Stepwise Synthesis of Metal–Organic Frameworks

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1. INTRODUCTION

One-pot metal–organic framework (MOF) syntheses are often developed through trial and error. The Yaghi group has described the customization of MOF structures through the “reticular approach” of functionalizing and lengthening the linkers of known structures, and mixed-ligand MOFs are often “multivariate”, or distributed randomly. This allows customization of the pore sizes of known structures, and the placement of many functional groups within them, but it can also make detailed control of the shapes of the pores and the placement of the functional groups within the pores difficult.1,2 Many early MOFs made from divalent metals show exceptional porosity and promise for a wide variety of applications, but some proved

CONSPECTUS: Metal–organic frameworks (MOFs) are a category of porous materials that offer unparalleled control over their surface areas (demonstrated as higher than for any other material), pore characteristics, and functionalization. This allows them to be customized for exceptional performance in a wide variety of applications, most commonly including gas storage and separation, drug delivery, luminescence, or heterogeneous catalysis. In order to optimize biomimicry, controlled separations and storage of small molecules, and detailed testing of structure–property relationships, one major goal of MOF research is “rational design” or “pore engineering”, or precise control of the placement of multiple functional groups in pores of chosen sizes and shapes. MOF crystal growth can be controlled through judicious design of stepwise synthetic routes, which can also allow functionalization of MOFs in ways that were previously synthetically inaccessible. Organic chemists have developed a library of powerful techniques over the last century, allowing the total synthesis and detailed customization of complex molecules. Our hypothesis is that total synthesis is also possible for customized porous materials, through the development of similar multistep techniques. This will enable the rational design of MOFs, which is a major goal of many researchers in the field. We have begun developing a library of stepwise synthetic techniques for MOFs, allowing the synthesis of ultrastable MOFs with multiple crystallographically ordered and customizable functional groups at controlled locations within the pores. In order to design MOFs with precise control over pore size and shape, stability, and the placement of multiple different functional groups within the pores at tunable distances from one another, we have concentrated on methods which allow us to circumvent the lack of control inherent to one-pot MOF crystallization.

Kinetically tuned dimensional augmentation (KTDA) is an approach using preformed metal clusters as starting materials and monotropic carboxylates as equilibrium shifting agents to make single crystals of ultrastable MOFs. Postsynthetic metathesis and oxidation (PSMO) takes advantage of the fast ligand exchange rate of a metal ion at the low oxidation state as well as the kinetic inertness of the same metal at high oxidation state to make ultrastable and highly crystalline MOFs. Multiple similar strategies have been successful for the metathesis of Fe-based MOFs to Cr3+. Several highly crystalline Ti-MOFs have also been prepared. Kinetically controlled linker installation and cluster metatation methods utilize a stable MOF with inherent coordinatively unsaturated sites as matrix and postsynthetically install linkers or grow clusters on the matrix, so that a robust MOF with precisely placed functionalities is realized. This method has diverse applications especially when specific functional groups or metals having synergistic effects are desired in the proper proximity.

Exceptional porosity and stability are required for many potential applications. We have demonstrated several of these, including entrapment of nanoscaled functional moieties such as enzymes. We have developed a series of metal–organic frameworks (PCN-333) with rationally designed ultralarge mesoporous cages as single-molecule traps for enzyme encapsulation. We successfully incorporated metalloporphyrins, well-known biofunctional moieties, into robust MOFs for biomimetic catalytic applications. By rationally tuning the synthetic conditions, we obtained several different porphyrinic Zr-, Fe-, and Ti-MOFs with distinct pore size and concentrated acid or base stability, which offer eligible candidates for different applications. These and other stepwise kinetic tuning and catalyst incorporation methods are small steps toward achieving the grand challenge of detailed control of the placement of matter on an atomic and molecular level.
unsuitable for many applications because of their lack of long-
term stability to ambient moisture. Therefore, researchers such
as Fe{	extdegree}rey et al. and Lillerud et al. developed stable MOFs based
on trivalent and tetravalent metals (M\textsuperscript{3+} and M\textsuperscript{4+}) which tend
to possess much greater chemical stability due to the decreased
lability of the M\textsuperscript{−}O bonds. The exceptional stability of M\textsuperscript{3+}
and M\textsuperscript{4+} based MOFs have made them feasible for use in wide-
scale practical applications. However, the stability of the high-
valent metal–ligand bonds also causes challenges in MOF
crystal growth and functionalization.

