Perspectives on titanium-based metal–organic frameworks

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Abstract

Chemistry of titanium metal–organic frameworks (Ti-MOFs) encompasses the linking of various titanium-oxo clusters formed mainly by hydrolysis of titanium precursors and organic linkers. Owing to the high reactivity of such titanium precursors, the crystallites of Ti-MOFs are hardly obtained without applying tricky synthetic approaches. For the past decade, scientists have exhaustedly pursued many methodologies to overcome the synthetic challenges of Ti-MOFs. Achievements are indeed observed. However, challenges remain, which not only hinder the versatility of Ti-MOF chemistry but also limit their applications in photocatalysis. This perspective seeks to concisely summarize the Ti-MOF chemistry and discuss viewpoints of the author on how to promote the diversity of Ti-MOFs. The author hopes that future perspectives of this work will help direct the research in this field.

1. Introduction

Reticular chemistry of metal–organic frameworks (MOFs) lies at the heart of linking discrete metal clusters and organic linkers (both are denoted by secondary building units or SBUs) by strong bonds [1, 2] that rigidify the connectivity of metal SBUs and organic building units in the form of porous, crystalline, and extended structures. Key factors to the success of MOF chemistry include the diversity of metal-oxo clusters with various geometrical arrangements and unlimited numbers of organic linkers that can be functionalized in the manner that perfectly fits with the metal SBUs [3–5]. MOF chemistry has recently been exponentially developed given that the number of new MOF structures reaches greater than 80 000, of which the metal component of MOFs spans from s-block elements, transition metals to rare-earth metals in the periodic table [6]. Especially, MOFs consisting of transition metal clusters are most dominant due to the pronounced characteristics of p- and d-block elements [7]. The transition metals of d-block include one of the most applicable metals in chemistry: titanium. The chemistry of Ti-based MOFs, however, suffers great challenges of synthesis—the extremely reactive activity of titanium precursors. Therefore, combination of organic linkers and titanium salts for constructing Ti-MOFs is incompatible [8–11]. As a result, there lacks diversity in the Ti-MOF chemistry which the outstanding features of Ti-oxo clusters combined with intrinsic properties of MOFs can be employed for many kinds of applications that require highly robust architectures and stable frameworks which otherwise is arduous or even cannot be achieved.

One may say that if we only focus on the chemistry of Ti-MOFs, that would be very limited due to the small number of reported MOFs based on Ti-oxo clusters. I would say ‘no, the chemistry of Ti-MOFs is not limited but lack methodologies to diversify it.’ In order to corroborate this statement, let us consider the following example: MOFs themselves whose chronological advances have been gone through the early state of coordination solids, Werner complexes, Hofmann clathrates, then coordination networks, and the recent large state of MOFs [12]. It is apparent that the extended chemistry of crystalline materials, now preferred reticular chemistry, has been grown during two centuries. And recently, how great of the MOF diversity compared to the predecessor, coordination networks? The key to this answer relies on methodologies to link metal clusters by organic building units through strong bonds [1, 2, 12]. It is quite similar to the recent state
of Ti-MOF chemistry where we are looking for different approaches to alleviate the reactivity of titanium precursors so that they can further react with organic linkers to form crystalline structures.

Recently, we are facing the energy shortage and related global energetic issues due to the major activity of heavy industry and vast energy consumption originating from the population growing [13]. Ameliorating the fossil-fuel reliance, therefore, is one of the urgent tasks. In light of photochemistry, using photocatalysts to create renewable energy through chemical reactions (e.g. water splitting, CO₂ photoreduction, H₂ evolution, etc) can solve this global problem [14]. This lofty task turns out that it is necessary to develop novel photocatalysts for such photochemical reactions. In this context, Ti-based MOFs are promising candidates due to their well-known photoredox properties of Ti-oxo clusters and the linkers acting as antenna entities to absorb visible light irradiation [8–11]. Correlating the aforementioned purpose and the one to diversify the chemistry of Ti-MOFs, in this special issue, I briefly summarize the foundational chemistry of Ti-MOFs and methods to promote their chemical diversity. Additionally, I would like to take this opportunity to discuss future perspectives on new designs of Ti-MOFs as well as photocatalytic applications that needs to be focused on and improved. Due to the scope of this perspective, synthesis, structural characterizations, and detailed applications are not the main focuses. Interested readers are directed to the literature.

