Stable Metal–Organic Frameworks with Group 4 Metals: Current Status and Trends

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ABSTRACT: Group 4 metal-based metal–organic frameworks (MIV-MOFs), including Ti-, Zr-, and Hf-based MOFs, are one of the most attractive classes of MOF materials owing to their superior chemical stability and structural tunability. Despite being a relatively new field, MIV-MOFs have attracted significant research attention in the past few years, leading to exciting advances in syntheses and applications. In this outlook, we start with a brief overview of the history and current status of MIV-MOFs, emphasizing the challenges encountered in their syntheses. The unique properties of MIV-MOFs are discussed, including their high chemical stability and strong tolerance toward defects. Particular emphasis is placed on defect engineering in Zr-MOFs which offers additional routes to tailor their functions. Photocatalysis of MIV-MOF is introduced as a representative example of their emerging applications. Finally, we conclude with the perspective of new opportunities in synthesis and defect engineering.

INTRODUCTION

Metal–organic frameworks (MOFs),1,2 as a class of organic–inorganic hybrid materials, have attracted considerable research interest in the past two decades because of their intrinsically porous structures and unlimited tunability.3–9 MOFs are usually constructed by connecting inorganic nodes and organic linkers through coordination bonds. The inorganic nodes can be metal clusters or metal ions,10,11 while the organic linkers are usually carboxylates or heterocyclic compounds.12 The structures and functions of MOFs are often tailored by the design of organic linkers with specific lengths, geometries, and functional groups.7 Meanwhile, the inorganic nodes also dictate some MOF properties. For example, the chemical stability of a MOF is mainly determined by the inorganic node, as the metal–ligand bonds are usually the most labile sites of the framework. Almost all the metal cations in the Periodic Table, including some radioactive ones, have been used as inorganic nodes to construct MOFs (Figure 1). Generally, the inorganic nodes of MOFs can be constructed from monovalent (Cu+, Ag+, etc.), divalent (Mg2+, Mn2+, Fe2+, Co2+, Ni2+, Cu2+, Zn2+, Cd2+, etc.), trivalent (Al3+, Sc3+, V3+, Cr3+, Fe3+, Ga3+, In3+, lanthanides3+, etc.), or tetravalent (Ti4+, Zr4+, Hf4+, Ce4+, etc.) metal cations. In the early stages of MOF research, divalent metals such as Zn2+ and Cu2+ were widely used in MOF synthesis.1,13 Despite their numerous advantages, applications of these divalent metal-based MOFs are ultimately limited by their instability under harsh conditions. Therefore, researchers have turned their efforts to more stable framework structures in recent years.14–16

A method to enhance the stability of MOFs is to use high-valent metal cations and carboxylate linkers.16–18 With the same ligands and coordination environment, high-valent metal cations with high charge densities can form stronger coordination bonds and a more stable framework. Group 4 metal cations generally exist in the oxidation state of +4, which is expected to form stable MOFs when combined with...
carboxylate-based ligands.\textsuperscript{19,20} In addition to the stronger metal–ligand bonds, these 4+ metal cations require more ligands to balance their charge. Therefore, their inorganic nodes tend to have high connectivity, which, to some extent, enhances the stability of the framework by preventing the attack by guests such as water molecules.

Compared to the well-studied Zn\textsuperscript{2+}– and Cu\textsuperscript{2+}–based MOFs, group 4 metal-based MOFs (M \textsuperscript{IV}–MOFs) are a relatively new research field. The first Zr-MOF was reported in 2008\textsuperscript{19} followed by the discovery of Ti-MOF in 2009.\textsuperscript{20} Nevertheless, they have drawn increasing attention since their discovery particularly because of their high stability and wide application scope. Previous reviews have provided comprehensive summaries of Zr- and Ti-based MOFs, including their syntheses, structures, properties, and applications.\textsuperscript{18,21} This Outlook will not repeat these reviews but will briefly introduce the history of M \textsuperscript{IV}–MOFs, highlight their unique properties, and explore the current challenges and emerging opportunities in this area.

\section*{A BRIEF HISTORY}

\textbf{Zr-MOFs.} The first Zr-MOF, UiO-66, was reported in 2008 (UiO stands for University of Oslo).\textsuperscript{19} It is constructed by linking 12-connected \([\text{Zr}_6(\mu_3-O)(\mu_3-OH)(\text{COO})_4]_{12}\) clusters (Figure 2a,b) with linear BDC linkers into a network with fcu topology (Figure 2c). It possesses two types of micro pores, tetrahedral and octahedral (Figure 2f), and a BET surface area close to 1200 m\textsuperscript{2}g\textsuperscript{−1}. Isoreticular expansion of UiO-66 with elongated linkers successfully generated two isostructures, namely, UiO-67 and UiO-68. After this publication, there were few reports on new Zr-MOFs until 2011, aside from some works exploring the functionalization and applications of UiO-type structures.\textsuperscript{24–27} The discovery of new Zr-MOFs is largely hindered by synthetic difficulties. The strong Zr–O bonds slow down the ligand exchange rate and thus inhibit the crystallization process. Direct synthesis of stable MOFs using a mixture of metal salts and organic linkers usually leads to quick precipitation of low crystalline powders. In fact, the UiO series were initially obtained as polycrystalline powders. Without single crystals, their structures need to be determined by complicated Rietveld refinements against synchrotron powder X-ray diffraction (PXRD) data, which further impedes the discovery new Zr-MOFs.

