

The Postsynthetic Renaissance in Porous Solids

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ABSTRACT: Metal–organic frameworks (MOFs) have rapidly grown into a major area of chemical research over the last two decades. MOFs represent the development of covalent chemistry “beyond the molecule” and into extended structures. MOFs also present an unprecedented scaffold for performing heterogeneous organic transformations in the solid state, allowing for deliberate and precise preparation of new materials. The development of these transformations has given rise to the “postsynthetic renaissance”, a suite of methods by which these materials can be transformed in a single-crystal-to-single-crystal manner. Postsynthetic modification, postsynthetic deprotection, postsynthetic exchange, postsynthetic insertion, and postsynthetic polymerization have exploited the unique features of both the organic and inorganic components of MOFs to create crystalline, porous solids of unique complexity and functionality.

INTRODUCTION

Metal–organic frameworks (MOFs) have exploded as a new area of materials research in the last two decades. MOFs are hybrid materials constructed from a combination of organic ligands and metal ions, the latter of which are often found as metal clusters within the framework, often termed secondary building units (SBUs). The inherently low density and high surface area of many MOFs, along with their crystallinity, has made them intriguing materials for a wide range of potential technologies. A large number of reviews have been published on various aspects of MOF chemistry, including a recent Perspective in this journal.¹

Beyond the crystallinity and porosity inherent to MOFs, the hybrid nature of these materials offers special opportunities when compared with many other solid-state materials. Unlike materials that are predominantly (if not exclusively) composed of only organic or inorganic building blocks, MOFs merge these two components together. Particularly with respect to conventional inorganic materials, the organic constituent of MOFs offers special opportunities for tuning and functionalization in ways not accessible for other inorganic materials.

Taking advantage of the organic component of MOFs has allowed the development of a number of postsynthetic methods that have introduced rich chemical functionality into MOFs.² “Postsynthetic” refers to the fact that these reactions are performed after the MOF has already been formed/assembled. The original use of the term “postsynthetic modification” (PSM)³ was made in reference to the biological process of post-translational modification, whereby as-synthesized proteins are covalently modified with new chemical functionality. Postsynthetic methods most often associated with covalent

modification of the ligand struts include postsynthetic modification (PSM), postsynthetic deprotection (PSD), and, more recently, postsynthetic polymerization (PSP) (Figure 1).

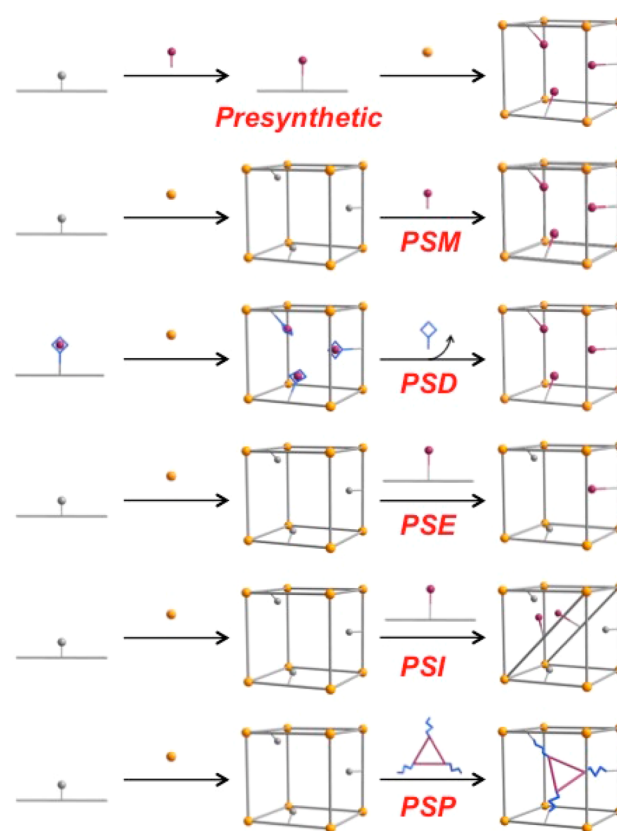


Figure 1. Schematic depiction of presynthetic modification, postsynthetic modification (PSM), postsynthetic deprotection (PSD), postsynthetic exchange (PSE), postsynthetic insertion (PSI), and postsynthetic polymerization (PSP). SBUs are represented as gold spheres, and ligand struts are represented by gray rods.

Abundant reviews of the use of these methods with MOFs are available, including several from the author.^{2,4,5} This Perspective provides an update on each of these topics as separate sections, except for PSD. Although it is an important method in the postsynthetic toolbox, new reports of PSD reactions are rather limited compared with the rapid development of other postsynthetic methods, but PSD remains an area for further discovery and development. Similarly, there is a growing body of literature on postsynthetic rearrangement reactions, which can be generally categorized as lattice

Received: October 28, 2016

Published: January 24, 2017

rearrangements^{6–9} or rearrangements of functional groups on the organic linkers,^{10–14} the latter of which has largely consisted of thermally driven ligand rearrangement reactions (e.g., Claisen rearrangements). Again, these rearrangement reactions represent a burgeoning area of research and an opportunity for additional discovery, but they will not be explicitly discussed in this Perspective.

In addition to exploiting the organic component of MOFs, the kinetically labile nature of metal–ligand coordination bonds in MOFs (compared with covalent bonds in organic materials) has also enabled another set of postsynthetic methods (Figure 1). The ability to shift chemical equilibrium has allowed for the swapping of metal or ligand components in and out of MOFs in a process known as postsynthetic exchange (PSE) or solvent-assisted linker exchange (SALE). More recently, the ability to add metal ions or ligands to existing frameworks has also been reported, in a process termed here as postsynthetic insertion (PSI) or solvent-assisted linker incorporation (SALI). Several reviews of these exchange reactions are also available.^{15–17} In this Perspective, a brief history of these postsynthetic reactions is provided, followed by recent, state-of-the-art advancements and selected examples of postsynthetic transformations of MOFs.

