³⁰ The material was built from $\text{Zn}(\text{II})$ trimer SBU and an enantiopure tartrate derivative containing a pyridyl moiety. Although all the carboxylate groups coordinate to the $\text{Zn}(\text{II})$ trimers within the MOF, only half of the pyridyl units are engaged in coordinate bonding, with the other half exposed in the channels without any interaction with the framework metal ions. It was speculated that these free pyridyl groups were essential to the enantioselective catalytic activity of the MOF for the transesterification of 2,4-dinitrophenyl acetate. Treatment of the crystalline, chiral MOF in DMF with excess CH_3I at room temperature for 2 h was shown to convert the free pyridyl groups to *N*-methylpyridinium ions (Fig. 3), as indicated by ^1H NMR analysis. PXRD suggests the framework structure remains unchanged after the modification, whereas Raman spectroscopy confirms the presence of I_3^- counterions, which can be reversibly exchanged for other anions. The MOF can be similarly modified by other reagents such as 1-iodohexane. Interestingly, in contrast to the unmodified MOF, the alkylated MOF showed very little catalytic activity for the same transesterification reactions, supporting the importance of free pyridyl groups for catalysis and confirming the successful PSM on the MOF.

Recently, Cohen and co-workers initiated a systematic investigation on the covalent PSM of porous MOFs.^{56,58,59,70,87,104} IRMOF-3, which is the amino-substituted version of IRMOF-1, was chosen as a model system for the study of covalent PSM due to its highly porous, crystalline structure, and the presence of non-coordinating amino groups on the 2-aminobenzenedicarboxylate (NH_2 -BDC) linker.^{19,93} The initial study focused on acetylation by targeting the amino groups of IRMOF-3 with acetic anhydride (Fig. 4).⁵⁶ Activated IRMOF-3 crystals (treated by guest exchange and removal) were treated with dilute acetic anhydride solution in CDCl_3 under ambient conditions. The generation of an acetic acid byproduct in the mother liquor became apparent within hours, as determined by ^1H NMR, suggesting that the modification of the MOF was proceeding. No appreciable amount of NH_2 -BDC ligand was detected in the bulk solvent, corroborating the structural integrity of IRMOF-3 and indicating that the observed reactivity is *via* a heterogeneous reaction mechanism. ^1H NMR of the MOF crystals after

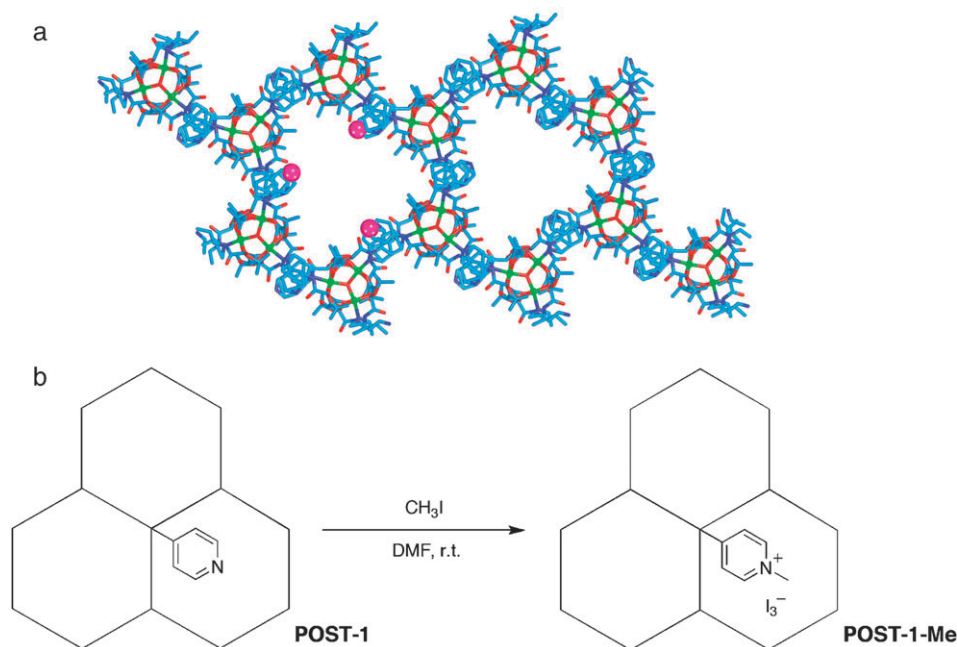


Fig. 3 Structural representations of POST-1 MOF (top); some sites of postsynthetic modification are highlighted with magenta spheres. Scheme of the postsynthetic modification (alkylation) of POST-1 (bottom). This example represents the earliest report of covalent postsynthetic modification of a MOF.