In order to produce MOFs that are chemically robust, a
pre requisite for most applications, a few basic approaches have
been developed over the last several years, which can be
rationalized by the application of hard–soft acid–base theory.
MOFs based on copper and zinc with carboxylate ligands are
both easy to crystallize as large single crystals and are
chemically unstable for the same reason: their metal–ligand
bonds are relatively labile. Those bonds can be made less labile,
increasing MOF chemical stability, by using softer, better
matching ligating moieties such as those based on nitrogen
heterocycles, or by using carboxylate linkers modified to protect
the SBU or increase bond strength, or by using harder higher-
valence metals that naturally have less labile bonds with
relatively hard carboxylates. The first two approaches often
require complicated or expensive organic synthesis that limits
the large-scale synthesis of the resulting MOFs, so our group
has focused mostly on the use of high-valence metals. However,
this often results either in noncrystalline, nonporous
amorphous products, or MOFs that could not be grown as
single crystals for characterization, with other characterization
methods taking far more time and effort overall. To overcome
this difficulty, we have in the past few years developed several
MOF synthesis, crystallization, and postsynthetic modification
(PSM) methods, building on years of advancements in these
techniques by a large number of research groups.

When high-valence metal salts such as FeCl\textsubscript{3} and
polycarboxylate linkers are mixed under traditional solvother-
mal conditions, the carboxylate linkers quickly bind to the iron
to form noncrystalline, amorphous metal–ligand coordination
polymers. Modulated synthesis using a monocarboxylic acid
was developed by the Kitagawa group to alter crystal growth
and morphology, and was used by the Behrens group to grow
single-crystals of high-valence Zr-MOFs that had previously
only been characterized using nanocrystalline powder. This
method slows nucleation both through lowering solution
pH(slowing and reducing ligand deprotonation) and through
competitive ligation of the metals in solution. Depending on
the metal and ligand used, the exact concentration of
modulating reagent can be increased over several trial reactions
to allow the synthesis of amorphous products, to polycrystalline
powders, typically in high yield, to large single crystals of the
same MOF in lower yield, and
finally to clear solutions
producing no products at a high concentration of acid. These
methods allow the synthesis of high-valence, chemically robust
MOFs with tunable crystallinity and yield. However, they still
typically require the use of acidic solutions at temperatures
exceeding 100 °C, which limits direct one-pot incorporation of
some functional groups. Our research has focused on enabling
the rational design of MOFs through finding methods to
overcome these and similar limitations. By using these stepwise
pre- and postsynthetic modification methods, multiple func-
tional groups can be placed at controlled positions within the
structure in order to customize materials for biomimicry, gas
separation, catalysis, and other new applications.

Figure 1. (a) Four different connecting modes of the [Fe\textsubscript{3}M(\mu\textsubscript{3}-O)]
cluster. Carboxylates on ligands and terminal acetates are represented by black
and purple, respectively. (b) Thirty different ligands and two types of mixed ligands used in constructing Fe-MOFs. Reprinted by permission from Macmillan Publishers Ltd.: Nature Communications copyright 2014.
2. Kinetically Tuned Dimensional Augmentation