■ PREDICTION AND DEMONSTRATION

The concept of PSM was outlined more than 25 years ago by Robson,¹⁸ with the most visionary of statements being, “Relatively unimpeded migration of species throughout the lattice [MOF] may allow chemical functionalization [PSM] of the rods [ligands] subsequent to the construction of the framework. The introduction of one or more catalytic centers per rod may thereby be straightforward. The very open structure should again ensure both easy access of substrates to catalytic sites and ready release of catalytic products.” Here Robson unambiguously states the concept of PSM as well as the use of PSM to place catalytic sites in MOFs, which indeed has matured into a rich area of research (vide infra). It is worth noting that the concept of postsynthetic reactions in other materials has also been explored. For example, cation exchange (i.e., PSE) in colloidal semiconductor nanocrystals has been demonstrated and is an important synthetic method for these materials,¹⁹ just as in MOFs.

Robson’s prediction of PSM predates proof-of-concept experiments by almost a decade. Starting in 1999, Lee and Kim separately provided experimental evidence for PSM via acetylation²⁰ and alkylation²¹ reactions in MOFs, respectively. For the next ~7 years, the field and concept of PSM was relatively dormant, even as MOF chemistry was exploding with activity. The most notable exception was the work of Lin, who had been using postsynthetic metalation to make MOF catalysts.²² However, starting in 2007, a number of publications appeared in rapid succession demonstrating a variety of covalent postsynthetic modifications to MOF ligands. To the best of the author’s knowledge, the first two reports during this renaissance in PSM were by Cohen³ and Fujita.²³ It is important to note that the Cohen report concerned direct PSM of a MOF ligand component,³ while the example from Fujita involved modification of a strongly bound guest molecule within the framework.²³ Although the modification reported by Fujita was on a guest that was not formally part of the MOF, the study demonstrates many of the core principles and concepts of PSM and hence is cited as an important contribution to the early findings on PSM. Reports by many

groups soon followed, including Yaghi,^{24,25} Long,²⁶ Burrows,²⁷ Hupp,²⁸ Reedijk,²⁹ and others. As a predecessor to his “molecular sponge” concept,³⁰ Fujita even reported the crystallographic characterization of an unstable hemiaminal intermediate formed by PSM,³¹ providing added significance to PSM. Within approximately three years, PSM had become an active area of study and a widely used tool. The first comprehensive review of the subject, by Wang and Cohen, appeared in 2009.⁵

Just as with solution-phase synthetic chemistry, the yields of postsynthetic reactions can vary depending on the reactivity of the components, steric factors, and the like. More importantly, when discussing postsynthetic reactions, it is critical that the reactions proceed in a single-crystal-to-single-crystal (SCSC) fashion to be considered valuable transformations. Only modifications that preserve the crystallinity, porosity, and overall structural integrity of the MOF are considered true postsynthetic reactions. Although many postsynthetic reactions do result in a reduction of surface area,³² this is the result of pore filling as opposed to pore collapse. Many transformations are hypothetically possible on MOFs, but preservation of the MOF structure during the reaction is essential. If the MOF loses its structure, crystallinity, and porosity after a postsynthetic reaction, then the material is no longer useful, as the reaction has resulted in degradation of the framework. In this regard, postsynthetic reactions share parallels with bioorthogonal chemistry,³³ where the latter requires a selective chemical transformation in a complex and delicate environment that does not result in harm to the biological milieu or the target of interest. Although few postsynthetic reactions have been directly demonstrated to occur in a true SCSC manner, the characterization data obtained on the materials discussed in this Perspective at least suggest that the reactions occur in a SCSC manner and that the resulting MOFs have the expected physical and chemical characteristics.

■ POSTSYNTHETIC MODIFICATION

Once a topic of fundamental exploration, PSM of MOFs has now become a commonplace tool for the synthesis and derivatization of MOFs. Research groups from around the world routinely use PSM to add a diverse range of functional groups to these materials, enhancing their physical properties or endowing them with new chemical properties. A summary of the many reactions that have been reported will not be provided here, but this topic has been reviewed elsewhere,^{2,4,5} and a recent Perspective on MOFs contains an excellent summary of covalent PSM reactions.¹ Needless to say, PSM has become ubiquitous in MOF chemistry and is used for many purposes, from making MOFs more robust against chemical insults (e.g., moisture) to endowing them with new physical properties to preparing catalytic MOFs. With respect to physical properties, in one recent example, Shustova and co-workers used PSM to introduce the 4-hydroxybenzylidene imidazolidinone (HBI) chromophore,³⁴ found in green fluorescent protein (GFP), into MOFs. These studies showed that the MOF matrix can recapitulate the β -barrel of GFP, generating highly emissive HBI fluorophores.³⁵

Catalysis continues to be a very rich subject for MOFs, and one where PSM has played a prominent role. Indeed, Robson was prophetic in his vision of the role MOFs and PSM would play in catalysis, stating (in addition to the earlier quote, vide supra) that “they [MOFs] may, after appropriate functionalization of the rods [ligands], provide tailor-made materials for the

heterogeneous catalysis of a wide range of transformations.³⁶ Indeed, PSM has been frequently used to derivatize both the ligands and SBUs of MOFs to generate molecular single-site-type catalysts bound within the MOF lattice. These types of reactions were investigated in the early days of the PSM renaissance,³⁷ and they continue to be popular, with numerous examples appearing in the contemporary literature. A number of important ligands, such as β -diketiminato (NacNac)³⁸ and pincer ligands,³⁹ have recently been introduced into MOFs by PSM to produce catalytic materials.