In 2011, this problem was overcome by modulated synthesis, using terminal carboxylic acids as modulators.\textsuperscript{28} The terminal carboxylic acids competitively coordinate with the metals and suppress the deprotonation of linkers. As a result, nucleation and crystal growth are slowed to allow for the formation of highly crystalline products. Using benzoic acid as modulator, single crystals of UiO-68-NH\textsubscript{2} were obtained, providing the first single-crystal structure of Zr-MOFs. Modulated synthesis has proved effective for most Zr-MOFs and thus has dramatically accelerated the discovery of new structures.\textsuperscript{18,29,30} According to the Cambridge Structural Database (CSD),\textsuperscript{31} about 200 Zr-MOFs have been recorded so far.

A unique feature of the \([\text{Zr}_6(\mu_3-O)(\mu_3-OH)(\text{COO})_4]_{12}\) core is the capability to vary the connection number without altering the robust \([\text{Zr}_6(\mu_3-O)(\mu_3-OH)(\text{COO})_4]_{12}\) core. Besides the aforementioned 12-connected \([\text{Zr}_6(\mu_3-O)(\mu_3-OH)(\text{COO})_4]_{12}\) clusters, 11-connected \([\text{Zr}_6(\mu_3-O)(\mu_3-OH)(\text{OH})(\text{H}_2\text{O})(\text{COO})_{11}]_{12}\), 10-connected \([\text{Zr}_6(\mu_3-O)(\mu_3-OH)(\text{OH})(\text{H}_2\text{O})(\text{COO})_{10}]_{12}\), 8-connected \([\text{Zr}_6(\mu_3-O)(\mu_3-OH)(\text{OH})(\text{H}_2\text{O})(\text{COO})_8]_{12}\), and 6-connected \([\text{Zr}_6(\mu_3-O)(\mu_3-OH)(\text{OH})(\text{H}_2\text{O})_6(\text{COO})_6]_{12}\) clusters have also been documented in which each missing carboxylate was replaced by a terminal monocarboxylate ligand or a pair of −OH−/H\textsubscript{2}O to balance the charge. Note that the proton assignments for these clusters with −OH−/H\textsubscript{2}O groups are not clear, although simulations indicated that the −OH− and −H\textsubscript{2}O are interconvertible by rapid proton transfers.\textsuperscript{37}

This variable connection number further enriches the structural abundance of Zr-MOFs. Meanwhile, the maintained \([\text{Zr}_6(\mu_3-O)(\mu_3-OH)(\text{COO})_4]_{12}\) core facilitates structural prediction. As an example, the possible structures formed by Zr\textsubscript{6} clusters and tetracarboxylate linkers can be predicted by a reverse topological approach.\textsuperscript{38} First, possible geometries of organic linkers and Zr\textsubscript{6} clusters are analyzed: the tetratopic linkers are represented by 12-connected cuboctahedrons, 8-connected triangular antiprisms, 6-connected hexagons, or 6-connected triangular antiprisms. Possible topologies formed by the combination of two nodes were then listed including ftw, csq, scu, sqc, and she. These topologies were used as templates to construct hypothetical MOFs by replacing the topological

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure2.png}
\caption{Topological representation (a) and structures of \([\text{Zr}_6(\mu_3-O)(\mu_3-OH)(\text{COO})_4]_{12}\) (b), \([\text{Ti}_8(\text{OH})(\text{COO})_8]_{12}\) (c), and \([\text{Ti}_8\text{Zr}_2\text{O}_{12-}\text{O}_6]_{12}\) (d) clusters. Topology (e) and structure of Zr-MOF UiO-66 (f), Ti-MOF MIL-125 (g), and Ti–Zr bimetallic MOF PCN-415 (h). Color scheme: Zr, cyan; Ti, green; O, red; C, black; tetragonal cage, yellow; octahedral cage, light green.}
\end{figure}
nodes with Zr₆ clusters and organic linkers. Finally, the predicted structures were carefully examined, geometrically optimized, and experimentally synthesized. Guided by topological analysis, a series of Zr-MOFs based on a 4-connected linker, TCeP, were constructed, including MOF-525 (fw)₃⁹ PCN-222 (esc)₄⁰ NU-902 (scu)₄⁰ PCN-224 (she)₄¹ and PCN-225 (sqc)₄¹ (TCeP = tetraakis(4-carboxyphenyl)-porphyrin); NU stands for Northwestern University; PCN stands for poruous coordination network). Using the same strategy, the Snurr group has predicted 204 hypothetical Zr-MOFs and examined their performance in CH₃OH adsorption, which guided the syntheses of Zr-MOFs for targeted applications.

