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Use of the Advantages of Titanium in the Metal-Organic Framework

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Abstract

Titanium is one of the most attractive elements, due to its unique advantages such as stability, recyclability, activity under light absorption, cheapness, and safety. The special characteristics of titanium include different oxidation states, high coordination number of Ti^{4+} , and the ability to form strong bonds with oxygen and different ligands, making it a good candidate for the construction of the new composite named metal-organic framework or briefly MOF. MOFs are composites that have opened a new window toward the scientific world due to their special structure that makes them have some properties, including the highest surface activity, high porosity, tunable pore, and high flexibility in design that make them useful in different applications, such as gas storage and separation, liquid separation and purification, electrochemical energy storage, catalysis, and sensing. Titanium, due to the mentioned properties, has been used as a node in the structure of different MOFs and applied in different fields.

Keywords: titanium, MOF, photocatalyst, modification

1. Introduction

Coordination polymers (CPs) are a class of compounds formed by metal ions (or clusters) coordinated to multidentate organic and/or inorganic ligands. Metal-organic frameworks (MOFs) are a special group of CPs with porous and crystalline one-, two- or three-dimensional structures. These compounds are composed of metal ions or well-defined secondary building units and organic linkers that are connected by coordination bonds and other weak interactions or noncovalent bonds, such as H-bonds, π -electron stacking, or van der Waals interactions [1]. In the 1960s, the MOF kind of structure was firstly introduced by Tomic and others [2–4]. In the 1990s, research on MOF was developed by Robson et al. [5, 6] and later by Yaghi et al. [7].

After the discovery, synthesis, and characterization of the first known MOF structure, MOF-5 ($[Zn_4(BDC)_3(DMF)_x]$) by Yaghi and coworkers in 1999, a rapid advancement has been made in the chemistry of MOFs [8]. The increasing interest in MOF research can be attributed to their amazing properties, including high specific surface area, ultra-high porosity, tunable surface chemistry, functional diversity, and crystallinity [9].

The main goal of this chapter is the use of titanium as a node in the design of metal–organic frameworks. To achieve this goal, we will specifically investigate the characteristics and properties of titanium as a component in the design of metal–organic frameworks. In the following, considering the features and advantages mentioned in the text for titanium, we will introduce the types of titanium-based MOFs, synthetic methods, and applications. Eventually, the comparison of the properties and performance of titanium-based MOFs with other metal–organic frameworks is discussed.

2. Synthesis of MOFs

MOFs are constructed by connecting inorganic and organic building units through coordination bonds. The inorganic units can be monovalent (Cu^+ , Ag^+ , etc.), divalent (Mg^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , etc.), trivalent (Al^{3+} , Sc^{3+} , V^{3+} , Cr^{3+} , Fe^{3+} , Ga^{3+} , In^{3+} , lanthanides³⁺, etc.), or tetravalent (Ti^{4+} , Zr^{4+} , Hf^{4+} , Ce^{4+} , etc.) metal cations or clusters, namely secondary building units (SBUs) (e.g., $\text{Zn}_4\text{O}(\text{COO})_6$, $\text{Cu}_2(\text{COO})_4$, $\text{Cr}_3\text{O}(\text{H}_2\text{O})_3(\text{COO})_6$, and $\text{Zr}_6\text{O}_4(\text{OH})_{10}(\text{H}_2\text{O})_6(\text{COO})_6$) [10]. These inorganic units are connected by coordination bonds to organic linkers, which commonly contain carboxylate, phosphonate, pyridyl, and imidazolate, or other azolate functional groups [11].

Different synthesis methods have been developed and applied to synthesize MOFs to achieve the required properties in terms of shape, surface morphology, and others for various applications. The major synthesis methods of MOFs include hydrothermal (solvothermal) synthesis, mechanochemical synthesis, microwave-assisted synthesis, sonochemical synthesis, and electrochemical synthesis [12–15].