The use of PSM reactions, particularly for the metalation of MOF ligands, can be very effective compared with other synthetic approaches. In the case of kinetically labile metal complexes, PSM is the obvious choice, as these complexes are unlikely to stay intact during solvothermal or PSE reactions. However, even for some kinetically inert metal complexes, PSM has proven to be quite efficient. For example, numerous studies on incorporating polypyridyl metal complexes into MOFs have been reported.^{34,40} Specifically, several laboratories have examined the incorporation of polypyridyl Ru²⁺ complexes and related cyclometalated Ir³⁺ complexes into frameworks such as those of the UiO-67 family.^{41–43} In our efforts to prepare Ru–polypyridyl MOFs for use as photocatalysts, we compared direct synthesis, PSM, and PSE approaches and found the PSM approach to be superior (Figure 2).⁴⁴ Similarly,

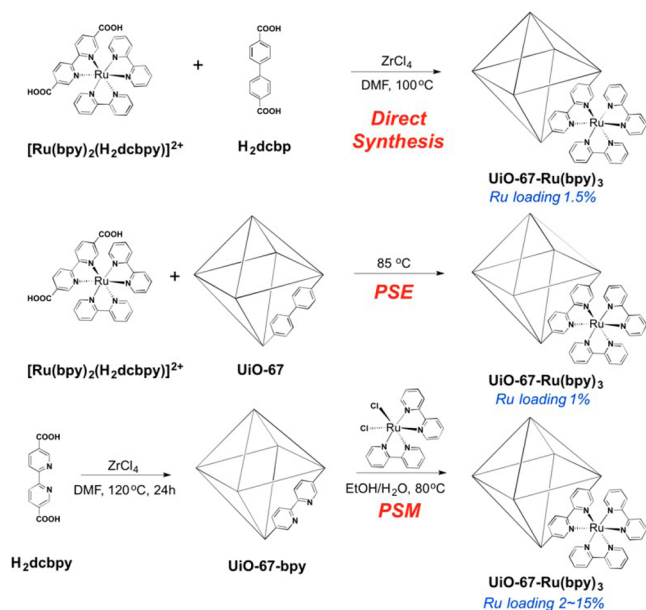


Figure 2. Preparation of UiO-67-Ru(bpy)₃ using different synthetic approaches shows PSM to be the preferred method for achieving high loading. Adapted from ref 44.

for the preparation of Ir-cyclometalated MOFs, PSM was the preferred method.⁴⁵ Although PSM of ligand sites with labile metal ions has been known for some time,³⁷ these recent examples show that PSM may often be the method of choice for the formation of even more complex and kinetically inert metal complexes as well.

Representing the state of the art in PSM for catalysis, an impressive example was recently reported by Toste and Yaghi.⁴⁶ In that study, MOF-74(Mg)-III was subjected to repeated rounds of peptide coupling to obtain what the authors called “enzyme-like complexity”. MOF-74(Mg)-III is an extended, isorecticular derivative of the popular MOF-74

system.^{47,48} A mixed-ligand version of MOF-74(Mg)-III, using 3,3′-dihydroxy-(1,1′:4′,1′′-terphenyl)-4,4′′-dicarboxylic acid and a Boc-protected amine derivative, resulted in a MOF with massive 25 Å one-dimensional channels that can accommodate sterically demanding PSM reactions (Figure 3). It was determined that having only 40% of the Boc-protected amine ligands was optimal for PSM derivatization.

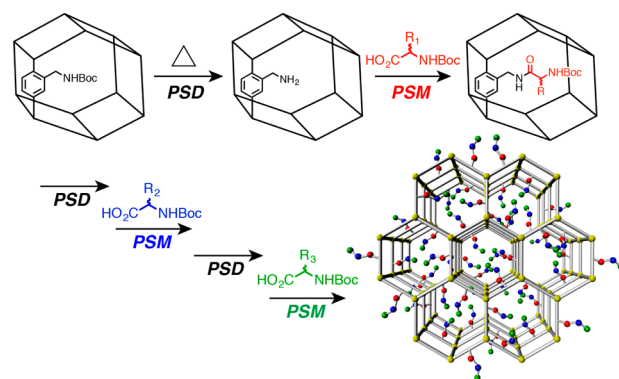


Figure 3. Scheme of multistep PSM/PSD in a MOF-74(Mg)-III derivative to generate MOFs bearing polypeptides (amino acids represented by colored spheres) with enzyme-like catalysis. By repeated rounds of PSM and PSD, polypeptide chains were constructed within the pores of this MOF. Adapted from ref 46. Copyright 2016 American Chemical Society.

In a manner resembling solid-phase peptide synthesis, the MOF was subjected to a series of deprotection (Boc removal via microwave heating, PSD) and peptide coupling reactions. In all, the MOF was subjected to as many as seven sequential PSM reactions (several of which were PSD reactions, i.e., removal of Boc protecting groups; Figure 3) to generate tripeptides within the large one-dimensional pores (Figure 3).⁴⁶ This was a record-setting number of consecutive PSM/PSD reactions on a MOF, exceeding the prior record of four transformations on a single framework.⁴⁹ One limitation of the reported work was that the yield of the PSD steps (i.e., Boc removal) was only ~76%, which upon multiple reaction cycles (Figure 3) resulted in a heterogeneous mixture of peptides within the MOF. Nonetheless, these PSM transformations were then used to install two different tripeptides into MOF-74(Mg)-III. The first, MOF-Ala-Gly-Pro-NH₂ (loaded onto 20% of the MOF struts) was shown to be a competent catalyst for the α -chlorination of butyraldehyde. This was predicted on the basis of the ability of proline derivatives to catalyze this reaction. The MOF-based catalyst showed improved enantioselectivity compared with a homogeneous analogue (20% vs 2% ee), presumably due to confinement effects within the MOF pores. The second peptide, MOF-Asp-His-Cys-NH₂ (loaded onto 10% of the MOF struts) was modeled on a known protease, and indeed, the MOF demonstrated low but measurable protease activity on a model pentapeptide substrate (5% conversion after 24 h at room temperature).⁴⁶ With other studies of biomolecules being coupled to MOFs via PSM,⁵⁰ it is clear that these kind of efforts represent what is to come for PSM.