Besides the [Zr₆(μ₃-O)₄(μ₃-OH)₄] core, Zr-clusters featuring other core structures have also been occasionally observed in MOFs. Polymeric double chains were found in MIL-140 (MIL stands for Materials of Institut Lavoisier) which was composed of edge sharing ZrO₂ polyhedra connected through linear ligands. The 1D building unit has also been observed in CAU-22 (CAU stands for Christian-Albrechts-Universität), which is perceived as 6-connected Zr₆ clusters bridged by μ₂-OH. Recently, the [Zr₁₂(μ₃-O)₆(μ₂-OH)₆(μ₂-OH)₆(μ₂-OH)₆(μ₂-OH)₆(μ₂-OH)₆] cluster was discovered, which can be viewed as a pair of Zr₆ clusters linked by μ₂-OH groups. Note that most Zr-MOFs have Hf-based analogs. Due to lanthanide contraction, Hf has the same d⁶ electronic configuration and a nearly identical radius as Zr⁴⁺. Therefore, the Hf-MOFs usually show identical structures and properties as their Zr-based counterparts, except for the formula weight. Considering the diversity of Zr-clusters and the ever-increasing research interest in stable MOFs, the number of Zr-MOFs will continuously grow in the near future.

**Ti-MOFs.** Ti-MOFs possess several advantages over Zr-MOFs such as high photocatalytic activities, earth abundance, and relatively low toxicity. The first Ti-MOF, MIL-125, was reported in 2009, one year after the discovery of Zr-MOFs. It is constructed from 12-connected [Ti₈O₆(OH)₁₆(COO)₁₆] clusters (Figure 2c) and BDC linkers affording a fcu network (Figure 2g). It has the same topology as the Zr-MOF, UiO-66, although the [Ti₈O₆(OH)₁₆(COO)₁₆] cluster is less symmetric than the [Zr₆O₄(OH)₄(COO)₁₂] cluster. It demonstrates permanent porosity with a BET surface area of 1550 m² g⁻¹. The amine functionalized BDC linker also forms the MIL-125 structure. One would expect that isostructural Ti-MOFs can be obtained with longer linear linkers such as BPDC (BPDC = biphenyl-4,4’-dicarboxylate). However, the synthesis of MIL-125 isostructures using elongated linkers was carried out but to no avail.

Inspired by the success of modulated synthesis of Zr-MOFs, the modulated synthesis of Ti-MOFs was attempted by our group using a [Ti₈O₈(OH)₁₆(COO)₁₆] cluster as the metal resource and carboxylic acids as modulators, in expectation of a Ti₈-based MOF (ABZ = 4-aminobenzoate). However, despite the similarity between Ti⁴⁺ and Zr⁴⁺, the modulated synthesis of Ti-MOFs was not successful. The Ti₈-cluster tends to reassemble during MOF synthesis. Recent developments in synthetic technique have partially overcome this difficulty by combining the synthetic strategies of MOFs and covalent organic frameworks (COFs). In this method, the same hexameric Ti-oxo-cluster with amino groups, [Ti₈O₈(OMe)₆-(ABZ)₆], was in situ generated and further extended into a 2D layer by dialehyde spacers through an imine condensation reaction. Two Ti-MOFs, namely, MOF-901 and MOF-902, are successfully obtained. They represent a combination of MOFs and COFs with both coordination bonds and dynamic covalent bonds. The formations of both Ti₈-clusters and imine bonds are favored under the synthetic conditions, although it is not clear which bond is the labile one that controls the crystallization process.

Until now, only a limited number of Ti-carboxylate-based coordination polymers (MIL-125 and its derivatives) have been reported (PCN-22, COK-69, MOF-901, MOF-902, NTU-9, MIL-167, MIL-168, and MIL-169) have been reported (NTU stands for Nanyang Technological University). Among all these coordination polymers, permanent porosities were proven for MIL-125, PCN-22, MOF-901, and MOF-902. Different clusters were observed in each of these MOFs ([Ti₆] for MIL-125, [Ti₇] for PCN-22, and [Ti₈] for MOF-901/902). Compared with the well-established synthetic method for Zr-MOFs, there is still a lack of an efficient way to take control over the formation of Ti-MOFs.