Solvothermal/hydrothermal synthesis is the most conventional method for the synthesis of these compounds. If water is used as a solvent, this method is termed as a hydrothermal method. This method generally consists of the self-assembly of soluble precursors, which contain the metal and the organic component. The key point of this method is the selection of the appropriate solvent because the solvent acts not only as a reaction medium but also as a structure-directing agent. Some examples of this synthesis include MOF-5 [16], MOF-74 [17], ZIF-8 [18], and Uio-66 [19]. The advantages of this technique are a large operating temperature range, relatively easy transposition, and high yield. Disadvantages include high energy consumption and a long reaction time [20].

Another commonly used method is mechanochemical synthesis, which is a green approach performed by grinding a mixture of the organic linker and metal salt in an agate mortar and pestle or in a ball mill and in the absence of solvent. Examples of this method include HKUST-1 [21], ZIF-4, and ZIF-8 [22].

In microwave-assisted synthesis, energy for the reaction is provided in the form of microwave radiation (MW). Advantages include a reduction in crystallization time and higher yields, on the other hand, disadvantages include difficulty in controlling the shape and size and the lack of a direct method for scale-up [20]. Examples include CoMOF-74 [23] and Cr-MIL-100 [24].

The ultrasonic/sonochemical method is another efficient synthesis of MOFs under ultrasonic irradiation. The impact of ultrasound on liquid and colloid systems is mainly caused by acoustic cavitation, which would be the production, growth, and implosion of bubbles within the solvent. The advantages of this method include homogeneous particle size and morphology in short periods of time and the

formation of stable structures due to the high energy and high pressure created during this process [20]. Fe-MIL-53 [25] and MOF-177 [26] are some examples of MOF materials synthesized through this ultrasonic method.

In the electrochemical method, metal ions rather than metal salts are introduced in the anode, whereas an organic linker is placed at the cathode and the electrochemical cell is filled with conducting salt. This technique was reported by BASF in 2005. The advantages of this method are avoiding anions, such as nitrates, from metal salts, lower temperatures of reaction, and extremely quick synthesis [12]. Some examples of this synthesis are ZIF-8 and MIL-53 (**Table 1**) [27].

Synthetic method	Advantages	Disadvantages	Examples	Ref.
Hydro(solvo)thermal	<ol style="list-style-type: none"> 1. Large operating temperature range (i.e., between 80 and 250°C) 2. Easy transposition 3. High yield 	<ol style="list-style-type: none"> 1. High energy consumption 2. Long reaction time 3. Expensive pressure-sealed metal vessels and heating ovens 	MOF-5 ZIF-8	[16, 18]
Mechanochemical	<ol style="list-style-type: none"> 1. Solvent-free synthetic method 2. No need for temperature and pressure 	<ol style="list-style-type: none"> 1. Difficult isolation single-crystals for X-ray diffraction studies 2. Formation of Secondary phases 	HKUST-1 ZIF-4	[21, 22]
Microwave	<ol style="list-style-type: none"> 1. Reduction in crystallization time 2. High yields 3. Possibility to control morphology, phase selectivity, and particle distribution 4. Simple method and easy to control the reaction parameters 	<ol style="list-style-type: none"> 1. Difficult to isolate large single crystals 2. The lack of a direct method for scale-up 	CoMOF-74 Cr-MIL-100	[23, 24]
Ultrasonic	<ol style="list-style-type: none"> 1. Homogeneous particle size and morphology 2. Short reaction time 3. Formation of stable structures 4. Suitable method for the preparation of nanosized MOFs 	Destruction of crystallites hindering the formation of large single crystals for X-ray diffraction studies	Fe-MIL-53 MOF-177	[25, 26]
Electrochemical	<ol style="list-style-type: none"> 1. Avoiding anions such as nitrates from metal salts 2. Low temperatures of reaction and extremely quick synthesis 	Rarely reported method for synthesis of MOFs	ZIF-8 MIL-53	[27]

Table 1.
 The advantages and disadvantages of the different methods.

3. Applications of MOFs

MOFs have been attracting great attention in the past several decades mainly because of their outstanding properties, including high specific surface area, ultra-high porosity, tunable surface chemistry, functional diversity, and crystallinity [9]. These properties make them good candidates for use in gas storage and separation [28, 29], catalysis, drug delivery, and sensing [30].