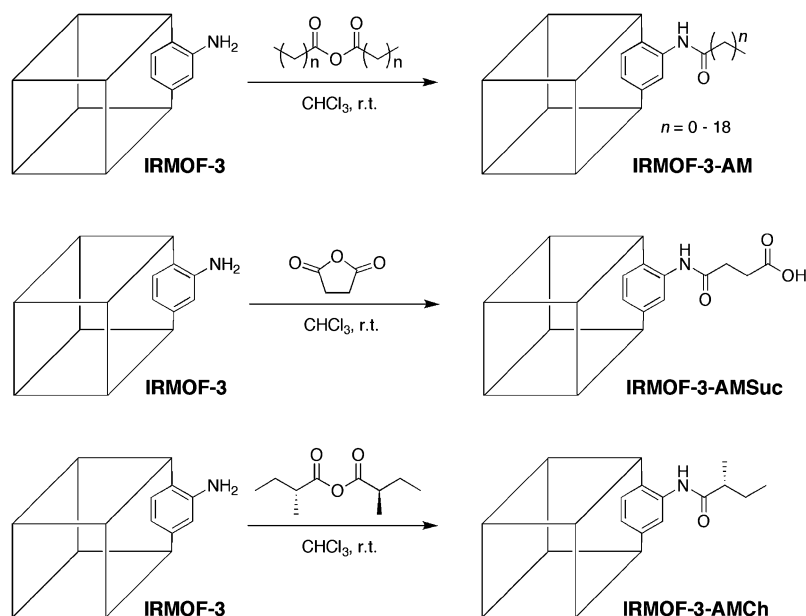


Fig. 4 Scheme of representative postsynthetic modification reactions with IRMOF-3 and various anhydrides that have been performed and characterized.

modification and digestion showed that the product, IRMOF-3-AM1, was comprised of >85% acetylated NH_2 -BDC ligand. This provided compelling evidence for the efficient, covalent modification on the MOF. PXRD and thermal gravimetric analysis (TGA) further revealed the well-retained crystallinity and thermal stability of IRMOF-3-AM1. More significantly, under optimized conditions, IRMOF-3 was quantitatively transformed into IRMOF-3-AM1 by acetic anhydride in a single-crystal-to-single-crystal fashion. The MOF structure

was confirmed by single-crystal X-ray diffraction, although the acetyl groups could not be located as a result of positional disorder over the four positions of the NH_2 -BDC ring and the weak diffraction quality of the crystals. However, subsequent electrospray ionization mass spectrometry (ESI-MS) analysis, performed on the single-crystals from which the framework structure was confirmed by X-ray diffraction, unambiguously showed the presence of the acetyl functionality in IRMOF-3-AM1 crystals.

Covalent transformation of IRMOF-3 was subsequently expanded to reactions with larger acid anhydrides.⁵⁸ A series of ten straight-chain alkyl anhydrides (with the general formula $O[CO(CH_2)_nCH_3]_2$, where $n = 1-18$) were used as the acylating reagents (Fig. 4). It was demonstrated that, similar to the case of acetic anhydride, IRMOF-3 can be readily modified by each of the linear alkyl anhydrides (corresponding products designated IRMOF-3-AM($n + 1$)). The degree of modification ranges from essentially quantitative (for $n \leq 5$) to less than 10% (for $n = 18$). Under similar conditions (*i.e.*, nearly identical reactant concentrations and reaction times), the degree of modification strictly follows an inverse correlation to the size of the anhydride. This trend of reactivity can be accounted for by a heterogeneous reaction mechanism where steric effects play an increasingly critical role as the size of reagents gets larger. Based on steric and solubility arguments, it was suggested that some of these MOFs, including IRMOF-3-AM9, -AM13, -AM16, and -AM19 in particular, would be extremely difficult, if not impossible, to prepare *via* traditional solvothermal methods. Although only partially modified, these new MOFs represent the first examples of polymeric metal–organic systems that are functionalized with long, hydrophobic alkyl chains. The porous structures of the ten modified IRMOF-3 samples were also evaluated in a systematic fashion. To more accurately describe the porosity of these materials, the concepts of ‘apparent surface area’ and ‘molar surface area’, which are surface area on a per mass and per mole basis, respectively, were described. Interestingly, when Brunauer–Emmett–Teller (BET) surface area expressed in either term was plotted *versus* alkyl chain length, a distinct “well-shaped” curve was observed, in which porosity of the MOF decreases from IRMOF-3-AM2 to -AM6 but increases from -AM7 to -AM19. Simple calculations taking into account both the percent conversion and the length of substituents reconcile this perplexing result by showing that the surface area of the modified MOFs correlate inversely with the number of additional atoms added by PSM per unit volume. This strongly suggests that the PSM approach is a highly viable route to fine-tuning MOF architectures and their pore structures.

In addition to the linear alkyl anhydrides, it was shown that IRMOF-3 can also react with cyclic anhydrides such as maleic anhydride and succinic anhydride.¹⁰⁴ ¹H NMR and ESI-MS data showed that the reactions with these two reagents under ambient conditions resulted in the open-form amide products and generated new MOFs decorated with free carboxylic groups (Fig. 4), consistent with the findings of a recent X-ray diffraction study.⁶⁴ Similarly, chiral anhydrides, such as (*R*)-2-methylbutanoic anhydride can modify IRMOF-3

quantitatively (Fig. 4), converting an achiral MOF to a chiral MOF material.¹⁰⁴ Interestingly, preliminary results suggested that a mixture of both open-form amide and closed-form imide products were obtained when IRMOF-3 was treated with (*S*)-(-)-2-acetoxysuccinic anhydride under similar conditions. This latter result is of significance as it demonstrates the feasibility and efficiency of generating multifunctional (*e.g.*, chiral and free-acid functionalized) MOFs using the PSM approach.