**Ti–Zr Bimetallic MOFs.** The synthetic difficulties of Ti-MOFs are attributed to the incompatible formation condition of Ti-clusters with those required for MOF synthesis. In contrast, the robust [Zr₆O₄(OH)₄(COO)₁₂] cluster affords the formation of various Zr-MOFs via modulated synthesis. The combination of Ti and Zr in a bimetallic [Ti₈Zr₂O₁₂(COO)₁₆] cluster has brought new opportunities in the synthesis of Ti-containing MOFs. Starting from [Ti₈Zr₂O₁₂(McCOO)₁₆] clusters and linear linkers with different lengths and functional groups, a series of isoreticular bimetallic MOFs, the PCN-415 and PCN-416 series, were synthesized under synthetic conditions similar to those used for Zr-MOFs.

The robust [Ti₈Zr₂O₁₂(COO)₁₆] clusters were maintained in the resulting MOFs. The decanuclear [Ti₈Zr₂O₁₂(COO)₁₆] cluster is composed of a Ti₈-cube capped by two Zr₆ clusters on the top and bottom (Figure 2d). The Ti₈ and Zr₆ were further bridged by four μ₂-O, eight μ₂-Oₐ, and 16 carboxylates generating the [Ti₈Zr₂O₁₂(COO)₁₆] cluster. Interestingly, the [Ti₈Zr₂O₁₂(COO)₁₆] cluster can be regarded as a derivative of the [Zr₆O₄(OH)₄(COO)₁₂] cluster by replacing four equatorial Zr⁴⁺ by Ti₈-cube. As a result, PCN-415 and PCN-416 share the same topology as their Zr-analogues, UiO-66 (Figure 2h). Both PCN-415 and PCN-416 are highly porous with BET surface areas of 1050 and 1337 m² g⁻¹ respectively. They also demonstrate excellent chemical stability, tunable photoresponsiveness, and good activity toward photocatalytic hydrogen evolution reactions. Considering the synthetic difficulties of Ti-MOFs, the [Ti₈Zr₂O₁₂(COO)₁₆] cluster is believed to be a Ti-containing replacement of the [Zr₆O₄(OH)₄(COO)₁₂] cluster, which promises the construction of various robust and photoactive MOFs.

By comparing the history of Ti-MOFs and Zr-MOFs, some useful information can be provided. The field of Zr-MOFs has developed rapidly since 2011 when an effective synthetic method was developed. Modulated synthesis allows for the facile production of high quality MOF materials, which contributes to the success of Zr-MOFs. Over the past few years, Zr-MOF UiO-66 has almost dethroned MOF-5 and HKUST-1 (HKUST stands for Hong Kong University of Science and Technology) as a benchmark MOF material. Unfortunately, the Ti-MOF field remained relatively silent for almost 10 years with sporadic reports of new structures. Once the synthetic challenges are overcome, we believe that new Ti-MOFs will begin to burgeon. On the other hand, the discovery
of Ti−Zr bimetallic clusters may offer an opportunity for the development of new Ti-containing photoactive MOFs.58

STABILITY

The outstanding chemical stability makes MIV-MOFs an attractive research area. It is necessary to introduce the fundamentals of MOF stability in a tutorial manner in order to understand the stability of MIV-MOFs. The stability of MOFs is affected by multiple factors, including the metal nodes, organic ligands, metal−ligand coordination, operating environment, hydrophobicity of the pore surface, defects, etc.14−16 The metal−ligand bond strength is an important factor that determines the thermodynamic stability of MOFs. Since it is not always easy to quantify the bond strength, the stability of MOFs can be roughly compared according to the Pearson’s hard/soft acid/base principle.17 Strong coordination bonds are expected between hard Lewis acids and bases4,19 or soft Lewis acids and bases.60−62 Carboxylate-based ligands can be regarded as hard bases, which form stable MOFs with group 4 metal cations. Besides the influence of bond strength that determines thermodynamic stability, the stability of MOFs can also be affected by kinetic factors. Dense and rigid framework structures formed by highly connected metal-oxo clusters and rigid organic linkers enhance the overall stability of MOFs. This also partially explains the good stability of M4+-based MOFs, because M4+ cations require more ligands to balance their charge.

Since it is not always easy to quantify the bond strength, the stability of MOFs can be roughly compared according to the Pearson’s hard/soft acid/base principle.