Common methods of gas storage require high-pressure tanks and multistage compressors, which are difficult and expensive. MOFs provide a simpler and safer storage method, owing to their high surface area, high porosity, and tunable pore structure. To date, numerous MOFs have been applied for gas storage. PCN-12 [31], MOF 210 [32], and NU-100 [33] are some examples for H₂ storage. MOFs also have great potential to perform gas separations as adsorbents. In 2014, Yang et al. reported a hydroxyl-functionalized Al-MOF (NOTT-300) with high selectivity for C₂H₄/C₂H₆ separation [34].

MOFs have shown great capability in heterogeneous catalysis due to their unique features. Numerous MOFs have been reported as catalysts in photocatalysis reactions, electrocatalysis reactions, and organic transformations, such as oxidation, epoxidation, and Knoevenagel condensation [35]. These compounds are commonly employed as heterogeneous catalysts in the form of pristine solids or post-synthetically modified ones. One of the earliest studies in the field of MOF catalysis was reported in 1994 by Fujita et al. They constructed a two-dimensional (2D) network of Cd(4,4'-bpy)₂(NO₃)₂ by reaction between Cd(NO₃)₂ and (4,4'-bpy), and used it as a heterogeneous catalyst for the cyanosilylation of aldehydes [36]. The first experimental evidence of photocatalytic activity on a MOF (MOF-5) was published in 2007 [37]. To date, many researches have been made in the area of MOF-based photocatalysts. For example, Leng et al. reported an indium-based MOF, USTC-8(In), which exhibits an excellent photocatalytic activity for H₂ production [38].

Researches on MOFs as drug carriers have been developed in biomedical fields due to their features, such as drug loading ability, biodegradability, and adaptable functionality. According to the enhanced stability, enormous porosity, and large pore volume of the MIL family, they are an attractive candidate for the storage and controlled release of biologically important molecules [39]. Serrey and Férey et al. demonstrated encapsulating drug molecules (Ibuprofen) in chromium carboxylate MOFs, MIL – 100 and MIL – 101, exhibiting drug storage capacities of 35 wt% and 140 wt%, respectively, and controlled drug release behavior of 5 to 6 days under physiological conditions [40].

In addition to the applications mentioned above, MOFs can be used as sensors in different fields. A sensor is a device that can receive, respond, and detect a signal. In MOF-based devices, the sensor responds to different external stimulations, such as stress, mass, optical, and environmental changes. MOFs, which can be excited by absorbing UV-visible light, are considered as photoluminescent. Both the metal and the linker increase luminescence. Lanthanides like Eu, Tb, Dy, Sm, Nd, Gd, Er, and Yb are employed as luminescent metal ions owing to their electronic transition from d- to f-orbitals. Naphthalene, anthracene, pyrene, perylene, and stilbene types of ligands are used for the synthesis of luminescent MOFs [15]. As an example, HKUST-1 has shown a color change from turquoise to green as a result of the exchange of Cu²⁺-coordinated water with pyridine (**Table 2**) [44].

MOF	Metal node	Linker	Application	Ref.
UiO-66	Zr ₆ O ₄ (OH) ₄	Benzene-1,4-dicarboxylic acid	Ring-opening reaction cyclization	[41, 42]
HKUST-1	Cu(II)	1,3,5-Benzene tricarboxylate	Esterification	
Ti-MOF- Ru(tpy) ₂	Ti(IV)	Bis(4'-(4-carboxyphenyl)- terpyridine)Ru(II) complex	Photocatalytic H ₂ production	[43]
PCN-12	Cu(II)	5,5'-Methylene-di-isophthalate	H ₂ storage	[31]
Al-MOF (NOTT- 300)	Al(III)	Biphenyl-3,3',5,5'- tetracarboxylic acid	C ₂ H ₄ /C ₂ H ₆ separation	[34]
MIL - 101	Cr(III)	1,4-Benzenedicarboxylate	Drug delivery	[40]
HKUST-1	Cu(II)	Benzene-1,3,5-tricarboxylate	sensor	[44]
Al-ATA-Ni MOF	Al(III)	2-Aminoterephthalate	Photocatalytic water splitting	[45]
Zr-MOF,	Zr ₆ O ₄ (OH) ₄	Dibenzoate-substituted 2,2'-bipyridine dibenzoate	Oxidation	[46]
IRMOFs (MOF-5)	Zn ₄ O	Benzene-1,4-dicarboxylic acid	Alkylation	[47]

Table 2.
 Different applications of MOF.