■ POSTSYNTHETIC EXCHANGE

Perhaps more than any other subtopic within the realm of postsynthetic methods, the exploration of postsynthetic exchange (PSE) within MOFs (Figure 1) has gathered the

greatest interest. Playing on the kinetically dynamic nature of many metal–ligand bonds, PSE involves the exchange of either metal or ligand components within a preformed MOF lattice with alternative components (either metal ions or ligands) from solution. Exchange of metal ion and ligand components of MOFs via PSE have been reported, with early examples described by the groups of Kim⁵¹ and Choe,⁵² respectively. Recent examples show that both the ligand and metal components can be exchanged in the same MOF.⁵³

Metal ion exchange, either at the SBUs or appended to other sites within the framework (e.g., on binding sites within the ligand struts), has been successfully demonstrated, and several recent reviews of the subject are available.^{15,16} Importantly, Dincă and co-workers have initiated mechanistic studies to better understand the metal ion exchange process in PSE.^{54–56} These investigations will certainly prove valuable for gaining even greater control over these processes, and similar studies of ligand-based PSE are needed.⁵⁷

With respect to ligand exchange, which is also referred to as solvent-assisted linker exchange (SALE, an acronym coined by Farha and Hupp¹⁷), many impressive examples have been described, including both exchange of ligands and addition of new ligands (the latter of which is technically not an exchange reaction; *vide infra*). In this section, some recent advancements in PSE are highlighted.

Work from our own laboratory in 2013 helped to establish the synthetic power of PSE. In a collaborative effort with the Ott group (Uppsala University, Sweden),⁵⁸ our laboratories sought to incorporate a synthetic mimetic of the metalloenzyme hydrogenase within the confines of a MOF. Hydrogenase is an important enzyme for advancing technologies relevant to renewable energy, as the enzyme catalyzes the reversible two-electron reduction of protons to H₂. The goal was to immobilize a functional mimic of this enzyme into a MOF (Figure 4) in order to produce a more robust and active

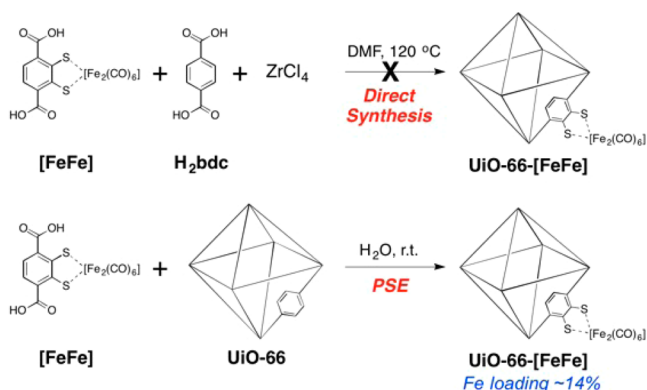


Figure 4. Incorporation of a hydrogenase model catalyst into UiO-66 using PSE. Attempts to include the model catalyst using direct solvothermal synthesis were not successful because the [FeFe] complex was not sufficiently stable at elevated temperatures.

catalyst. The model catalyst, a diiron carbonyl complex with a bridging thiocatecholato ligand,⁵⁹ was integrated into the UiO-66 MOF using a modified thiocatecholato ligand. Several strategies were examined, as depicted in Figure 4. Direct solvothermal synthesis failed, as the carbonyl complex proved unstable at elevated temperatures, and PSM using a diiron carbonyl precursor was also ineffective. Other examples of postsynthetic metalation of the thiocatecholato and related

ligands have since proven successful,^{60,61} but ultimately, in this case it was found that PSE was the best method for incorporating the catalyst into UiO-66. By simple immersion of UiO-66 in an aqueous solution of the catalyst at room temperature for 24 h, PSE resulted in a material with 14% incorporation of the catalyst via displacement of the native 1,4-benzenedicarboxylate (bdc²⁻) ligands. The catalyst was characterized spectroscopically within UiO-66, which unambiguously demonstrated that the diiron cluster remained intact.⁵⁸ Indeed, the MOF-immobilized catalyst proved to be more active than the corresponding molecular species. This work was an important, relatively early demonstration that complex, fragile, and highly functionalized building units could be incorporated into MOFs by PSE.

Many other exceptional advancements in PSE have been made in recent years. One interesting example is related to the original report by Choe et al.,⁵² where ligands were replaced in a stepwise manner in a layered MOF structure. Rosi and co-workers examined the sequential replacement of functionalized dicarboxylate ligands in bMOF-100 (bMOF = bioMOF).⁶² bMOF-100 is a mesoporous material containing clusters of Zn²⁺ ions and adeninate ligands connected through trimeric “bundles” of 4,4'-biphenyldicarboxylate (bpdc²⁻).^{63,64} Rosi and co-workers showed that PSE is capable of “extending” this MOF structure in all three dimensions by the introduction of elongated ligands that replace the native bpdc²⁻.⁶⁵

In a related study, it was also shown that three different bpdc²⁻ derivatives, containing a pendant formyl (F-bpdc²⁻), amine (NH₂-bpdc²⁻), or azide (N₃-bpdc²⁻), could be introduced into the framework.⁶² Importantly, the authors noted that the exchange kinetics and PSE yield of the derivatized ligands differed depending on the functional group. The authors used this observation to prepare ternary MOFs containing controlled ratios of the three functionalized ligands. Importantly, they noted that the azide ligand was always the least abundant (most readily exchanged) and that the most abundant ligand was always the last one introduced by PSE, suggesting that the reactions were under kinetic control.⁶²

By means of PSE, a binary bMOF-100 containing an ~1:1 ratio of the formyl and azide ligands was synthesized.⁶² A fluorescent dye and quencher were introduced onto the struts of the MOF using orthogonal PSM reactions, such that dye molecules were coupled only with azide groups and quencher molecules were coupled only with formyl groups. Examination of the resulting crystals by microspectrophotometry showed strong quenching of the dye molecules. This suggests that the dye and quencher molecules are in close proximity and evenly distributed throughout the MOF crystal, indicating that PSE resulted in a homogeneous distribution of the functionalized ligands throughout the MOF lattice (as opposed to the formation of a core–shell structure).⁶²