While the modulated synthesis method alone seemed to be sufficient for the synthesis of single-crystals of a variety of Zr-MOFs, Fe- and Ti-MOFs remained difficult to synthesize or characterize. Growing single crystals, as opposed to powders, is still difficult in these systems. This is likely because crystal nucleation is too fast and widespread, creating many microporous powder particles which do not have the opportunity to continue to grow into single crystals. It may also be influenced by the lesser reversibility in the metal–ligand bond. The modulating acid concentration zone between polycrystalline powders and clear solutions was small or nonexistent. At a very high modulating reagent concentration, starting materials such as solvated metal salts may be favored, as the pH would be too low for a resulting MOF framework to be stable. Soluble metal-carboxylate clusters may also be favored when the concentration of nonlinking monocarboxylates is too much higher than that of linkers. Inspired by concepts like “scale chemistry” introduced by Férey,1 we decided not to use highly soluble metal salts as a starting material. Instead, we started from soluble metal-acetate preformed clusters, [Fe₂M-(μ₂O)(CH₃COO)]₆ (M = Fe²⁺/³⁺, Co²⁺, Ni²⁺, Mn²⁺, Zn²⁺).₁₀

This alters the equilibria in favor of slowing nucleation and allowing larger crystal growth in several ways. First, the less labile cluster-carboxylate bond is far slower to be displaced by an energetically very similar linking-carboxylate bond. Entropic effects, with the displacement into solution of multiple monocarboxylates per linker, play a major role in the crystallization, and the amount of modulating acetic acid can be tuned to slow linker ligation and framework growth even further. This was validated experimentally with the synthesis and single-crystal X-ray diffraction (SCXRD) characterization of 34 different Fe-MOFs based on this cluster and 30 distinct ligands (Figure 1).

The trends observed in this work provide key insight into MOF kinetics and crystallization equilibria. We found that higher-connected ligands of similar size always required more acetic acid to produce large single crystals, with in some cases 10 times higher concentrations of acetic acid required to get single crystals of a MOF with the same SBU, when using a tetracarboxylate linker instead of a dicarboxylate linker. This implies that the larger coordination number of the linker, displacing more acetate from the starting clusters, was a highly important factor in the MOF crystallization, though higher connectivity may increase the thermodynamic stability of the framework as well. When starting from carboxylate clusters instead of metal salts such as FeCl₃, less acetic acid or other nucleation-disfavoring changes were required to grow single crystals. Starting from a preformed cluster allows the chemist to incorporate other metals such as Co²⁺ into the (μ₂O) cluster and thus tune the SBU for other properties, and acts as a lever for crystallization control.

However, the preassembled inorganic clusters are not always preserved during the MOF formation process. The cluster should be kinetically stable under the synthetic conditions used. We aimed at using the KTDA method for the synthesis of a porphyrin-based titanium MOF. A preformed Ti₆O₆(OiPr)₆(abz)₆ (abz = 4-aminobenzoate) cluster was selected as starting material which is expected to form a she topology when combined with tetratopic porphyrinic linker (TCP). Starting from a preformed Ti₆O₆ cluster, a single crystalline porphyrinic titanium MOF, PCN-22, was obtained. A large excess of benzoic acid was required to produce single crystals, as is typical for tetracarboxylate linkers with high-valence metals. As far as we know, this was the first report of a single-crystalline Ti-carboxylate MOF and one of very few Ti-MOFs ever reported.₁₂ However, the Ti₆O₆ cluster was transformed into a Ti₆O₆ cluster in PCN-22 (Figure 2). This shows how a robust cluster under the MOF synthetic conditions is required for the KTDA method, but as starting from a titanium salt did not produce the MOF products, it shows that even attempted KTDA can be a useful kinetic modulation method. This is similar to other examples found by our group where attempted KTDA resulted in new MOFs with different SBUs than that which were added, under conditions where the attempted original SBU was not completely stable.₁₃