The substrate scope and reactivity of covalent PSM on IRMOF-3 were further investigated using isocyanates as the modifying reagents.⁵⁹ The prospect of generating urea derivatives of MOFs from these reactions was extremely attractive because ureas are known as an important family of organocatalysts¹⁰⁵ and anion-binding moieties.^{106–108} Eight different isocyanates with a wide range of substituents were examined for their reactivity with IRMOF-3. ¹H NMR and ESI-MS confirmed that the reactions indeed led to formation of the desired urea-functionalized MOFs, with percent conversions varying from ~99% (for trimethylsilylisocyanate) to essentially no reaction (for *tert*-butyl isocyanate), depending on the nature of the substituents. Surprisingly, the product of the reaction with TMS (TMS = trimethylsilyl) isocyanate was not the trimethylsilylurea, but rather a simple primary urea. This finding indicated that the TMS isocyanate was hydrolyzed, most likely by residual water, during or after the reaction with IRMOF-3 (Fig. 5).

Most recently, Cohen *et al.* have demonstrated the generality of their approach, by performing covalent PSM on two additional porous MOF topologies.⁷⁰ NH₂–BDC was found to readily substitute for BDC in the synthesis of two previously reported MOFs: the first is based on a square-grid layered structure linked by DABCO (1,4-diazabicyclo[2.2.2]octane) ligands,^{109,110} and the second is based on the work of Matzger, which employs both a BDC and BTB (4,4',4''-benzene-1,3,5-triyl-tribenzoate) ligand.²² These two MOFs, designated DMOF-1-NH₂ and UMCM-1-NH₂ (Fig. 6), respectively complement the work performed with IRMOF-3, as they differ in several ways: (a) their topologies are notably different, which places the NH₂–BDC groups in dissimilar local environments, (b) unlike IRMOF-3, they each use a co-ligand in addition to NH₂–BDC, and (c) they have significantly different surface areas when compared to IRMOF-3 (DMOF-1-NH₂ is lower at ~1500 m² g⁻¹; UMCM-1-NH₂ is greater at ~3900 m² g⁻¹). DMOF-1-NH₂ and UMCM-1-NH₂ were successfully modified with a series of linear and branched anhydrides in a manner analogous to that previously reported with IRMOF-3. The degree of conversion when using linear anhydrides generally followed the trend UMCM-1-NH₂ > IRMOF-3 > DMOF-1-NH₂. This

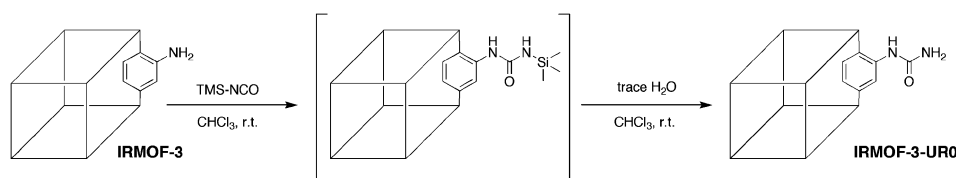


Fig. 5 Scheme of representative postsynthetic modification reaction of IRMOF-3 with trimethylsilylisocyanate that results in the formation of a primary urea group within the MOF upon hydrolysis.

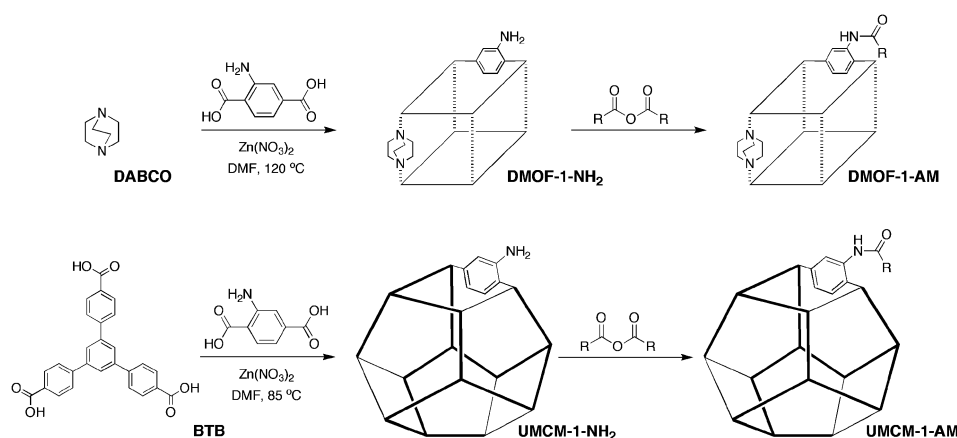


Fig. 6 Scheme for the synthesis, and representative postsynthetic modification reactions with anhydrides, of DMOF-1-NH₂ and UCMCM-1-NH₂.

correlates well with the relative BET surface areas for these three materials (*vide supra*), with the highest surface area material showing the highest conversion. Interestingly, with certain branched anhydrides (*e.g.* isobutyric anhydride), the modification of IRMOF-3 was more efficient than with UCMCM-1-NH₂; this was attributed to the different local environments of the NH₂-BDC ligands in these structures. This extensive study demonstrates several key points about covalent PSM: (a) NH₂-BDC can substitute for BDC in several MOFs thereby expanding the scope of PSM, (b) PSM is a broadly applicable approach to functionalizing MOFs, and (c) the topology of a MOF can affect the efficacy of PSM reactions.