In ongoing studies from Rosi, another significant advancement in understanding and controlling the ligand distribution via PSE has been achieved.⁶⁶ As mentioned above, bMOF-100 is capable of undergoing ligand expansion via PSE.⁶⁵ Elaboration of these investigations showed that expansion occurs in a stepwise fashion when using a series of increasingly longer ligands, as shown in Figure 5. Interestingly, PSE experiments indicated that only modest, incremental changes in ligand size can be accommodated, which also suggests that the PSE process occurs via a SCSC reaction and not a crystal dissolution–recrystallization process. With this information in hand, a short (10 min) PSE reaction was performed on bMOF-

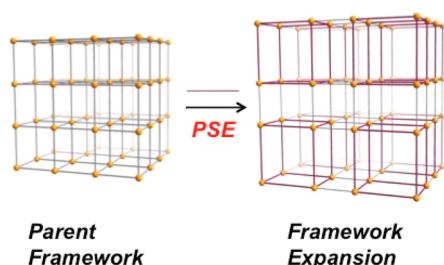


Figure 5. Demonstration of incremental ligand elongation achieved via PSE. This strategy was used to create MOF crystals with a gradation in pore size, with larger pores on the exterior and smaller pores on the interior of the crystal. The parent ligands are shown as gray rods and the extended ligands as magenta rods.

100. Under these reaction conditions, both microspectrophotometry and single-crystal X-ray diffraction (SCXRD) showed that a bMOF-100 core crystal transitioned in a gradual manner to a bMOF-102 lattice on the exterior of the crystals. Similar experiments were used to obtain bMOF-102 to bMOF-106 gradient crystals.⁶⁶ PSE was essential to achieving this important advancement in MOFs whereby a gradient from small to large pores moving from the center to the periphery of the crystal was achieved. The importance of these collective findings by Rosi and co-workers is manifest in the progress made toward major challenges in postsynthetic methods. First, these studies demonstrate exquisite control over the introduction of ligand functionality; second, the findings display an ability to determine the localization of the PSE reaction in the product; and, third, the results show the use of PSE to control the formation of hierarchical MOF structures.

■ POSTSYNTHETIC INSERTION

Although not formally coined as a term in the literature, a new class of postsynthetic reactions have emerged in MOFs that is perhaps best described as postsynthetic insertion (PSI) (Figure 1). When referring to ligand addition, Hupp and Farha have utilized the term solvent-assisted linker incorporation (SALI),⁶⁷ and Zhou has termed the phenomenon sequential linker installation (SLI).⁶⁸ These reports represent impressive advancements in postsynthetic chemistry that encompass a wide range of powerful transformations. In some PSI reactions, metal ions are added to decorate existing SBUs. In others, ligand components are added to vacant/labile sites on SBUs and thereby inserted into the existing MOF framework. For example, early reports established the ability of PSI with linkers to convert two-dimensional structures into three-dimensional frameworks.^{69,70} In this section, a few exceptional examples of PSI will be highlighted, including an interesting example where ligands and metals are removed from a MOF followed by PSI of new ligands and metals.

An important report by Li established some foundational observations for PSI involving both metals and ligands.⁷¹ An IRMOF-1 (MOF-5) analogue (**1**) was prepared from Zn^{2+} and 4-pyrazolecarboxylate (PyC) ligands. During self-assembly, framework **1** forms two distinct but similar SBUs: one formed exclusively from the carboxylate side of PyC and the other from only the pyrazole end of PyC. Upon immersion of MOF **1** in water, 50% of the ligands and 25% of the Zn^{2+} ions (one from each SBU) are removed in an SCSC manner to generate the new porous framework **2** (Figure 6). Despite the loss of these components, the new framework **2** remains intact. To quote the

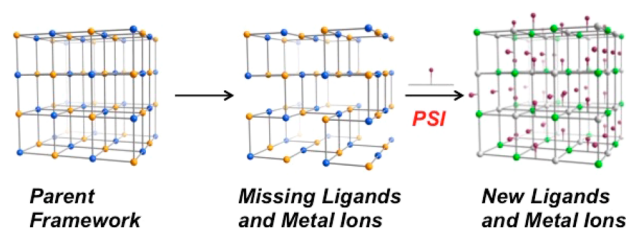


Figure 6. Systematic ligand and metal removal from a parent MOF (left to center, MOF **1** to **2**) is followed by PSI of new linkers and metal ions into crystallographically defined positions within the final MOF (MOF **3**, right). Blue, yellow, green, and silver spheres represent SBUs with different metal ions and ligand sets. Ligands inserted via PSI are designated with red tags (right).

authors, “In a way, the conversion of the **1** to **2** process is akin to the removal of nonload-bearing walls of a building.”⁷¹

Exposure of framework **2** to various metal ions (Li^+ , Co^{2+} , Cd^{2+} , or La^{3+}) and/or ligand derivatives of PyC (methyl, CH_3 -PyC; amine, NH_2 -PyC) allows for PSI and introduction of these metals and ligands into the framework, making new materials containing mixed-metal, mixed-ligand, or both mixed-metal and mixed-ligand compositions. In one particularly successful example, the use of Co^{2+} and either CH_3 -PyC (MOF **5-CH₃**) or NH_2 -PyC (MOF **5-NH₂**) gave MOFs with precisely one Co^{2+} ion per SBU and derivatized ligands (methyl or amine) in strictly, crystallographically defined positions within the MOF lattice.⁷¹

These advancements demonstrate the increasing power of postsynthetic methods: not only were new metals and ligands introduced into the parent MOF, but this could be achieved with exquisite control over composition and positioning within the MOF lattice. Indeed, the authors highlight that neither direct solvothermal synthesis nor PSE reactions could produce the same MOF,⁷¹ as these other reaction conditions do not allow for replacement of components with a specific spatial (and in this case periodic) arrangement. It is this high level of tunability and spatial control that will further elevate the utility of postsynthetic methods in making new porous materials.