It is worth noting that use of different amounts and types of modulating reagents can produce effects both during and after crystallization. For example, lower pKₐ modulators such as trifluoroacetic acid have been reported to increase the Lewis acidity, pore volume and/or surface area, and proportion of mesoporous defects in UiO-66-type Zr MOFs when compared to use of higher temperatures and higher pKₐ modulators, which can produce UiO-66 with few defects.₁₄ Some MOFs can even be synthesized under basic conditions in order to influence their porosity.₁₅ It is possible to tune the properties of UiO-66 and many other MOFs by using different modulating reagents of different solubility and pKₐ. This should be tried when attempting to grow single crystals, as each solvothermal system only crystallizes in a certain range of modulator concentration. The pKₐ of the modulating reagent is another kinetic parameter that we can tune as part of our crystallization toolbox. However, certain systems and metals, such as Cr(III)-based MOFs which possess even less labile metal–ligand bonds than Fe(III) or Zr(IV)-based MOFs, are still difficult to crystallize directly, even with these tools. Furthermore, this method does not directly allow the rational design of new...
MOFs. However, KTDA is still a useful part of the synthetic toolbox, even if it does not directly provide structural control. This is because the empirical “kinetic control” methods developed as part of KTDA are used in the later structural control methods. In methods such as postsynthetic metathesis and oxidation or sequential linker installation, a MOF with a known structure is modified using the kinetic methods developed in KTDA.

3. POSTSYNTHETIC METATHESIS AND OXIDATION

Some extremely stable high-valence MOFs such as Ti- and Cr-based MOFs are extremely rare, due to the aforementioned difficulties in their synthesis and characterization. Building on a large variety of postsynthetic modification techniques developed by many researchers in the MOF field, our group has developed a variety of approaches based on metal metathesis in order to produce MOFs based on these metals, which then demonstrate much higher chemical stability than the isoreticular parent frameworks they are based on. Postsynthetic metathesis and oxidation (PSMO) refers to the synthesis of a targeted MOF based on metals such as Sc$^{3+}$, Zn$^{2+}$, or Mg$^{2+}$. The use of scandium$^{3+}$ here, along with example such as Zr$^{4+}$ MOFs, is actually a useful example of how “high-valence” and “low-valence” MOF is a shorthand that is too simplistic to be completely accurate. Sc$^{3+}$-based MOFs, as d$^0$ metals, actually tend to be less or similarly chemically stable than, for example, d$^9$ Cu$^{2+}$-based MOFs, despite their increased valence, possibly because ligand exchange is not energetically destabilized by the ligand field stabilization energy (LFSE) of the metal. Similarly, d$^0$ Zr$^{4+}$ and Ti$^{4+}$ MOFs tend to be less stable than d$^3$ Cr$^{3+}$ MOFs. There are also many other factors affecting stability, such as SBU and ligand connectivity, porosity, and the functionalization and ligating moieties of the linker.

Because the original MOFs are made with labile metals, an excess of less labile metal in solution after synthesis should be entropically driven to exchange. The speed and completeness of this metal metathesis depends on both the metal concentration and the relative thermodynamic stability of each metal in the MOF SBU’s coordination environment. Building on previous work by the Dinca and Cohen groups, we reasoned that care must be taken to select MOFs with SBUs that the new metal will be stable in. Furthermore, direct exchange of low-valence to low-valence metals, while fast, did not produce an increase in MOF chemical stability, while direct exchange from low to high-valence metals was incomplete and slow. One of the solutions was to select MOFs with SBUs and coordination environments that were highly stable with the new metal, exchange for a lower-valence, unstable ion of that metal under an anoxic environment, and then allow the air to oxidize the metal to its stable higher oxidation state. This was demonstrated in PCN-426, where Mg$_2$(μ$_2$-O) clusters serve as an SBU which can be easily exchanged for Fe(II) and Cr(II), which remain labile in those oxidation states. After oxidation, this process produced a MOF which was to our knowledge the first example of a Cr-MOF of sufficient crystal size and quality for characterization on a nonsynchrotron single-crystal diffractometer. This is an example of how even materials that cannot be directly crystallized can be synthesized and characterized through stepwise methods that change environmental conditions to “climb” over an energetic barrier into a local energy minima.