Rosseinsky *et al.* reported an investigation that used both covalent and coordination chemistry to transform IRMOF-3 (Fig. 7).⁶² The initial modification was performed using salicylaldehyde as an imine condensation reagent. The reaction produced a partially modified MOF with ~13% conversion of the NH₂-BDC ligands, which was characterized by elemental analysis, TGA, PXRD, solid-state UV-Vis, and solid-state ¹H-¹³C CP-MAS NMR. These data confirmed that the resulting MOF contained the expected salicylidene moiety, which is an effective bidentate ligand for metal complexation. The metal binding ability of the modified IRMOF-3 was examined by treating the material with V(O)acac₂·H₂O (acac = acetylacetonate) in dry CH₂Cl₂ (or CD₂Cl₂) solutions. Solution phase ¹H NMR was indicative of the appearance of new resonances attributable to the byproducts (*i.e.*, acetylacetonate) within a few days. After repeated washing and subsequent evacuation, the modified MOF was characterized by combined elemental, TGA, and energy dispersive X-ray (EDX) analysis, which supported the presence of V(O)acac species coordinated to the salicylidene groups in an expected 1 : 1 molar ratio. A preliminary catalytic investigation revealed that the final modified MOF is active for the oxidation of

cyclohexene with tBuOOH, although both conversion and turnover frequency were relatively low, with a possible problem involving framework collapse. Nevertheless, the results from this study highlight the opportunities provided by the covalent PSM approach to produce materials that may be useful as solid-state catalysts.

It has been established that covalent PSM can be performed on IRMOF-3 in a single-crystal-to-single-crystal fashion.^{56,58,59,87}

Unfortunately, characterization by single-crystal X-ray diffraction has proven unsuccessful for directly identifying the newly introduced functional groups in modified IRMOF-3 samples due, in part, to positional disorder of the substituents.¹⁹ A study by Gamez and co-workers showed that, by synthesizing a less symmetric MOF, covalent PSM can be characterized by X-ray diffraction.⁶³ In this case, a 3D MOF with a triclinic symmetry, given the name MOF-LIC-1, was prepared from Gd(III) and NH₂-BDC. There exist three types of crystallographically independent, uncoordinated amino groups in this MOF. Upon treating with ethylisocyanate at 120 °C (which is above the boiling point for ethylisocyanate) for 1 h, one of the amino groups was found, by single-crystal X-ray diffraction, to have transformed into urethane functionalities (Fig. 8), presumably *via* a urea intermediate. Reaction with acetic acid under similar conditions led to formation of amide substituents on the same amino sites, which was also confirmed by X-ray diffraction. These modification results draw a clear contrast to those found in the IRMOF-3 system described above, where reactions with ethylisocyanate at room temperature gave rise to urea products and no detectable reactivity was observed for acetic acid. The different outcomes might be ascribed to the high temperature conditions involved in the modification of MOF-LIC-1.

The Fujita laboratory has also taken advantage of X-ray diffraction in several covalent PSM investigations.^{60,64} These

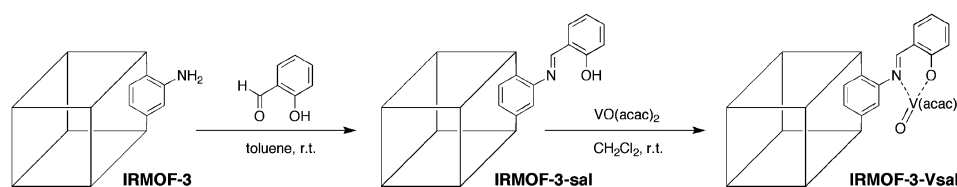


Fig. 7 Scheme of the postsynthetic modification of IRMOF-3 with salicylaldehyde, followed by metallation to create a solid-state catalyst.

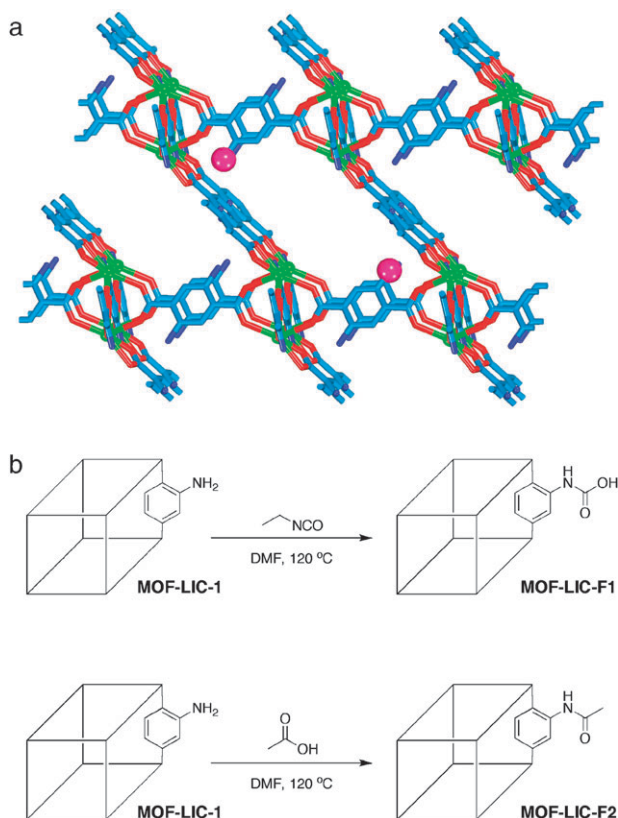


Fig. 8 Structural representation of MOF-LIC-1 (top); some sites of postsynthetic modification are highlighted with magenta spheres. Scheme of the postsynthetic modification reactions on MOF-LIC-1 that were confirmed by single-crystal X-ray diffraction studies (bottom).