4. Different types of MOFs

MOFs can be divided into different types based on their metal nodes. Metal nodes may vary from the s-block, p-block, transition metals, or even rare earth metals. S-block main group elements, alkali and alkaline earth metals are rarely used because of their low stability and difficulties in the structural formation of MOFs. In spite of their limitations, they have some advantages, including naturally high abundance, less toxicity, and low density, which lead to different applications [48]. Most reported MOFs are based on transition metals that can divide into different groups.

4.1 Transition-metal-based MOFs

4.1.1 Zr-based MOFs

Zr-based MOFs are useful in different fields according to their extraordinary mechanical, thermal, chemical stability and high oxidation state of Zr(IV) compared with M(I), M(II), and M(III)-based MOFs (M stands for metal elements). Zr-MOFs are applied in catalysis, molecule adsorption and separation, drug delivery, and fluorescence sensing, and as porous carriers [49]. For instance, Feng et al. reported Zr-PCN-221(Fe) as the catalyst for the selective oxidation of cyclohexane with tert-butyl hydroperoxide (TBHP) as the oxidant [50]. Additionally, Zr-based MOFs

can act as a semiconductor in photocatalytic reactions. As an example, Lillerud and coworkers reported the first Zr-based MOFs including UiO-66 and UiO-66(NH₂) for photocatalytic water splitting [51].

4.1.2 Cu-based MOFs

Copper (Cu) as an abundant and inexpensive metal with divalent copper ions having tetra- or hexa-coordinated structure can be used as another metal node in the synthesis of MOFs. Also, it has different oxidation states, such as Cu⁰, Cu^I, Cu^{II}, and Cu^{III}, leading to a wide variety of redox reactions [52].

Park and coworkers reported the green synthesis of PNU-25 applied in the cycloaddition reaction of CO₂ and epoxide [53]. In another study, a semi-conductive copper organic MOF, that is, {[Cu^ICu^{II}₂-(DCTP)₂]NO₃·1.5 DMF}_n with 2.1 eV bandgap was involved in UV/visible photocatalytic H₂ generation and oxidation of holes for photocatalytic degradation of methyl blue with use of visible light and without the aid of photosensitizer [54].

4.1.3 Fe-based MOFs

According to the Earth's abundance of iron, development in various applications of Fe-based MOFs in CO₂ reduction, photo-degradation, water splitting, and organic transformations occurred [55]. They are widely applied in photocatalytic reactions like H₂ production. For example, the photocatalytic visible light H₂ production of MIL-100(Fe) in presence of MEOH was reported by Wang et al. [56].

4.1.4 Co-based MOFs

Based on the inexpensiveness and availability of cobalt salts, cobalt-based MOFs have been widely used in different applications, such as oxygen and hydrogen evolution, catalysis, electrocatalysis, synthesis of nanomaterials, and more [57–59]. These structures can provide a transition porous framework and ultra-high surface area for photocatalytic H₂ production. For instance, Yang et al. reported Co-based zeolitic imidazolate MOF (ZIF-67) with RuN₃ as a photosensitizer for efficient photocatalytic H₂ production from H₂O [60]. In another study of Co-MOFs, Dirk Volkmer and coworkers reported the synthesis and the catalytic performance of MFU-1 MOF in the oxidation of cyclohexene using TBHP as an oxidant [61].

4.1.5 Ni-based MOFs

Ni-based MOFs are another useful group of metal–organic frameworks with properties such as high porosity, presence of coordinatively unsaturated Ni²⁺ sites and Lewis acid sites so they can be used in different fields. Miyake et al. first described the synthesis and application of MOFs with Ni-bipyridyl complex as the linker along with Ni as the nodes in ethylene oligomerization [62]. In another study, [Ni(phen)(oba)]_n·0.5nH₂O 2D MOF has been studied as supporting material for metal sulfides as a visible light active photocatalyst for effective H₂ production [63].