The stability of a MOF also depends on the operating environments. Generally, MOFs constructed from high-valent metal ions and carboxylate-based ligands exhibit excellent stability in acids, while their resistance to base is weak. In acid, the degradation of MOFs is mainly caused by the competition of proton and metal ion for the coordinating linkers (Scheme 1).63 The low pKa of carboxylic acids and strong coordination bonds endow these MOFs with excellent stability in acids. However, the strong affinity between high-valence metal cations and OH− facilitates the replacement of linkers by OH−, which results in their lability toward basic solutions. The Zr-MOF UiO-66, Ti-MOF MIL-12S, and Ti−Zr bimetallic MOF PCN-415 show similar stability in aqueous solution from pH = 1 to pH = 12, indicating a better stability in acid than in base. Note that different synthetic procedures may give rise to MOFs with different defects and particle sizes, which may also affect the stability. Another extreme example is Zr-MOF PCN-222 (also known as MOF-545) constructed from Zr4+ and carboxylate linkers.34,39 It can maintain its crystallinity in concentrated HCl (12 M) but readily decomposes in dilute NaOH solutions (0.1 mM). Therefore, MIV-MOFs can find application in acidic environments, but one should be cautious when using them under basic conditions.

DEFECTS

It has been proven that defects exist in almost any MOFs, such as MOF-5 and HKUST-1.64−68 However, Zr-MOFs have attracted particular attention because of their remarkable tolerance toward a high concentration of defects without suffering from severe loss of crystallinity or stability.69,70 This is related to the high connectivity of Zr6 clusters (Figure 3a) and their capability to reduce their connection number. Take the Zr-MOF, UiO-66 as an example (Figure 3b,d), two types of defects were observed: missing-linkers and missing-clusters.71 The missing linker defect is generated by the removal of an organic linker from a pair of adjacent Zr-clusters, leaving coordination vacancies.70 The coordination vacancy on the Zr-cluster is believed to be terminated by a monocarboxylate or a pair of −OH−/H2O to balance the charge.72 Structural evidence of the missing linker defects in UiO-66 is provided by neutron powder diffraction in which the defects are described by a linker occupancy of 0.917, corresponding to an 8.3% missing linker vacancy.71 Single crystal X-ray diffraction (SCXRD) allows further insight into the defect sites. The replacement of carboxylate by terminal −OH−/H2O was proven by the electron densities around the carboxylate oxygens.71,74
The pore size distributions derived from N₂ adsorption isotherms of UiO-66 indicate the existence of large pores with a diameter of 1.7 nm, which cannot be explained by missing linker defects. This is attributed to the missing cluster defect, which results from the removal of a Zr₆ cluster, along with the 12 surrounding linkers (Figure 3c). Intuitively, the missing linker defects and missing cluster defects are believed to be randomly distributed throughout the MOF particle. However, synchrotron PXRD in combination with pair distribution function (PDF) analysis, anomalous X-ray scattering, and electron diffraction suggested a secondary crystalline phase formed by the missing cluster defects. In this case, a framework with reo topology is locally created and exists in the form of nanodomains, in which each cluster is only 8-connected (Figure 3c,e). Later, similar missing linker defects and missing cluster defects have been observed in other UiO-type structures with 3c,e. Later, similar missing linker defects and missing cluster defects are believed to be created in a one-pot reactions are still limited, because highly defective structures with relatively low stability cannot survive harsh solvothermal synthetic conditions.

Tuning MOF Properties by Defect Engineering. As many properties are strongly affected by defects, it is possible to tailor the performance of MOFs by defect engineering. The concentration of defects can be affected by synthetic conditions including the metal to ligand ratio, type of modulators, modulator concentration, reaction temperature, and so on. Generally, a less defective MOF can be generated with low metal to ligand ratios at high temperature. However, defects that can be created in a one-pot reactions are still limited, because highly defective structures with relatively low stability cannot survive harsh solvothermal synthetic conditions.

Linker labilization was developed to create a high concentration of defects in Zr-MOFs in a stepwise manner. A defect free Zr-MOF was initially synthesized with a mixture of stable linker and imine-based pro-labile linker. The pro-labile linkers are subsequently labilized by breaking the imine bond under acidic conditions to introduce missing linker defects. Taking advantage of the acid stability of Zr-clusters, the crystallinity of Zr-MOFs can be well maintained after the removal of labile linkers. This method allows controlled generation of defects in Zr-MOFs by changing the labile linker ratio and acid concentration. Later, this method was extended using thermolabile linkers instead of acid-labile linkers, which generates defects by thermal decomposition of linkers. A direct consequence of defects is the increased maximum pore volume and BET surface areas as a result of the expanded cavity and decreased material density.