2. Notion of discovery of extended titanium frameworks

Common titanium resources including TiCl₄, Ti(alkoxide)₄, and Ti(alkylamido)₄ are commercially available. Considering the coordination number of these available titanium compounds which is 4, it is understandable that such titanium salts are highly reactive: they most strongly hydrolyze under humidity conditions, especially in the aqueous medium to form compounds whose structures possess higher coordination number (e.g. 6 or even higher). Titanium oxide (TiO₂; Ti atoms bear coordination number of 6) is formed under this mechanism. This hydrolysis behavior is observed for the formation of well-known, multiple, and diverse titanium-alkoxide clusters. Indeed, such formation of titanium-based complexes was first evidenced by Bradley in 1955 [15, 16]. Especially, the crystal structure of the first titanium heptameric clusters formed by the hydrolysis of titaniumtetraethoxide was then reported by Watenpau using single-crystal x-ray diffraction (SXRD) technique in 1967 [17]. Along with SXRD, characterization methods using oxygen nuclear magnetic resonance (¹⁷O-NMR) spectroscopy were also developed to aid the rich versatility of the chemistry of titanium alkoxides and carboxylates [18]. Recently, such titanium-oxo clusters bearing the number of titanium atoms from 3 to 28 can be synthesized under solvothermal synthesis, ionothermal synthesis, inert conditions, and aqueous medium [19, 20].

Titanium-oxo clusters are discrete complexes so they are dissolvable in common organic solvents and therefore are applied for thin film deposition. Particularly, due to the low stability, titanium-oxo clusters are straightforwardly transformed into TiO₂ in forms of sol, gel, or powders under solvothermal or ambient conditions [19, 20]. Exploiting these two properties of titanium-oxo clusters, scientists have studied their photoresponsivity by applying the thin film deposition techniques: Titanium-oxo clusters are first dissolved in solvents and then drop-casted onto specific electrodes.

Although the photoactivity of titanium-oxo clusters is pronounced and can easily be tailored by altering their crystal structures via linker modifications, the low stability hinders their practical applications [20]. The solubility of titanium-oxo clusters also limits their recyclability. In order to further employ the potential photoresponsive behavior of titanium-oxo clusters, such clusters should be rigid, stable, and even infinite. Therefore, it is imperative to reticulate such kinds of titanium clusters into extended structures so that their photoactivity will be incorporated with the porous characteristic of infinite structures, for example TiO₂, zeolites, and most recent developed materials, reticular materials.

Before discussing the chemistry of Ti-based MOFs, let us consider the widely applicable oxide, TiO₂ whose structure presents infinite backbone, porosity, and semiconductor aspects [21].

The applicability of TiO₂ as a semiconductor was discovered by Fujishima and Honda who, in 1972, observed the groundbreaking behavior of TiO₂ hydrolyzing water under ultraviolet (UV) irradiation [22]. This discovery paved the way for scientists working on photochemistry to study and develop many kinds of semiconductors (e.g. metal alloys, nanowires, quantum dots, graphene composites, polymers, etc) applied for a variety of photocatalytic applications (photoreduction of CO₂, water splitting, hydrogen evolution, organic transformation, and many more) [23–25]. These photocatalysts work well under either UV light or visible light irradiation, of which the latter is more beneficial because the use of ubiquitous attributes of the solar energy can be employed, thus eliminating the required input energy of UV light for activating the photocatalysts.

Although TiO₂ has been commercially used for a long time, it remains one big drawback: TiO₂ adopts a large bandgap energy of 3.2 eV, therefore it can only be activated under UV irradiation (scheme 1). The surface area, active sites, and pore structures of TiO₂ are difficult to be customized. Therefore, looking for a
new class of photocatalysts whose structures rely on the visible light photoresponsiveness and inherit, even surpass the structural measures of TiO$_2$ (i.e. porosity, crystallinity, and structural modification), is highly encouraged. At this juncture, we consider and endorse Ti-MOFs.

3. Promoting structural diversity in Ti-MOFs

It is undoubted that MOFs, albeit being developed just 25 years, are one of the most interesting materials that have been researched in over 100 countries and manifested by over 80,000 structures [6, 26]. Of these, the metal-oxide SBUs constituting MOF structures are very diverse, which include almost all metal elements in the periodic table [6]. However, MOFs based on titanium-oxo clusters are sparse and only hold a very small fraction (less than 0.1%) compared to those MOFs comprising of other metal clusters.