Much of the recent and most impressive work in PSI has been reported by the groups of Farha, Hupp, and Zhou on Zr^{4+} -based MOFs. Farha and Hupp have reported SALI reactions that insert ligands onto existing SBUs as well as decoration of SBUs with metal ions.^{72,73} However, the work by Zhou and co-workers, focused on PCN-700 (PCN = porous coordination network), is distinguished by its amazing level of control and high level of atomic precision, as confirmed by SCXRD studies.^{68,74,75}

PCN-700 is a Zr^{4+} -based MOF based on 2,2'-disubstituted biphenyl-4,4'-dicarboxylate (R_2 -bpd c^{2-}) ligands and an eight-connected $Zr_6O_4(OH)_8(H_2O)_4$ SBU. Formation of PCN-700 competes with that of UiO-67, which possesses a similar SBU but higher ligand connectivity and hence is thermodynamically more stable. However, Zhou has shown that the formation of PCN-700 can be preferred by use of the correct substituent on R_2 -bpd c^{2-} (with $R = CH_3$ being the system of choice for forming PCN-700).⁷⁵ In one report, it was shown that metal PSI could be performed on PCN-700 to generate a new MOF with heterometallic SBUs (PCN-800).⁷⁴ In PCN-800, four Co^{2+} or Ni^{2+} ions could be added at precise locations (as shown by X-ray crystallography) to generate new SBUs with the generic formula $[Zr_6M_4O_8(OH)_8(H_2O)_8]$ ($M = Co^{2+}, Ni^{2+}$). Amazingly, the MOF is so stable and highly crystalline that X-

ray crystallography could be used to obtain “snapshots” of the metalation process, giving insights into the mechanism of the PSI reaction.⁷⁴ The ability to capture such transformations in MOFs via crystallographic characterization are known but quite rare.⁷⁶

Even more impressive than metal-based PSI in PCN-700 is its compatibility with ligand-based PSI. In a series of reports, Zhou and co-workers showed that PCN-700 is highly amenable to stepwise PSI by up to two additional ligands.^{68,75} A geometric analysis was used to predict ligand combinations that would be compatible with PSI, enabling the preparation of several new MOF structures. The resulting products are MOFs with three distinct ligands (the original R_2 -bpd c^{2-} to form PCN-700 and two new ligands from PSI; Figure 7), all placed

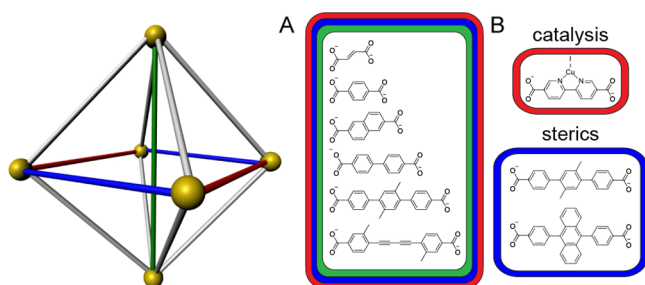


Figure 7. PSI reactions have been demonstrated with the PCN-700 MOF. Left: Illustration of ligand arrangement between SBUs (shown as gold spheres) and possible sites of PSI (blue, red, and green sticks). (A) Some of the ligands that can be inserted into these positions. (B) Two sequential PSI reactions were used to introduce a catalytic copper site (red box) and a second, flanking ligand to control the sterics of the catalytic site (blue box). Adapted from ref 75. Copyright 2016 American Chemical Society.

into crystallographically defined positions within the framework. Not all of the ligands could be inserted with equal efficiency, and conversions as low as 50% and/or substantial ligand disorder (as determined by XRD) were observed in several cases of incomplete PSI.⁷⁵ Nonetheless, this level of structural control is quite remarkable and was further exploited by the authors to prepare a $Cu(bpy)^+$ catalyst for alcohol oxidation. One ligand introduced by PSI harbored the Cu^+ center, with the Cu^+ ion introduced by PSM and crystallographically characterized at $\sim 50\%$ occupancy disorder over two positions. The second ligand was decorated with substituents to control substrate access to the active site, thereby producing a size-selective catalyst (Figure 7).⁷⁵ Despite some limitations, these results represent a substantial advancement in MOF engineering for designing highly tunable, metalloenzyme-like MOF catalysts.⁷⁷

POSTSYNTHETIC POLYMERIZATION

One of the most exciting possibilities with the development and advancement of postsynthetic methods is the opportunity to use these methods to harness MOFs as templates for other materials or to directly transform MOFs into other materials and form factors. Current efforts have largely focused on transforming MOFs into polymer materials or into polymer–MOF composites, which in some studies has been termed postsynthetic polymerization (PSP) (Figure 1).

Some fascinating studies that used MOFs as templates for forming new materials in a postsynthetic manner were reported by the Sada group, where PSM was used to cross-link a MOF

lattice to create a polymer monolith. One report built off of earlier efforts that described the use of “clickable” groups (i.e., azides) on the organic ligand struts (Figure 8).⁷⁸ By the use of