PSMO was also applied to the synthesis of multiple titanium frameworks based on appropriate SBUs. MIL-100(Sc), PCN-333(Sc), MOF-74(Zn), and MOF-74(Mg) were all quickly exchanged with Ti(III), (Figure 3) which was then oxidized in air to Ti(IV) with varying rates of metathesis ranging from 35% in MOF-74(Mg–Ti) to 100% in MOF-74(Zn–Ti), combined with promising photocatalytic activity measurements.

We soon worked to extend this process in order to stabilize and functionalize a framework, PCN-333, that was useful due to its extremely large 5.5 nm mesopores, but had relatively high chemical stability, but slightly lower than other MOFs synthesized with the same SBU, presumably due to those mesopores. Modulated synthesis using 4,4′,4″-tris(4-fluoroacetic acid produced frameworks which were isoreticular with MIL-100. Due to the many-sided shapes of the larger pores in their MTN topology, isoreticular expansion produces greater pore size increases than it does in frameworks with pores that have fewer “sides” or windows. These large pores proved useful in the encapsulation and protection of several enzymes, which retained catalytic activity within the pores under conditions that unprotected enzymes were denatured under. The chemical stability of this framework, remaining intact under conditions of pH 3–9, is high for such a highly porous material, but needed to be improved for certain catalytic applications requiring more concentrated acid or basic solutions.

One metal produces MOFs which typically have higher chemical stability than that of Fe(III)–Cr(III). However, growth of PCN-333(Fe) already pushed the limits of our earlier kinetic tuning and crystallization methods, with only powder synthesized, which had to be characterized using synchrotron powder X-ray diffraction methods. Attempts to directly synthesize PCN-333(Cr) produced only amorphous, nonporous products. Furthermore, directly synthesized Cr-MOFs such as MIL-101 have proven highly difficult to functionalize, as the high-temperature, high-pressure conditions necessary for the synthesis of even powders of these MOFs decompose many functional groups that have been used in other MOFs. Both of these problems were solved simultaneously by the “dual exchange” of PCN-333(Fe) to PCN-333-N$_2$(Cr). Postsynthetic ligand exchange of PCN-333(Fe) allowed the functionalization of the framework with moieties that are too fragile to survive solvothermal synthesis, or that formed another framework.

Figure 3. Stepwise PSMO synthetic method allows high-valence metals to be used in a MOF structure that was not found through one-pot methods. Ref 20. Published by The Royal Society of Chemistry.
such functionalities into the Cr-MOF, which was too kinetically inert for successful postsynthetic ligand exchange. Interestingly, PCN-333(Sc) showed only 64.8% exchange for Cr under conditions that produced a 99.8% exchange ratio when starting from PCN-333(Fe) at 150 °C over two 30 min incubations in CrCl3 DMF solution, due to framework collapse when starting from PCN-333(Sc); it is not stable enough to survive the exchange conditions, while PCN-333(Fe) was. Unlike in the case of PCN-426, replacing Fe(III) with Cr(III) via metathesis of Fe(II) to Cr(II) followed by oxidation was not necessary, due to the more similar ligand exchange rate constants of Fe(III) and Cr(III).

Another method that takes advantage of redox changes to control the metathesis reaction, “reductive labilization,” was demonstrated through an alternative preparation of PCN-333(Cr). In this case, anoxic Cr(II) solutions were used for an outer-sphere reduction of Fe(III) in PCN-333(Fe) to Fe(II), which quickly exchanged with the Cr(III) that was produced by this reaction. PCN-333(Cr) was also shown to be much more chemically robust than PCN-333(Fe), showing stability over 24 h in solutions of pH 0–11, and surviving uptake of alkylamines, used to increase the CO2 uptake of the material through chemisorption, while PCN-333(Fe) was degraded by the alkylamine molecules.