studies focused on a 3D 2-fold interpenetrated porous MOF prepared from ZnI_2 and a TPT ligand (TPT = 2,4,6-tris-(4-pyridyl)triazine).¹¹¹ In contrast to the other covalent PSM studies described above, the modifications in the MOFs from Fujita target not the MOF itself, but rather immobilized guest molecules, namely triphenylene derivatives that are engaged in strong π - π interactions with the TPT ligands of the MOF. In their initial report, it was shown that the 2-aminotriphenylene guest inside the MOF can undergo imine condensation upon treating with acetaldehyde, hexanal, and *p*-anisaldehyde (Fig. 9).⁶⁰ Remarkably, the single-crystal-to-single-crystal transformation of the modifications facilitated the direct observation, by X-ray diffraction, of the highly unstable imine product from the reaction with acetaldehyde. Subsequent studies confirmed that, within the MOF lattice, modification of the 3-aminotriphenylene guest with acetic anhydride, octanoic anhydride, phenyl isocyanate, succinic anhydride, and maleic anhydride, and modification of a 3-formyltriphenylene guest with aniline (Fig. 9) could be characterized by single-crystal X-ray diffraction.⁶⁴ These exciting studies provide unambiguous confirmation and validation for the PSM approach to MOF modification.

Recently, Yaghi *et al.* prepared a sodalite-like zeolitic imidazolate framework (ZIF) from Zn(II) and imidazolate-2-carboxyaldehyde that was amenable to PSM (ZIF-90).⁶⁷ The presence of the free aldehyde functionality inside the

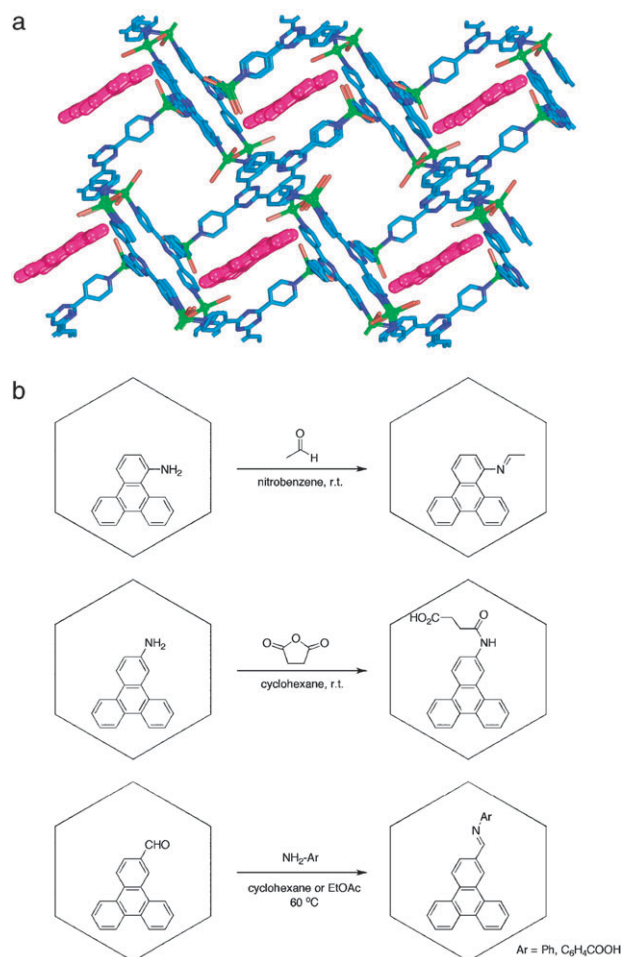


Fig. 9 Structural representation of a MOF based on Zn(II) and the TPT ligand (top); the immobilized triphenylene guests where postsynthetic modification occurs are highlighted in magenta. Scheme of some of the postsynthetic modification reactions on these MOFs that were confirmed by single-crystal X-ray diffraction studies (bottom).

framework permits the covalent modification of ZIF-90 with ethanolamine via an imine condensation (Fig. 10). Quantitative conversion to the imine was complete within three hours as verified by ^{13}C CP-MAS NMR and FTIR. The high crystallinity of the imine-functionalized ZIF-92 was maintained as evidenced by the PXRD pattern. N_2 adsorption measurements revealed an extremely low uptake, presumably due to the severe constriction of the pore aperture as a result of modification. The unusual thermal and chemical stability of ZIF-90 allowed the framework to be modified under relatively harsh reaction conditions. This was demonstrated by the reduction of the aldehyde to an alcohol functionality achieved by reacting ZIF-90 with NaBH_4 in methanol at 60 °C for 24 h. Solid-state ^{13}C CP-MAS NMR, solution ^1H NMR, and ESI-MS all support the transformation of aldehyde into alcohol (Fig. 10). It is worth noting that porosity of the ZIF-91 was well maintained with only a slight decrease in surface area.