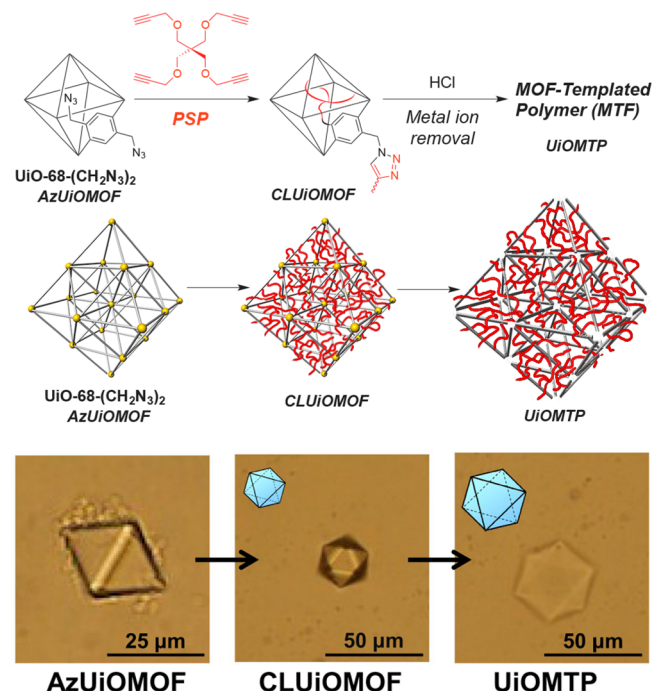


Figure 8. Top: By means of PSM of a MOF with multifunctional ligands and reagents with several reactive sites, transformation into a cross-linked MOF (CLM) and MOF-templated polymer (MTP) was achieved. This effectively results in intraparticle postsynthetic polymerization (PSP) of the MOF, and subsequent removal of metal ions generates a new polymeric material. Bottom: The original crystal habit of the MOF (AzUiOMOF) is preserved in the cross-linked MOF (CLUiOMOF) and even in the metal-free MOF-templated polymer (UiOMTP) after hydrolytic removal of metal ions. Swelling of the particle occurs upon transforming from the MOF to the CLM to the MTP. Reprinted from ref 79. Copyright 2013 American Chemical Society.

struts that possessed more than one “clickable” group (i.e., two azides per ligand) and reactants with more than one reactive site (i.e., three or more alkynes), it was demonstrated that PSM results in a complex, extensive cross-linking of the MOF lattice (Figure 8).⁷⁹ In this scenario, multiple click reactions occur throughout the lattice, connecting ligands to each other until ligand polymerization is achieved to produce a cross-linked MOF (CLM). Indeed, rather than simply a PSM reaction, the resulting transformation might be better categorized as an intraparticle (or intra-MOF) postsynthetic polymerization (although the authors did not use this terminology).

With the extensively interconnected CLM, it was shown that the metal ions could be removed from the CLM by hydrolysis with HCl, leaving behind a solid, monolithic polymer gel termed a MOF-templated polymer (MTP) (Figure 8).⁷⁹ Remarkably, the shape of the parent MOF crystal and even crystal defects (e.g., cracks) were preserved in the MTP. Although the CLM and MTP would swell in the presence of solvent, the overall topology of the original MOF crystals was preserved (Figure 8). In addition, partial metal removal by HCl hydrolysis at only one face of the crystal resulted in a chimera particle with both CLM and MTP domains continuously connected through the cross-linked components. The Sada

group obtained similarly impressive templated gel particles using cyclodextran-derived MOFs and a bis(epoxide) cross-linking reagent.⁸⁰ Collectively, these studies from Sada propelled PSM beyond the concept of ligand modification to complete materials transformation via intra-MOF PSP.

In another example of PSP, Matzger and co-workers applied atom transfer radical polymerization (ATRP)⁸¹ to encapsulate a MOF crystal within a polymer (Figure 9), specifically

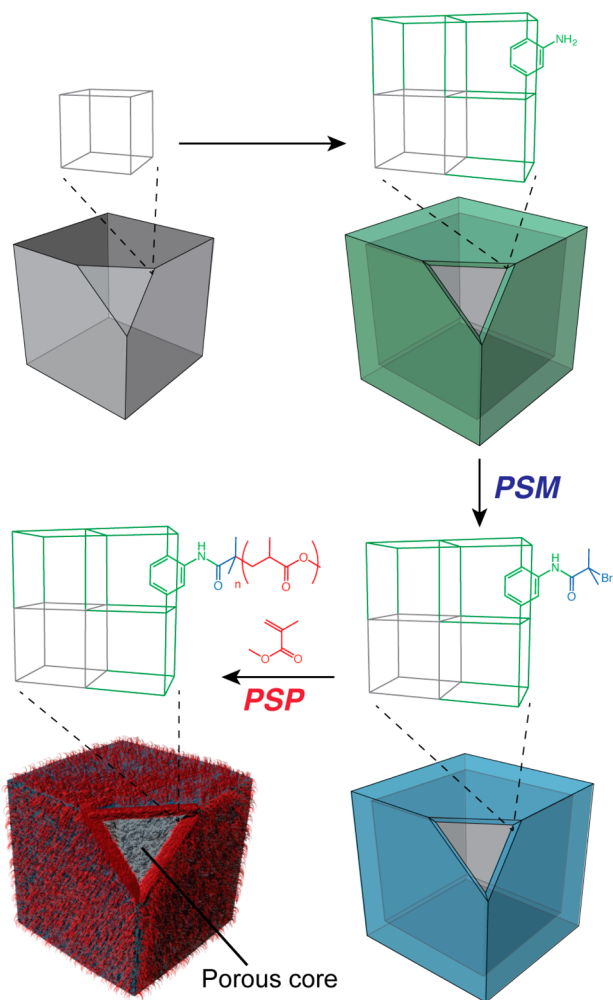


Figure 9. Use of postsynthetic polymerization (PSP) to graft a PMMA polymer coating onto an IRMOF-3@MOF-5 core-shell crystal. Different colors are used to highlight the core-shell structure. Adapted with permission from ref 82. Copyright 2015 The Royal Society of Chemistry.

poly(methyl methacrylate) (PMMA).⁸² This report applied two very specific strategies in order to maximize the degree of polymer encapsulation while preserving the internal surface area of the MOF (i.e., avoiding polymer clogging of the pores). To maximize the polymer loading on the particle, the authors pursued a “grafting from” rather than a “grafting on” approach. That is, the polymers were directly grown from the surface of the MOF particles (“grafting from”) rather than trying to attach fully formed, end-functionalized polymer chains to the MOF crystal (“grafting on”). It was suggested that the grafting on strategy would likely lead to lower polymer densities on the MOF due to the increased steric bulk as the crystal surface became modified with an increasing number of large polymer chains.