4.1.6 Ti-based MOFs

4.1.6.1 The overall properties of titanium (Ti)

4.1.6.1.1 The chemistry of Ti

What makes titanium an attractive candidate to use as a metal node in several MOFs? Indeed, divalent transition metal cations, such as Zn^{2+} , Cu^{2+} , Co^{2+} , and Ni^{2+} , lead to thousands of extraordinary porous MOFs. Nevertheless, they are often unstable in the presence of water. To enhance the strength of cation–ligand bond and gain stability in MOFs, increasing the charge of a metal cation and its polarizing power charge over ionic radius are considered [64].

Among the elements in the periodic table, titanium or Ti has drawn considerable attention due to its fascinating intrinsic features. To mention about its abundance, it is the ninth most abundant element in the Earth's crust and is the second most abundant transition metal after iron. This element, located in the first row of the periodic table and above the zirconium, has a $[Ar] 3d^2 4s^2$ electronic configuration. In comparison with Zr^{4+} , it has a stronger interaction with oxygen due to its smaller ionic radius. Its common oxidation states are +2, +3, and +4. Ti^{4+} ion is a frequent oxidation state, which is the most stable in ambient conditions (air and water), while Ti^{3+} could be generated under reductive conditions but quickly oxidized back to Ti^{4+} in the presence of oxygen. The reasons for its tendency to hydrolyze into various titanium oxo clusters, or directly to generate TiO_2 precipitation are low electronegativity and high polarizability [65–67].

Due to the all features mentioned above, titanium is a highly desirable alternative to constructing stable and diverse MOFs. There are several Ti-MOFs that were published, including MIL-91 [68], MIL-125 [69], NTU-9 [70], MIL-101 [71], COK-69 [72], Ti-CAT-5 [73], MIL-167 [74], MIP-177 [75], MIL-100 [76], Ti-TBP [77], and ZSTUs [78], applied in different fields. However, Ti-MOFs have seldom been reported due to some reasons, which will be summarized into three main parts [79]:

- i. Strong interaction between reactive titanium sources and ligand as a result of the high charge to radius (Z/r) value on Ti^{4+} causes poor association/dissociation of metal–ligand bond and formation of crystalline products. To achieve a crystalline structure, choosing suitable synthetic conditions, such as the organic solvents, ratio of the reacted solution mixture, pH, and temperature, should be considered.
- ii. Another limitation is the extreme hydrolysis of reactive titanium sources
- iii. Some of the titanium carboxylates show low symmetry or inappropriate connectivity that leads to hinder the formation of periodic networks with organic linkers [80].

4.1.6.1.2 History

MIL-22 was the first Ti-MOF, synthesized by Serre, Fèrey, and coworkers, using phosphorus ligand and TiO_2 under high temperature in 1999 (**Figure 1a**) [81]. This

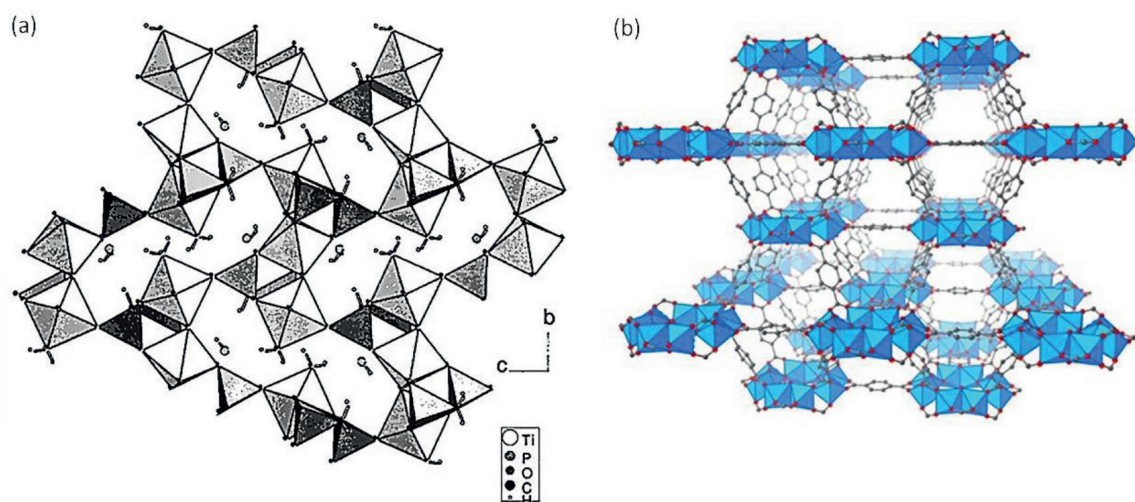


Figure 1.
(a) Structure of MIL-22, (b) structure of MIL-125.