4. SEQUENTIAL LINKER INSTALLATION AND CLUSTER METALATION

MOFs have been very widely studied due to their combination of ease of crystalline synthesis, high surface area, easy functionalization, and high chemical stability. They are promising for many applications due to these properties, especially as they have been demonstrated to be functionalized simultaneously with up to 8 different moieties in controlled ratios, as in multivariate MOFs.25 One limitation has been that placement of multiple functional groups at controlled positions, important for applications such as biomimetic catalysis, has been limited, though some postsynthetic modification approaches, such as those recently published by the Yaghi group, have been promising.26 The synthesis of mixed-ligand MOFs offers another solution to this limitation, as each ligand can be functionalized separately, and the distance and orientation of the functional groups from each other will be known and controlled by the MOF structure. Mixed ligand MOFs are rare, have had limited chemical stability, and have mostly been confined to two types of linkers, with mixed phases or domains forming when more symmetrically distinct linkers are mixed in one-pot reactions.27,28 In our experiments, one-pot solvothermal synthesis using linear linkers of different length always produced a mixture of different MOF phases, and so a kinetically controlled, stepwise approach was used to produce several new MOFs through single-crystal to single-crystal transformations.

To overcome these difficulties, we targeted the Zr6 SBU, which possesses tunable connectivity, from 6 to 12 connections depending on the linker used in the MOF. In the UiO-66 type structure, otherwise known as the fcu topology, the carboxylates on the linear linkers must be coplanar in order for the Zr6 SBUs to form 12-connected nodes. By using a linker that twists at a 90° angle, i.e., dimethyl biphenyl dicarboxylate, instead of the unhindered, nonfunctionalized biphenyl dicarboxylate of UiO-67, another structure, PCN-700, is produced at lower temperatures (Figure 5).29 The bcu topology of PCN-700 is similar to fcu, except that 4 equatorial linkers on the SBU are missing, producing an 8-connected node. (Figure 6).

The missing coordination areas on the Zr6 SBU in PCN-700 consist of terminal oxygens that can be, in turn, displaced by a...
postsynthetic ligation reaction. Two of the sites have different lengths than the other two, which allows the stepwise placement of two different types of linear linkers, which can be separately functionalized (Figure 6). Furthermore, all this takes place in a crystallographically ordered fashion, and so the precise distances of each of the three possible linkers and any functional groups attached to them can be measured, which was demonstrated through the synthesis and crystallographic characterization of PCN-701, -702, -703, and -704, with different ordered linkers. PCN-700 shows a high degree of flexibility, which allows the installation of linkers with different lengths and a combination thereof. Guided by geometrical analysis, 11 new MOFs were obtained by linker installation, each bearing up to three different functional groups in predefined positions (Figure 7). Systematic variation of the pore volume and decoration of the pore environment was realized by linker installation, which resulted in synergistic effects including an enhancement of H₂ adsorption capacities of up to 57%. In addition, a size-selective catalytic system for aerobic alcohol oxidation reaction was built in PCN-700 through linker installation, which shows high activity and tunable size-selectivity. Altogether, these results exemplify the capability of the linker installation method in pore environment engineering of stable MOFs with multiple functional groups, giving an unparalleled level of control.

In addition to multifunctional mixed-linker MOFs being made synthetically accessible through the control afforded by stepwise synthesis, mixed-metal Zr MOFs have also been produced. PCN-700s terminal oxygens on its equatorial plane are postsynthetically solvothermally reactive with other metals, which over time grow onto the Zr₆ SBUs, forming decanuclear Zr₆M₄ (M = Ni, Co) clusters, which can be shown stepwise with successive SCXRD "snapshots" if the reaction is interrupted every several hours (Figure 8).