To preserve the internal surface area of the MOF, a core-shell MOF architecture was employed by growing an shell of IRMOF-3 (based on 2-amino-1,4-benzenedicarboxylate, $\text{NH}_2\text{-bdc}^{2-}$) over a core of IRMOF-1 (MOF-5, based on bdc^{2-}). The IRMOF-3 outer shell was then selectively modified at the amines of $\text{NH}_2\text{-bdc}^{2-}$ with 2-bromoisobutyric anhydride to generate initiators for ATRP (Figure 9). These initiator sites were selectively located on the IRMOF-3 outer shell; therefore, upon polymerization with methyl methacrylate, the polymerization reaction was confined to the outer crystal shell (as confirmed by Raman microscopy),⁸² leaving the IRMOF-1 core intact and unadulterated. This overall strategy resulted in a multilayered PMMA@IRMOF-3@MOF-5 structure (Figure 9), containing MOFs with a high internal surface area ($S_{\text{BET}} > 2200 \text{ m}^2/\text{g}$), good crystallinity (as gauged by PXRD), and polymers with high molecular weights and narrow dispersities (as determined by gel permeation chromatography, $M_n = 421\text{--}615 \text{ kDa}$, $\text{PDI} = 1.36\text{--}1.44$).⁸² These grafting studies represent another interesting example in which PSP bridges the gap between MOFs and polymers.

Despite the previously described examples of PSP, it was Wang⁸³ who first coined the term PSP in an elegant study that used bona fide PSP to polymerize MOF crystals (i.e., inter-MOF PSP) to form a MOF-based polymeric film. Using an approach highly analogous to that described by Matzger (Figure 9), Wang and co-workers modified UiO-66- NH_2 crystals (also based on $\text{NH}_2\text{-bdc}^{2-}$) with methacrylic anhydride, resulting in MOF crystals decorated on the ligand struts with terminal, polymerizable olefin groups (UiO-66-NH-Met, Figure 10). Subsequent photopolymerization using UV light, the

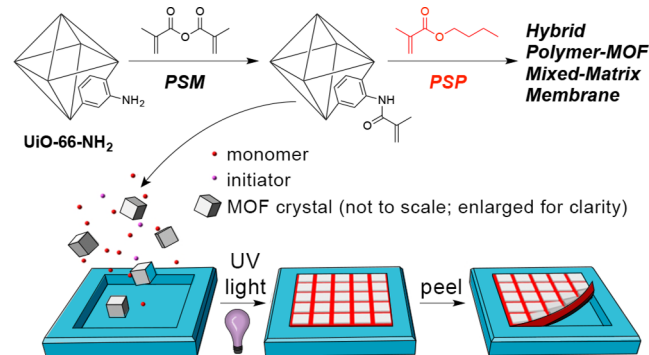


Figure 10. Schematic illustration of the PSP process to obtain an MMM-like film formed in a Teflon mold. MOF particles are depicted as gray cubes. Adapted with permission from ref 83. Copyright 2015 Wiley-VCH.

photoinitiator phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide, and butyl methacrylate resulted in a cross-linked polymer film that could be crafted into different form factors using a Teflon mold.⁸³ The process takes only a few minutes and can be used to produce MOF-rich, freestanding membranes. Through the discovery of PSP, Wang and co-workers effectively created an in situ strategy to prepare covalently linked MOF-based mixed-matrix membranes (MMMs).^{84–86} That work also showed the ability of these MMMs to extract toxic Cr^{4+} from aqueous solutions.⁸³ Overall, PSP represents an extremely clever and powerful approach to the synthesis of MOF-polymer hybrid materials, and it is certain that many more studies and applications of these PSP-derived membranes will be reported in the near future.⁸⁷

PROSPECTIVE

Postsynthetic methods are the manifestation of “Covalent Chemistry beyond Molecules”,¹ where the material is the molecule. In less than a decade, postsynthetic modification methods have rapidly grown from an area of exploratory chemistry to a mainstream tool within the MOF community. Continued efforts have developed new postsynthetic methods, such as PSE and PSI, that are complementary to earlier methods (e.g., PSM) and are often superior to these earlier approaches. The newest methods, such as PSP, are blurring the line between soft and hard, amorphous and crystalline materials (i.e., polymers and MOFs). Additional efforts to scale up both the synthesis and postsynthetic treatments of MOFs suggest that postsynthetic methods may find their way into those MOFs that are ultimately used in commercial applications.⁸⁸

Nonetheless, challenges remain for the field, particularly in the development of postsynthetic methods that allow for precise spatial control over new functionality within the MOF. Compared to molecular synthesis, postsynthetic methods are approaching the wide range of chemical functionality accessible in the realm of small molecules. However, where postsynthetic methods still fall short is the precise, relative location of different functional groups, which is not only achievable but has been mastered in molecular synthesis. Recent reports (e.g., PCN-700, vide supra) hold tremendous promise that this frontier will also be conquered in postsynthetic chemistry, and when this is achieved, then we will truly have mastered “chemistry beyond the molecule”.

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Notes

The author declares no competing financial interest.

ACKNOWLEDGMENTS

Studies on the synthesis, modification, and catalytic properties of MOFs for organic transformations were supported by a grant from the National Science Foundation under Award CHE-1359906. Other studies in our laboratory on the synthesis, modification, and catalytic activity of MOFs for energy-related small-molecule transformations were supported by a grant from the Office of Basic Energy Sciences, Department of Energy, under Award DE-FG02-08ER46519. A VIP fellowship (S.M.C.) from the Ruhr University Research School PLUS, funded by Germany's Excellence Initiative (DFG GSC 98/3), is gratefully acknowledged for providing support during the drafting of this Perspective. The authors thank Dr. Le Wang of U.C. San Diego and Dr. Mary O'Reilly of O'Reilly Science Art, LLC for assistance with the preparation of figures. The author thanks Joseph Palomba, Cy V. Credille, Michael Denny, Jr., Jessica Moreton, and Xiao Yu (U.C. San Diego) for careful reading and editing of the manuscript.

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