compound showed limited porosity. For a quite long time, no highly porous Ti-MOF was reported. Subsequently, in 2009, MIL-125 was discovered by the same group (**Figure 1b**) [82]. The discovery of this MOF created a scientific boom in the synthesis of new Ti-based MOFs material. It consists of 12-connected $[\text{Ti}_8\text{O}_8(\text{OH})_4(\text{COO})_{12}]$ clusters and 1,4-benzenedicarboxylate (BDC) linker and demonstrates permanent porosity with a BET surface area of $1550 \text{ m}^2\text{g}^{-1}$ [69]. Meanwhile, titanium oxo clusters, which can be seen as TiO_2 nanoclusters, affect the construction of novel Ti-based MOFs [83].

Up to now, different types of Ti-MOFs have been introduced. The development of a titanium-based MOFs timeline is presented in **Figure 2** [65].

4.1.6.1.3 Comparison of the Ti-MOF with other MOFs

In this regard, Ti-MOFs possess several advantages over other groups of MOFs, which are as follows:

- i. Strong Ti–O bonding, which is the result of the small ionic radius of Ti^{4+} , leads to rigid MOF structures.
- ii. The high coordination number of Ti^{4+} causes structural diversity in metal-oxo clusters.
- iii. Ti-based MOFs with large surface area and high porosity can be effective photocatalysts in which Ti–O clusters act as isolated titanium oxide quantum dots, making them like the Ti-grafted zeolites and the semiconducting titanium oxide.
- iv. Their ability to store charge effectively because of the reversible redox transition between $\text{Ti}^{4+}/\text{Ti}^{3+}$ under photo-excitation leads to using them in photo-driven catalytic redox reactions.
- v. Their photocatalytic properties can be developed and improved by functionalization of ligands and composition with other highly active species like metal nanoparticles and graphene.