5. CONCLUSIONS

Since the late 1990s, research interest in MOFs has been growing continuously. In a recent review article, Yaghi et al. proposed that the new materials should have multiple kinds of building units, and the arrangement of these building units within crystals should have specific sequences. Advanced functionalities in MOFs require more complex structures and
pore environments, accompanied by heightened challenges with their geometric design. Constructing metal–organic frameworks from multiple components is a pathway to enable sophisticated applications which require high complexity in highly ordered crystalline materials. The above-discussed research provides possible methods to increase MOF complexity while maintaining structural regularity to the maximum extent. We have begun developing a library of stepwise synthetic techniques for MOFs, allowing the synthesis of ultrastable MOFs with multiple crystallographically ordered and customizable functional groups at controlled locations within the pores. In the long term, we expect to realize total synthesis in MOFs for customized structures and functionalities, through the development of stepwise synthetic techniques. Although currently not possible, the high designability and diverse synthetic methodologies of MOFs discovered in recent years suggest that such a feat is feasible in the future, and represents one path toward “rational design” of MOFs that is a major goal within the field.

The kinetic tuning, crystallization, and postsynthetic modification methods described here are part of a growing synthetic toolbox for MOF researchers. Each of these methods can be used to achieve the synthesis and characterization of new, targeted MOFs that would not be possible in a simple one-pot solvothermal crystallization process. Eventually, we hope to help realize the dream of rational, stepwise design of metal–organic frameworks with precise control over pore size and shape, stability, and the placement of multiple different functional groups within the pores at tunable distances from one another. This precise control will be necessary to produce materials optimized for energy storage, catalysis, or other applications that can benefit from the engineering of pore environments.

We have developed and demonstrated the KTDA, PSMO, sequential linker installation, structure-assisted functional anchor implantation, single-enzyme encapsulation, and other methods for this purpose. Each of these methods, more than simply allowing the synthesis of the particular MOFs published with them, can be used to synthesize a limitless variety of MOFs customized for many different applications. The stepwise methods we have described allow researchers to overcome the harsh conditions necessary for MOF crystallization and the randomness of functional group placement that have previously limited biomimicry.

Small molecule separations are governed by selecting a separation material that has pore size, shape, and functionalization that select very preferentially between molecules that may be very similar to one another, such as racemic mixtures or different isomers of a molecule. Stepwise synthesis offers new opportunities to design MOFs for this purpose. Small molecular characterization can also be undertaken in this way, for example through the crystalline sponge or coordinative alignment methods. Using the PSMO and sequential linker installation methods to produce materials customized for preferential interaction by multiple aligned functional groups with small molecules of interest will be a rich avenue of future investigation. The KTDA method can be used for isoreticular manipulation of the SBU of known MOFs, and modulation of their surface area and catalytic activity, as well as synthesis of MOFs not synthetically accessible through in situ SBU assembly. Immobilization of enzymes and homogeneous molecular catalysts can be used to produce robust, reusable heterogeneous catalysts. Finally, development of new stepwise synthesis and modification techniques is vital to allow more precise pore engineering and to work toward the rational design of MOFs.

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The authors declare no competing financial interest.

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Shuai Yuan graduated from Shandong University in 2013, where he studied the design and synthesis of luminescent MOFs. He became a Ph.D. student in Dr. Hong-Cai Zhou’s group at Texas A&M University in 2013, and he focuses his research on the design and synthesis of metal–organic frameworks for gas storage, gas separation and catalysis.

William Rutledge graduated from Millersville University in 2014, after researching iridium N-heterocyclic carbene-based transfer hydrogenation catalysts, and became a member of Dr. Hong-Cai Zhou’s group at Texas A&M University as a Ph.D. student in 2015. His research is on the synthesis of new MOF materials specialized towards clean energy technologies.

Hong-Cai “Joe” Zhou graduated from Texas A&M University with his Ph.D. in 2000 under the supervision of Prof. F. A. Cotton. He then completed postdoctoral research with Prof. R. H. Holm at Harvard University in 2002, and became a faculty member at Miami University, Oxford. In 2008, he became a full professor at Texas A&M University, a Davidson Professor of Science in 2014, and a Robert A. Welch Chair in Chemistry in 2015. His research focuses on synthetic methods to obtain extremely stable framework and other porous materials with interesting and useful catalytic or clean-energy related properties.

ACCOUNTMENTS


REFERENCES