In addition to advanced aspects such as well-defined structures, large porosity, high concentration of active sites, and a high degree of flexibility inheriting from reticular chemistry of MOFs, Ti-MOFs possess three outstanding features that distinguish them from the other MOFs:

(a) Appealing photoresponsive properties (i.e. bandgap being engineered and structures being tailored for specific photocatalytic reactions are key factors to the success of Ti-MOFs in photocatalysis) which are necessary and the main concerns for sustainable photocatalysts used for various photochemical reactions.

(b) High stability under harsh working conditions thus making them be promising candidates for industrial applications.

(c) Low toxicity which renders Ti-MOFs to be potential for a wide range of photocatalytic applications and commerciality.

Although Ti-MOFs adopt many outstanding and attractive properties, synthesis of such materials suffers a great challenge that originates from the strong reactivity of titanium resources, as mentioned above, they are prone strongly to hydrolyze or react with water to form TiO$_2$. This negatively affects the formation of MOF structures and impedes the crystallization process. Moreover, being highly reactive, titanium salts quickly react with carboxylate-functionalized linkers to generate Ti–O bonds which are strong bonds and such bonding formation hinders the bonding association and dissociation process, thus preventing the self-correction error [8–11]. As a consequence, it is so difficult that common solvothermal conditions can lead to crystalline Ti-MOFs; such synthetic conditions must be precisely controlled, otherwise amorphous solids are usually obtained during the synthesis of Ti-MOFs.

In order to deal with this challenge, reticular community has focused on controlling pH environment [27], solvothermal conditions [28], and most recently, synthetic methods including cluster approach [29], mixed metal strategy [30], and high throughput procedure [31]. Indeed, using acetic acid as either a solvent or a pH controller, reported by Zhang et al [27], is a powerful synthetic method to synthesize Ti-MOFs with large crystal size. More specifically, this method is largely applied for many other synthetic procedures in producing new Ti-MOFs.

3.1. Early state of Ti-MOFs: the importance of the hydrothermal synthesis

The first two open frameworks of Ti-based MOFs date back to the early 2000s when Serre and Férey reported MIL-25 [32] and MIL-91 [33] whose structures are composed of Ti-oxo clusters tethered by methylenbis(phosphonate) and N,N’-piperazinebismethylene phosphonate, respectively. Both are
Figure 1. Crystal structure of MIL-125 consisting of eight-membered rings of Ti-oxo clusters tethered by 1,4-benzenedicarboxylates to generate a 3D structure based on \textit{fcu} topology. Atom colors: Ti, blue polyhedra; C, black; O, red. H atoms are omitted for clarity.

synthesized using hydrothermal conditions: autogenous pressure at a high temperature (>200°C). MIL-91 exhibited a permanent porosity of 500 m$^2$ g$^{-1}$, based on Langmuir method. This structure presents open pores that are suited for CO$_2$ capture because of its small size of 4 Å and the strong polarity of phosphonate-functionalized backbone which links to octahedral TiO$_6$ clusters sharing corners to form infinite units.

3.2. The first Ti-MOF made up of carboxylate linker—a breakthrough achievement
As discussed above, the high reactivity of titanium salts with carboxylate-based linking units leads to the difficulty of forming crystalline products as evidenced by the fact that the first Ti-MOF based on carboxylate linker (1,4-benzenedicarboxylate or BDC), termed MIL-125, was reported in 2009 by Férey \textit{et al} \cite{28} (figure 1). The success of making MIL-125 lies in the use of an appropriate solvent mixture ($N,N'$-dimethylformamide/methanol) at 120 °C. These solvothermal synthetic conditions are further applied to make an isoreticular version (MOFs with similar structure type) of MIL-125 using NH$_2$-BDC linker \cite{34}. It is worth mentioning that these two seminal materials open a new sky of using Ti-MOFs for photocatalytic applications. Furthermore, the solvothermal conditions along with the pH control pave the way for making many Ti-MOFs consisting of various carboxylate-functionalized linkers (MIL-177-HT \cite{35}, Ti-(Ti-TBP) \cite{36}, COK-47 \cite{37}, and ZSTU series \cite{38}).

3.3. Does the cluster approach the answer for making Ti-MOFs?
If we look into the literature from the discovery of MIL-125 (2009) until 2015, there almost exists no new chemistry of Ti-MOFs due to the vexed issue of hydrolysis of titanium precursors. In order to overcome this circumstance, we must alleviate the reactivity of titanium precursors in the MOF synthesis. There are two ways to achieve this purpose: either using preformed Ti-oxo SBUs or generating the targeted cluster \textit{in situ}.