Besides the increase of pore size and surface area, the defects also endow additional functions to the Zr-MOFs. The defect sites of Zr-MOFs were found to be active Lewis acidic sites for catalytic reactions, including cross-aldol condensation reactions, Meerwein–Ponndorf–Verley reactions, and the isomerization of α-pinene oxide. The Lewis acidity as well as the catalytic performance can be improved by defect engineering. For example, Vermootelen et al. used trifluoroacetic acid and HCl in the synthesis of UiO-66 to induce more defects as Lewis acidic sites after thermal activation. In another example, the degradation of chemical warfare agents by Zr-MOFs has been investigated. Hupp and co-workers have shown Zr-MOFs, NU-1000, can hydrolyze organophosphate-based nerve agents and simulants because of their Lewis acidity. The nerve agent simulant dimethyl 4-nitrophenyl phosphate is believed to bind to NU-1000 by hydrogen bonding with −H₂O/OH groups on the Zr₆-nodes as well as by weak π−π stacking interactions with the benzene ring of the organic linkers. The Zr-clusters with low connection numbers contain more Zr-OH and Zr-OH₂, leading to increased hydrolysis rates.

Functionalizing MOFs by Defect Modification. The existence of defects dramatically enhanced the versatility of Zr-MOFs, as the coordination vacancy provides a chemical handle for postsynthetic modifications. MOFs featuring low-connected Zr-clusters have been well-documented in which the connection number can be 11, 10, 8, or 6. These structures can be regarded as “intrinsically defective” MOFs with inherent coordination vacancies arranged in a crystallographically ordered manner. Taking advantage of these structures, a series of unique postsynthetic modification strategies have been developed, including linker incorporation and cluster metalation.

Ligand Incorporation. It was observed that the terminal linkages on the coordinatively unsaturated [Zr₆(μ₃-O)₆(μ₁-OH)₄(OH)₄(H₂O)₄(COO)₈] clusters (Figure 4b,e) can be replaced postsynthetically. This inspires the development of the solvent-assisted ligand incorporation (SALI) method by replacing the terminal linkages on the [Zr₆(μ₃-O)₆(μ₁-OH)₄(OH)₄(H₂O)₄(COO)₈] clusters with a different monocarboxylates, phosphates, and sulfates. For example, different perfluoroalkyl carboxylate entities were attached to the clusters of NU-1000 to enhance CO₂ uptake (Figure 4h,g). The postsynthetically attached linkages are believed to coordinate to the Zr₆ clusters by replace the −OH−/H₂O pairs (Figure 4a,d). Linker installation is an elegant example that takes advantage of the missing linker vacancy and postsynthetically installs linear linkers in the vacancy. A Zr-MOF, PCN-700, with 8-connected Zr₆ clusters and multiple missing linker sites at determined positions was constructed, and linkers with different lengths were sequentially installed at different defect sites. Systematic variation of the pore volume and decoration of pore environment were realized by sequential installation of multiple linkers with different lengths or functional groups, which
provides an effective method to functionalize Zr-MOFs.\textsuperscript{101} It was later demonstrated that the defect sites in UiO-66 and UiO-67 can be postsynthetically grafted with a monocarboxylic species. The missing linker defects in UiO-67 can also be “healed” postsynthetically by inserting a BPDC linker,\textsuperscript{79} a process similar to linker installation. These examples imply that the modification of defect sites by ligands can be a general method to functionalize Zr-MOFs.

Cluster Metalation. The Zr\textsubscript{6} cluster acts as an acid when reacting with carboxylates. Considering its amphoterism behavior, it is not surprising that the [Zr\textsubscript{6}(μ\textsubscript{3}-O)\textsubscript{4}(μ\textsubscript{3}-OH)\textsubscript{4}((OH)\textsubscript{3})(H\textsubscript{2}O)\textsubscript{4}(COO)\textsubscript{8}] clusters can also bind to metal cations as a base (Figure 4c). In fact, it has been reported that molecular Zr\textsubscript{6} clusters can bind with a heterometal through the bridging μ\textsubscript{3}-OH or μ\textsubscript{3}-O.\textsuperscript{102} In a Zr-MOF, the heteroatoms can be deposited on the coordinatively unsaturated Zr-cluster through gas-phase or liquid-phase methods.