Shortly after the report on the PSM of ZIF-90, a second study appeared that incorporated a reactive aldehyde 'tag' into a MOF structure.⁶⁸ Burrows *et al.*⁶⁸ synthesized an analogue

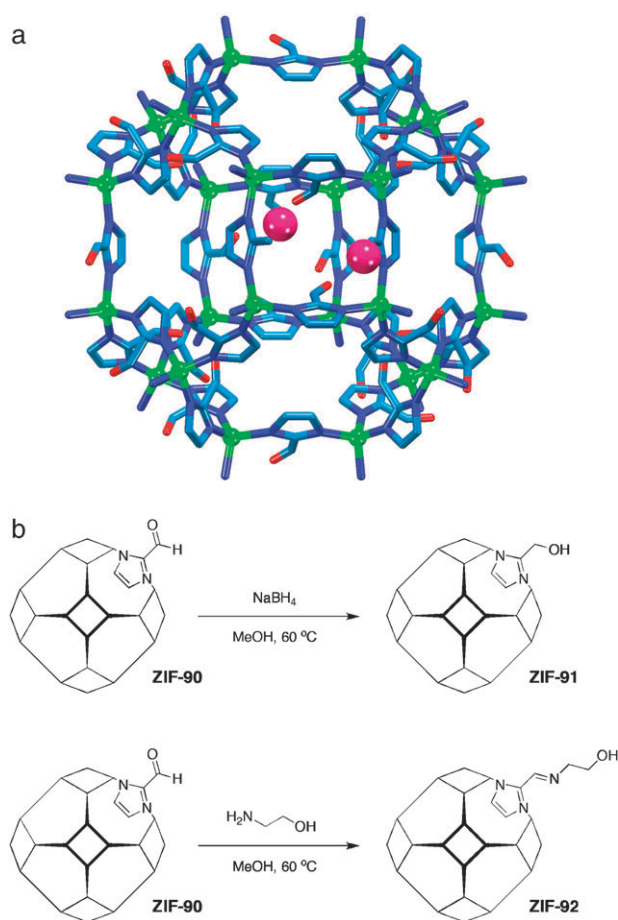


Fig. 10 Structural representation of ZIF-90 (top); some sites of postsynthetic modification are highlighted with magenta spheres. Scheme of the postsynthetic modification reactions described for ZIF-90 (bottom).

of 4,4'-biphenyldicarboxylate (bpdc) that included a single aldehyde group at the 2-position. This was combined with zinc(II) nitrate to obtain a doubly-interpenetrated MOF that was structurally similar to IRMOF-9.¹⁹ In this case the MOF was treated with a hydrazine to produce the expected hydrazone. The use of 2,4-dinitrophenylhydrazine (DPH) was selected as the intense color of the resultant hydrazone allowed for visual confirmation of the PSM reaction.

Two studies have been recently reported on the use of 'click' chemistry for the PSM of MOFs.^{66,69} The report by Hupp and co-workers is particularly interesting as it focuses on the covalent surface modification of a MOF using click reactions.⁶⁶ The parent MOF material in the Hupp study was based on a 2-fold interpenetrated jungle-gym type lattice constructed from dimeric Zn(II) paddle-wheel SBU, 2,6-naphthalenedicarboxylate (NDC), and bis(pyridyl) ligand **L1** (**L1** = 3-[(trimethylsilyl)ethynyl]-4-[2-(4-pyridinyl)ethenyl]pyridine). The silyl-protected alkyne functionality provides a suitable platform for covalent PSM. The MOF was initially treated with tetrabutylammonium fluoride in a THF solution to desilylate the surface. The deprotection process was confirmed by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry. Ethidium bromide monoazide was then chosen as the group to attach to the surface terminal

alkynes based on the Cu(I)-catalyzed click reaction.¹¹² The fluorescence of the azide allowed for direct visualization of the modification. Indeed, confocal microscopy imaging/depth profiling confirmed that the modification occurred exclusively on the surface. Further attempts to covalently 'click' the hydrophilic polyethylene glycol (PEG) chains onto the MOF surface were also successful. The increased hydrophilicity of the modified MOF was apparent from wettability tests and contact angle measurements. To our knowledge, this study represents the first example of surface-directed PSM of MOFs.

3.4 Tandem PSM of MOFs

The sufficient chemical and thermal stability of MOFs afforded by their robust structures means that it is possible to perform more than a single chemical reaction on the same MOF sample. The ease of separating small-molecule reagents from MOF crystals allows for facile control on the PSM process and hence the degree of modification by any one reagent. In this context, Cohen *et al.* generalized two post-synthetic strategies that, although conceptually distinct, similarly permit step-wise "tandem" modification of MOFs.⁸⁷ In strategy I, a MOF was partially modified with one reagent and then subsequently modified with a second reagent on the remaining reactive sites. In strategy II, a MOF was first modified with a reagent that contains a latent functional group that upon introduction into the MOF, is subject to further transformation with a second reagent. Whereas strategy II enables transformation cascades somewhat similar to those typically seen in organic synthesis, strategy I provides a simple, yet controllable approach to MOFs with multiple functional groups, a class of materials that would be challenging to prepare by conventional methods.