The first approach was reported by Zhou \textit{et al} \cite{29} and the latter was published by Yaghi \textit{et al} \cite{39}.

Especially, the preformed Ti-oxo method relies on employing the reticular synthetic approach whereby the targeted clusters were first synthesized and subsequently used to react with organic building units to finally create predictable structures. Bearing this idea in mind, Zhou \textit{et al} synthesized a hexameric titanium-oxo cluster \cite{40} whose structure is made up of trigonal prism of Ti hexanuclearity alternatively linking to trigonal prism of oxo atoms; this cluster under solvothermal conditions is not stable being decomposed and rearranged to unprecedented heptameric clusters that react to tetratopic porphyrine-based carboxylate linker to finally generate single crystals of PCN-22—the first single crystals of Ti-MOFs based on carboxylate linker and exhibiting large surface area (1284 m$^2$ g$^{-1}$) \cite{29}. 
Figure 2. Reticular design of MOF-901 and MOF-902. The hexameric Ti clusters are formed in situ and linked by benzenedialdehyde and biphenyldialdehyde to form MOF-901 and MOF-902, respectively. Both are isoreticular structures crystalizing in hxl topology. Atom colors: Ti, blue; C, black; O, red; H, light pink. Reprinted with permission from [41]. Copyright 2017, American Chemical Society.

It should be noted that the rearrangement of Ti hexanuclearity to Ti heptanuclearity possibly hinders the crystal structure determinations if single crystals are not obtained. This procedure additionally falls short of the designed synthesis of targeted structures, though it provides excellent strategy to diversify the chemistry of Ti-MOFs. In order to solve this issue, Yaghi et al later report the synthetic approach that relies mainly on the in situ formation of hexameric titanium-oxo cluster [39]. In particular, this cluster was formed under methanolic solution at a moderate temperature (120 °C) by the reaction of 4-aminobenzoic acid and titaniumtetraisopropoxide; such in situ clusters were subsequently linked together by benzene-1,4-dialdehyde through imine condensation. MOF-901 adopting hexagonal layer structure was obtained. This work combining the chemistry of MOFs and covalent organic frameworks (COFs) underlines the importance of reticular design in targeting the synthesis of novel Ti-MOFs. Interestingly, the isoreticular structure of MOF-901 can also be obtained using elongated aldehyde linker. This is the only Ti-MOF example having two isoreticular forms from linkers with different lengths at that time (figure 2) [41].

The cluster approach has influentially underpinned many research groups to synthesize novel Ti-MOFs. Particularly, this paves the way for the synthesis of DGIST-1 reported by Park et al [42].

3.4. De novo synthesis leads to a variety of Ti-MOFs with diverse topologies and high porosity
Inspired by the exquisiteness of reticular chemistry of Ti-MOFs, but at this point, the diversity and multiplicity of structures, topologies, and porosity of Ti-MOFs are at its infancy, Martí-Gastaldo et al developed the high-throughput synthesis that is based mainly on the hydrolysis control of titanium precursors over solvent mixture and pH environment for synthesizing MUV-10 [31] (the topology; 1041 m² g⁻¹), mesoporous MIL-100(Ti) [43] (mtt topology; 1321 m² g⁻¹), MIL-101(Ti) [44] (mtt topology; 2970 m² g⁻¹ reported by Long et al), and heterometallic Ti-MOFs [45] (MUV-101(Fe/Co/Ni/Zn): mtt topology and MUV-102(Cu): tbo topology). It is worth mentioning that the difficult synthesis of Ti-MOFs is main factor impeding the success of this area.

The de novo method here showcases that the resulting Ti-MOFs are reproducibly obtained independent on the use of titanium precursors. Additionally, the postsynthetic metalation induces the topological transfer which, for the first time, topologies of Ti-MOFs can be varied under mild conditions by adjusting the reaction time of the exchange process (figure 3). This work underlines the ability of employing postsynthetic modification to diversify the chemistry of Ti-MOFs that are based on multiple active metal sites which possibly open a new insight into the use of heterometallic Ti-MOFs for photocatalytic applications. This prospect is also evidenced by the recent work conducted by Martí-Gastaldo et al applying heterometallic photocatalyst MUV-101 for hydrolyzing nerve agent simulants (figure 3) thanks to their open metal sites [46].
4. New chemistry of Ti-MOFs: what are we looking for?