The gas-phase immobilization of heterometals reassembles the atomic layer deposition process which requires organometallic reagents or metals as salt precursors.\textsuperscript{103−105} For example, exposing the NU-1000 samples in Zn(Et)\textsubscript{2} or Al(Me)\textsubscript{3} vapor led to the metatation of Zr\textsubscript{6} cluster by Zn\textsuperscript{2+} or Al\textsuperscript{3+}, respectively (Figure 4f,i).\textsuperscript{103} This is a close remittance to the hydroxylated metal-oxide surface where surface −OH and −OH\textsubscript{2} bind to metal precursors. Later, this method was extended to liquid-phase by directly reacting MOF with a solution of metal salts.\textsuperscript{106} Compared with the gas-phase deposition, the liquid-phase method can be easily applied to a wider range of metal precursors. This method was systematically explored by the Hupp group using NU-1000 as a platform, generating a series of metal clusters or metal−organic complex-based catalysts.\textsuperscript{97,107} Definitive evidence of the positions and coordination environments of the incorporated metal ions was provided by SCXRD using single crystalline PCN-700 as a platform.\textsuperscript{108} Note that coordination environment of postsynthetically incorporated metal can be more complicated in other MOF systems such as NU-1000. The metals can be disordered, partially occupied, or form multi-nuclear clusters around the Zr\textsubscript{6} clusters. The metalation of clusters does not occur exclusively on low-connected Zr-clusters. In fact, the μ\textsubscript{3}-OH on the 12-connected [Zr\textsubscript{6}(μ\textsubscript{3}-O)\textsubscript{4}(μ\textsubscript{3}-OH)\textsubscript{4}((OH)\textsubscript{3})(H\textsubscript{2}O)\textsubscript{4}(COO)\textsubscript{12}] clusters can also be deprotonated by a strong base such as [AuMe(PMe\textsubscript{3})], CH\textsubscript{3}MgBr, BuOLi, or Me\textsubscript{2}Mg, leading to the replacement of protons by metal cations.\textsuperscript{109,110} Lin and co-workers use this method to stabilize a single-site Mg-alkyl catalyst for the ketone hydroboration in UiO-type MOFs with 12-connected clusters.\textsuperscript{11}\textsuperscript{11}

The defect sites can also be coordinated by metallates such as molybdates, tungstates, vanadate, chromates, and arsenates.\textsuperscript{112−114} For example, UiO-66 has been modified with vanadate as a catalyst for olefin epoxidation.\textsuperscript{114} Defective Zr-MOFs have also been used to capture chromates and arsenates from water.\textsuperscript{113,115} Although this behavior looks similar to the incorporation of low-valent transition metals, they are essentially different. The Zr\textsubscript{6} clusters act as acids, whereas the metallates act as bases. This process can be regarded as an analogue of ligand incorporation.

Modification of defects is a valuable addition to the existing toolbox of postsynthetic methods\textsuperscript{116,117} to functionalize Zr-MOFs. Considering the high chemical stability of Zr-MOFs and the abundant functional groups/metals that can be post-synthetically incorporated, it is apparent that unlimited potential exists by the modification of defective Zr-clusters for applications in gas storage, water purification, and catalysis.

**Photocatalytic Properties.** The high chemical stability of M\textsuperscript{IV}-MOFs offers a wide scope of potential applications, especially under harsh conditions. Besides their conventional role in gas storage, M\textsuperscript{IV}-MOFs find emerging applications in Lewis acid catalysis, Bronsted acid catalysis, redox catalysis, photocatalysis, electrocatalysis, sensing, and biomedicine.\textsuperscript{118−120} For example, M\textsuperscript{IV}-MOFs have been studied for air purification of toxic gases such as ammonia, carbon monoxide, nitrogen oxides, sulfur-containing gases, etc.\textsuperscript{121−123} Recently, M\textsuperscript{IV}-MOFs have also shown promising performances in catalytic degradation of chemical warfare agents such as sarin and sulfur mustard.\textsuperscript{124} These applications have been well discussed in some comprehensive reviews.\textsuperscript{125−128} We do not intend to cover the great number of publications in all these areas. Instead, we will focus the photocatalysis as a representative example that takes advantage of the high chemical stability, d\textsuperscript{0} configuration, and unique photoredox activity of group 4 metal cations.

MOFs represent an array of nanosized metal-oxide clusters periodically arranged within the crystal lattice. Many metal-oxide semiconductors are known as heterogeneous photocatalysts for hydrogen generation, CO\textsubscript{2} reduction, and organic transformations. One representative example is TiO\textsubscript{2}, which is considered as one of the most successful photocatalysts due to its high conductivity, efficient charge separations, chemical stability, earth abundance, and relatively low toxicity.\textsuperscript{129,130} As an analogue of TiO\textsubscript{2} nanoparticles, Ti-MOFs with nanosized Ti-oxo clusters have been explored for their potential applications in photocatalysis. Upon the discovery of the first Ti-MOF MIL-125, they have been studied as a photocatalysts. Reversible photochromic behavior in MIL-125 was observed upon UV irradiation in alcohol, indicating the photoinduced generation of Ti\textsuperscript{3+} species.\textsuperscript{20} Later, MIL-125 and amino-functionalized MIL-125 (MIL-125-NH\textsubscript{2}) have been studied as photocatalysts for hydrogen generation, CO\textsubscript{2} reduction, and decomposition of organic dyes.\textsuperscript{121−133} The presence of electron donating −NH\textsubscript{2} groups contributes to the light absorption in the visible light region and facilitates the ligand to cluster charge transfer.\textsuperscript{50} UiO-66 and the NH\textsubscript{2}-functionalized analogue (UiO-66-NH\textsubscript{2}) also show photocatalytic activity toward H\textsubscript{2} generation and CO\textsubscript{2} reduction.\textsuperscript{25,134} In most cases, sacrificial donors and cocatalysts such as Pt nanoparticles are used to assist hydrogen production.