To examine the synthetic feasibility of strategy I, IRMOF-3 was consecutively modified with two different anhydrides, namely, crotonic anhydride and acetic anhydride (Fig. 11). Initial reactions with crotonic anhydride under careful control of reaction time and reactant concentration led to the generation of a series of partially modified MOFs with an increasing degree of acylation. Such controlled modification of MOFs is by itself novel and deserves further attention as it immediately leads to new MOF structures with two distinct functionalities (*i.e.* amine and amide). The partially converted IRMOF-3 samples were further treated with acetic anhydride until the remaining amino groups were almost completely acylated. The presence of two different sets of signals in the ¹H NMR spectra of the digested products strongly suggested that IRMOF-3 was indeed modulated by these two reagents. Negative-mode ESI-MS performed on individual single-crystals confirmed that the resulting MOFs contain both substituents within a single framework and are not simply bulk mixtures (*i.e.* conglomerates) of monofunctionalized MOFs.

Tandem modification strategy II was also tested on IRMOF-3. Single-crystals of IRMOF-3 were treated with crotonic anhydride to yield a nearly fully converted, olefin-functionalized MOF. The newly incorporated alkenyl groups were then subject to bromination reactions with Br₂ in the dark. The reaction time and reactant concentration were carefully managed to allow a series of new MOFs with increasing degree

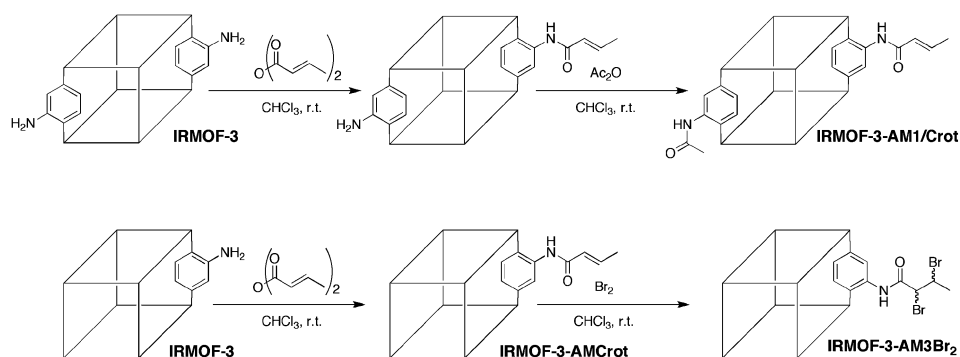


Fig. 11 Scheme of tandem postsynthetic modification reactions according to strategy I (top) and strategy II (bottom) with IRMOF-3.

of bromination to be isolated at different stages of the reaction. ^1H NMR spectra and ESI-MS supported the formation of the expected vicinal dibromides (Fig. 11). The final products were also characterized by X-ray diffraction, TGA, and gas sorption. N_2 isotherms revealed that, while the BET surface area decreases as degree of bromination increases, the overall microporosity was essentially maintained for all the samples.

The two tandem modification methods thus each exemplify a highly efficient and controllable approach to the functionalization of MOFs. Although only amide-coupling reactions and two different anhydrides were demonstrated for strategy I, it is not difficult to envision that the same principle could be easily applied to a wide variety of other types of reactions and reagents as well as much more complex combinations. In principle, it is also feasible to combine both strategies in the same MOF. This will in turn give rise to an even larger pool of diverse MOF structures. Therefore, the tandem modification approaches might be considered as a viable route to the solid-state version of diversity-oriented synthesis (DOS).¹¹³

3.5 Protonation as PSM of MOFs

While amino and carbonyl groups are particularly attractive in the context of covalent modification due to their versatile reactivity, PSM of MOFs based on very simple reactions have also been demonstrated. Indeed, protonation was found to be an effective and straightforward way for modifying the properties of some MOF structures. Zhou *et al.* discovered that adding acids HX ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) to a 3D mesoporous MOF greatly improves its framework stability.⁵⁷ The MOF was prepared from a trigonal TATAB ligand (TATAB = 4,4',4''-s-triazine-1,3,5-triyltri-*p*-aminobenzoate) and dimeric Cu(II) paddle-wheel SBU. It was believed that treatment with the acids led to protonation of the amino groups in the TATAB ligand and afforded ionic frameworks. The protonated frameworks showed significantly higher thermal stability than the unmodified analogue, as indicated by TGA analyses. Although no further characterization on the modified MOFs was provided, nitrogen sorption measurements on the protonated samples revealed a typical type IV behavior, indicating the mesoporous nature of these materials. Rosseinsky *et al.* also used a postsynthetic approach to generate solid Brønsted acid sites in a 3D chiral MOF.⁶¹ The amino acid-based starting MOF, Cu(L-asp)bpe_{0.5}(guest) (L-asp = L-aspartate; bpe = 1,2-bis(4-pyridyl)ethylene), was suspended in anhydrous Et_2O and treated with

HCl, which led to the isolation of the protonated phase Cu(L-asp)bpe_{0.5}(HCl)(H₂O). The composition of this new phase was confirmed by EDX and a combination of micro- and thermogravimetric analysis. IR spectroscopy supports the protonation on the carboxylate groups and the generation of COOH moieties. The catalytic activity of the protonated MOF was tested for the methanolysis of *rac*-propylene oxide, which showed a decent yield and turnover frequency. The enantioselectivity of the catalyst was subsequently examined in the methanolysis of *cis*-2,3-epoxybutane. Although only moderate ee values ($\leq 17\%$) were obtained in this case, the significance of using postsynthetic protonation to generate catalytically active MOF materials is still an important observation.