4.1. New designs for Ti-MOFs

It should be mentioned that it is complicated to predict the resulting products of Ti-MOFs. Unlike other MOFs, isoreticular forms with various linker lengths in Ti-MOFs are rare (except for a few) [39, 41, 42]. Up to now, only two examples of Ti-MOFs fall under the umbrella of reticular chemistry. They are MOF-901 and MOF-902 whose structures present the conceptual basis of reticular chemistry that is linking hexagonal clusters together by linear building units; in this case, the topology is subsequently formed [39, 41]. The others are generated based mainly on case-by-case synthesis and trials and errors. However, thanks to the high-throughput and de novo synthesis, we possibly predict the structure output of the Ti-oxo clusters [31, 43, 45]; therefore, the major challenge now is to control the reactivity and compatibility of organic linkers and titanium precursors. We are looking forward to having more multipotent linkers that can form crystalline Ti-MOF products with appealing structures. The main reason for pursuing Ti-MOF structures with multipotent linkers relies on the fact that such linkers will be able to not only create complex structures but also increase possibilities of having MOFs with large surface areas [47]. In this context, designed linkers that adopt multifunctionalities (carboxylate, hydroxyl, carbamate, hydroxamate, phosphonate, etc) would help expand the valency of Ti SBUs from discrete units to infinite clusters increasing the stability and activity in photocatalytic reactions. Furthermore, we think that the hydrophobic/hydrophilic balancing of a Ti-MOF backbone could be engineered by altering the multiple functionalized linkers. Such designs would maximize the interaction between MOF frameworks and adsorbates (water, CO$_2$, or H$_2$), thus increasing the adsorption/desorption rate between starting materials and photocatalysts during the photocatalytic process—one of the most important factors contributing to stabilizing intermediates and therefore enhancing the photocatalytic performance [48].

It should be noted that the synthesis of Ti-MOFs has recently attained notable achievements using cluster approach and de novo synthesis through pH control (via modulators). In terms of using cluster approach, the synthesis is recently based largely on hexameric titanium cluster (Ti$_6$O$_6$(OPr)$_6$(-COO)$_6$) which is decomposed under solvothermal conditions. The versatile chemistry of titanium alkoxides, however, is much further than that. It would be worth pursuing the synthetic approach that combines de novo synthesis and cluster approach using different kinds of Ti-oxo clusters in which the starting clusters retain their geometrical structures after linkage exchange reaction. This strategy will possibly expand the structural library of Ti-MOFs, as reported very recently by Zhang and Wang et al. The authors used Ti$_{44}$-oxo cluster as starting cluster source to synthesize three Ti-MOFs termed FIR-125, FIR-126, and FIR-127. Indeed, the Ti$_{44}$-oxo cluster was decomposed and transferred to Ti$_8$ cluster similar to those clusters of MIL-125 and MIL-125-NH$_2$ [49].

4.2. Linker modifications

For the past decade, many research groups have concentrated too much on using the cluster approach, mixed-metal approach, and acidic modulators for making new Ti-MOFs [27–31]. Such approaches worked well; more and more Ti-MOF structures have been prepared up to now. Nevertheless, the role of organic linkers is less investigated. In fact, as discussed above, very little data report the use of isoreticular structure of linkers for reticulating Ti-MOF frameworks, except for MOF-901, MOF-902, and ZSTU series [39, 41, 42], which means that there still exist empty rooms for examining the ability of organic linkers having similar geometrical structures in making Ti-MOFs. Such designed linkers may possess functional groups that change
the electronic structures, dihedral angles, or steric hindrance. This idea dates back to the early 2000s when Yaghi reported the applicability of bromide-functionalized carboxylate in directing the synthesis of nbo topology [50] instead of sql. This concept is recently employed to selectively crystallize jfh topology in 3D COFs [51]. Furthermore, the constrained linkers are widely used for the conformational design of various topologies in Zr-MOFs [52]. Taking this into account, we believe that the conformationally designed linkers will be of great interest to aid the diversity of Ti-MOF chemistry in near future.