The effects of metal clusters were investigated by comparing the photocatalytic hydrogen production efficiency of UiO-66-NH\textsubscript{2}, MIL-125-NH\textsubscript{2}, and PCN-415-NH\textsubscript{2}.\textsuperscript{48,58} The existence of Ti significantly improved the photocatalytic activity as indicated by the much higher activity of Ti-containing MOF (MIL-125-NH\textsubscript{2} and PCN-415-NH\textsubscript{2}) than the purely Zr-based UiO-66-NH\textsubscript{2}. Transient absorption spectra, electron paramagnetic resonance (EPR) spectra, and computations revealed that the Ti cluster allows for long-lived charge separation and efficient utilization of the photogenerated electrons by the generation of Ti\textsuperscript{3+} species, whereas the excitation lifetime of Zr-MOFs is...
much shorter. Computational results also suggest that the excitation of UiO-66-NH$_2$ is purely ligand-based, as the d-orbitals of Zr do not effectively overlap with the π* orbital of the ligand. In contrast, ligand to metal charge transfer (LMCT) can be achieved in Ti-MOFs to allow for long-lived charge separation and high photocatalytic performance in hydrogen production reactions. A LMCT mechanism was proposed for photocatalytic hydrogen generation. The BDC-NH$_2$ linkers absorb visible light and transfer the photoexcited electrons to the Ti-cluster, forming the Ti$^{3+}$ intermediate. The stabilized electrons on the Ti-cluster are then transferred to the Pt nanoparticles where the proton reduction takes place. Meanwhile the photogenerated holes on the BDC-NH$_2$ linkers were reduced by sacrifice donors, fulfilling the catalytic cycle (Figure 5).

Figure 5. Proposed mechanism of the hydrogen generation reaction catalyzed by Pt@MIL-125-NH$_2$.

While the visible light absorption of BDC-NH$_2$ is still limited, porphyrin-based linkers can significantly increase the light absorption efficiency of MOFs. In fact, porphyrin-based MOFs with metal-oxide clusters connected to porphyrin sensitizers are inherent dye sensitized photocatalytic systems that potentially mimics porphyrin-sensitized metal oxides. Our group integrated the Ti-cluster and photosensitizing porphyrinic linker into a MOF named PCN-22. As a proof of concept, PCN-22 was employed as a photocatalyst for an alcohol oxidation reaction. Later, the Zr-porphyrin MOFs, PCN-222 (also known as MOF-545) and MOF-525, were also investigated as a photocatalyst for CO$_2$ reduction. Compared with inorganic semiconductors, MOFs provide additional opportunities to control the light-absorption properties by functionalizing the organic linkers. The introduction of −NH$_2$ substituted linkers or specific chromophores can effectively enhance the photoresponse of MOFs. The porous structure makes each single metal-oxide cluster in MOFs accessible by the substrates, which facilitates the catalytic reaction. However, although the optical band-gaps of MOFs are similar to metal-oxide semiconductors, the located electronic states indicate that they are mostly insulators. The low conductivity of MOFs inevitably limits their applications especially in photoelectrochemical devices. So far, studies of MOFs in photoelectrocatalysis mainly focus on either oxidation or reduction half reactions, and their performances are still far from competing with other state of the art systems.

OUTLOOK

With escalated research interest in stable MOFs, the field of M$^{IV}$-MOFs has been flourishing in the past few years. An overview of the history of Zr-MOFs and Ti-MOFs suggests that the bottleneck of Ti-MOFs lies in the lack of a general synthetic method. The discovery of Ti–Zr bimetallic clusters provides a way to overcome these synthetic difficulties. A new class of Ti–Zr bimetallic MOFs is envisioned, and their applications await exploration.

The high concentration of defects in Zr-MOFs offers an additional opportunity to incorporate functional groups in the defect sites.

As a unique feature of Zr-MOF, defects are discussed with an emphasis on their effect on MOF properties. The high concentration of defects in Zr-MOFs offers an additional opportunity to incorporate functional groups in the defect sites. We introduced two methods to tether organic linkers or metals on the defect sites and their possible applications. These examples are not exhaustive, but represent the vast opportunities to functionalize Zr-MOF for specialized applications by the modification of Zr$_6$ clusters. Considering the similarity between Ti and Zr, defects are expected to exist in Ti-MOFs and Ti–Zr bimetallic MOFs. The Ti-MOFs and Ti–Zr bimetallic MOFs provide suitable platforms for the study of defects and their related applications. We anticipate that this research area has the potential to be greatly expanded, resulting in a new class of robust MOF materials with desired functionalities.
Outlook

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