3.6 PSM of MOFs by doping with metals

Recent simulation studies suggest that doping lithium in MOFs will greatly improve H_2 uptake capacity of the materials near ambient conditions.^{114,115} Inspired, in part, by these theoretical predictions, experimental endeavors to incorporate alkali metals or metal cations into MOFs have been demonstrated.^{78,79} A 'spillover' technique that involves loading of platinum on active carbon (Pt/AC) has been applied to MOF materials.^{80–83} Efforts to impregnate noble metals, including palladium,⁸⁴ ruthenium,⁸⁵ and platinum⁸⁶ inside MOFs have also been reported.

Mulfort and Hupp found that reductively doping a mixed ligand MOF with Li(I) substantially enhances its nitrogen and hydrogen gas uptake.⁷⁸ The starting MOF contains 2-fold interpenetrated networks derived from dimeric Zn(II) paddle-wheel SBUs and two types of bridging ligands, NDC and diPyNI (diPyNI = *N,N'*-di-(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide), the latter of which is known to be redox active.^{116,117} Immediately upon exposure to Li metal in DMF, the MOF changed color from bright yellow to brown, consistent with the color change observed in solutions of the diPyNI ligand alone. PXRD and TGA confirmed the structural integrity of the MOF even upon reduction and subsequent oxidation by exposure to air. Inductively coupled plasma (ICP) methods indicated that loading of lithium at ca. 5 mol% appears to be optimal for improving gas adsorption. Interestingly, the N_2 sorption isotherm of the Li(I)-modified MOF exhibits a large hysteresis loop at $P/P_0 \approx 0.01–0.5$, and the capacity at 1 atm is almost double that of the undoped MOF. Remarkable enhancements were also seen for H_2 sorption. At 77 K and 1 atm, the H_2 capacity of the modified MOF

(1.63 wt%) is nearly double that of the starting material (0.93 wt%). In addition, the isosteric heat of adsorption is also substantially greater over the entire loading range upon modification. It was proposed that framework displacement and/or enhanced ligand polarizability, as a result of reductive doping, largely accounts for the dramatic changes in gas sorption properties of the material. The study was further extended to include two other alkali metal cations, Na(I) and K(I), using metal naphthalenides as the reductive precursors.⁷⁹ At low-pressure and temperature, the reduced and doped materials exhibited enhanced H₂ uptake—up to 65% higher than the neutral framework. Notably, at similar doping levels, while H₂ binding is strongest with Li(I) and decreases as Li(I) > Na(I) > K(I), the uptake is highest with K(I) and decreases as K(I) > Na(I) > Li(I).

In a separate study, Li and Yang demonstrated that MOFs treated with a catalytic amount of Pt/AC show significantly enhanced hydrogen storage capacity *via* a spillover mechanism.^{80–83} A series of related studies employed porous MOFs as matrixes to stabilize the nanoparticle forms of catalytically active metals.^{84–86} From the viewpoint of MOF materials, these approaches can be justifiably considered as a form of PSM. However, they are beyond the scope of this review and will therefore not be discussed in more detail.

4. Concluding remarks

As evidenced by this themed edition of *Chemical Society Reviews*, MOFs have become a topic of central importance to inorganic and materials chemistry. Many studies on MOFs are flourishing with exciting new findings in the areas of gas sorption, catalysis, and simply the discovery of new materials and structure types. The concept of PSM was introduced at the inception of MOF materials. PSM was first evidenced as guest exchange processes, with encapsulated solvents, counterions, and the like being transported in and out of the open space within these frameworks. Only recently has the ability to chemically modify the framework itself, at either the organic struts or the metal ion nodes, become a prominent topic in MOF chemistry. Based on the tremendous number of PSM reports described within the last ~18 months, it is anticipated that the role of PSM in MOFs, particularly those involving chemical modification of the organic linkers, will grow substantially in the near future. The ability to develop heterogeneous catalysts, based on either organocatalytic or transition metal-based systems, is one area where PSM is likely to make important contributions. The capacity to systematically modify MOFs with various reagents will allow for the elucidation of structure–function relationships relevant to improving the chemical stability and gas sorption capacity of MOFs. Similarly, the surface functionalization of MOFs or MOF nanoparticles will allow for stabilization of these materials and the possibility of conjugation to biomolecules for use in biomedical and biotechnology applications. Indeed, the demonstrated ability to incorporate more than one functional modification onto a single MOF, *via* a tandem modification approach, bodes well for the use of MOFs as platforms for multifunctional, biocompatible nanoparticles. Ultimately, covalent PSM of MOFs will provide access to an otherwise

inaccessible class of MOF materials, which we anticipate will have a prominent and lasting impact on the future of these important compounds.

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