4.3. Postsynthetic modifications and beyond

Postsynthetic modification [53] is well-known in reticular chemistry whereby the pristine frameworks play an important role of host structures allowing the postsynthetic transformation including linker exchange, metalation, and reactions on the backbone. Metalation is largely applied and it is one of the important methods to introduce Ti atoms into the existent structures—diversifying Ti-MOFs by indirect synthesis [54–56]. In a recent study, Lin et al apply the postsynthetic metalation to introduce single Co$^{2+}$ catalytic sites into Ti-oxo cluster of MIL-125 (figure 4). The resulting heterometallic-based MIL-125 promotes arene hydrogenation with excellent performance [57]. The use of linker exchange, and considering the host titanium frameworks as solid complexes for organic transformations, however, are muted. A bold guess that lies mainly in the use of solid–solid transformations in which the pristine Ti-MOFs act as starting materials is likely emerging. In other words, by using appropriate linkers that allow postsynthetic modification, versatility of Ti-MOFs in terms of either fundamental chemistry or applications can be explored.

4.4. Photocatalytic applications

Applications of Ti-based MOFs were comprehensively discussed by Serre, Nguyen, Zou, and Zhang [8–11]. Indeed, the applicability of Ti-MOFs covers a wide spectrum spanning from dye degradation, organic transformation, hydrogen evolution, water splitting, and CO$_2$ photoreduction. It should be realized that such applications mainly resort to the photoresponsive behavior of the seminal material MIL-125-NH$_2$. The reasons why MIL-125-NH$_2$ has been used dominantly are:

(a) The synthesis of MIL-125-NH$_2$ is scalable for from-laboratory-to-pilot production since two components made up of the material are commercially available.

(b) Its bandgap energy is around 2.6 eV; the energy level of conduction band based on density functional theory calculation is around $-1.2$ eV which is more negative than the potentials of CO$_2$ reduction thus enabling MIL-125-NH$_2$ for CO$_2$ photoreduction under visible light irradiation.

(c) Last but not least, the structure of MIL-125-NH$_2$ can be precisely engineered using postsynthetic modification for targeted applications.

Recently, more Ti-MOF structures made up of commercial linkers (MUV series, ZSTU-2, and MIL-100(Ti)) have been reported. Applications in renewable energy using such materials are highly encouraged to expand the scope of applications using Ti-MOFs.

Table 1 summarizes some emerging Ti-MOF photocatalysts for various applications.
One of the big bottlenecks of using MIL-125-NH₂-based photocatalysts for CO₂ reduction is that the reduced products are formed with low yield and less selectivity. As discussed in my recent review [58], the chemistry of MOF catalysts used for photoreduction of CO₂ focuses on the bandgap engineering, active-site modifications, suppressing the combination of photoexcited electrons and holes, enhancing CO₂ interaction, and composites. Of these, MIL-125-NH₂ and mixed Zr/Ti-Uio-66 being engineered the bandgap energy and active-site mediators are able to catalyze the CO₂ photoreduction to HCOO⁻. However, the production yield is still low (16.3 µmol g⁻¹ h⁻¹) for MIL-125-NH₂ [59] and 11.6 µmol g⁻¹ h⁻¹ for Zr/Ti-Uio-66 [60]. We are curious about how Ti-MOFs with polar frameworks that enhance CO₂ interaction may improve the production yield since the CO₂ adducts can be stabilized during the photoreaction process. Additionally, heterojunction-based Ti-MOFs (composites) would be of great interest to solve the low yield issue and selectivity (we look forward to more photocatalysts capable of promoting 4-e, 6-e, or even 8-e CO₂ reduction products).

The same issue mentioned above for using Ti-MOFs as photocatalysts for water splitting including overall water splitting, hydrogen evolution, and oxygen evolution reactions. Indeed, overall water splitting remains many challenges (e.g. back reaction to water because of the uphill reaction, lack of stable catalysts, and inefficient photocatalytic activity since overall water splitting requires low bandgap, 1.23 eV) that cannot be solved within next few years [61, 62]. In this context, new chemistry of Ti-MOFs with impact solutions such as mixed metal clusters, co-catalysts, and/or composites is required. In contrast to inefficiency of Ti-MOFs in overall water splitting, Ti-MOF photocatalysts are able to promote H₂ evolution in the presence of sacrificial agents although there are few publications for this application [63]. Studies for enhancing the photocatalytic performance of Ti-MOFs for H₂ or O₂ evolution are still in the early stage and must be pursued relentlessly in the future. Ti-MOFs may hold promises for the near future as long as the diversity of this field is further expanded as similar to the Zr-MOF counterpart [51]. Finally, apart from the conventional photocatalytic applications (e.g. CO₂ photoreduction or photocatalytic water splitting) we encourage new applications using Ti-MOFs such as water uptake, polymerization, or degradation of nerve agents.

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