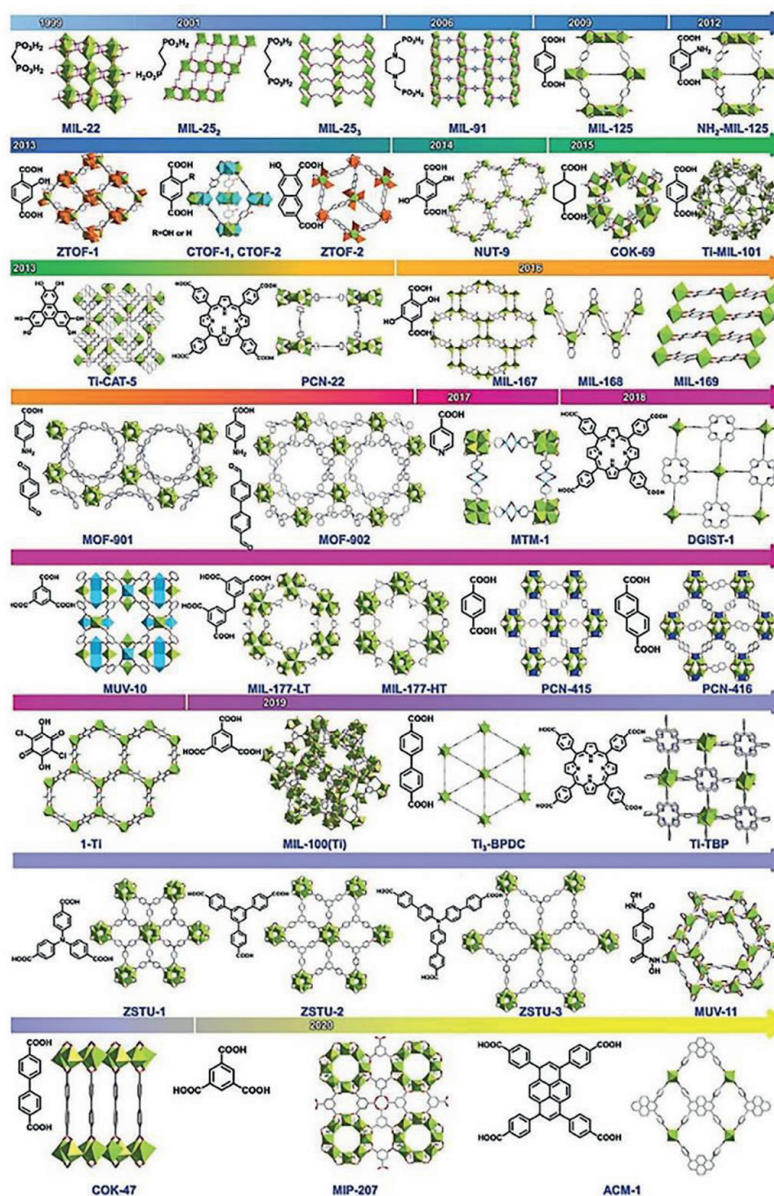


Figure 2.
 The timeline for the development of crystal structures of titanium-based MOFs.

- vi. They form rigid frameworks, which are the result of strong metal–ligand bonding.
- vii. Their well-defined porosity enhances photocatalytic activities.
- viii. Their low cost and low toxicity make them good candidates as catalysts [64, 84].

To realize the importance of Ti-MOFs among all families of MOFs, their properties should be discussed, most notably about two important ones such as porosity and optical properties [85].

Porosity is one of the most effective features in photocatalytic reactions accomplished by MOFs. Owing to this property, the transfer of photoelectric charge happens rapidly, thus the electron–hole recombination reduces. Moreover, porosity lets the active sites to be in contact with the substrate more effectively by reducing the

diffusion resistance [86]. In addition, this property prepares large spaces for encapsulating different types of catalysts [87]. As a result, Ti-MOFs can be used in different fields of chemistry.

There are various strategies used for the synthesis of porous Ti-MOFs, which are good to mention:

- i. Partial post-synthetic metal exchange; for instance, porous Ti^{III} -MOF-5 and Ti^{IV} -UiO-66 were synthesized by exchanging their metals with Zn^{II} and Zr^{IV} [88].
- ii. Assembly of clusters; MTM-1, a porous Ti-MOF, is synthesized by a combination of $\{[\text{Ti}_6\text{O}_6][\text{Oipr}]_6\}^{6+}$ cluster and cross-connected Cu_2I_2 dimer through isononanol (INA) [85].
- iii. The supramolecular template strategy [86].
- iv. Isorecticular expansion, an effective strategy, is used to increase the pore size, surface area, and porosity by self-assembly of metal centers and organic ligands. In this strategy, long and geometrically equivalent organic ligands influence the porosity of MOF. As an example, MOF-902 has a greater porosity in comparison with MOF-901 because of its longer organic building blocks [89]. In spite of the fact that the longer the organic ligands are, the higher porosity occurs, and the stability of Ti-MOFs diminishes.

The optical property of MOFs is an important factor for photocatalysis. In general, photocatalytic reactions consist of three main steps: light absorption, charge separation and transfer, and redox reaction [90]. To enhance the light absorption intensity, modification of organic ligands is utilized. In the same way, it can affect MOF's bandgap. As an example, inserting the $-\text{NH}_2$ functional group on the ligand of MIL-125 yields a small bandgap [91].

To conclude, compared to other MOFs, Ti-MOFs are fascinating structures with various applications in different fields due to their high thermal and chemical stability, novel structural diversity, photocatalytic properties, low cost, and low toxicity (**Figure 3**) [85]. The geometry and length of organic building blocks and metal nodes can affect the chemical stability and functional properties of MOFs. For instance, the carboxylate ligand-based MOFs with low-valent ions, such as Zn^{2+} , Co^{2+} , and Mn^{2+} , show lower chemical stability. However, those with high-valent ions, such as Zr^{4+} , Ti^{4+} , and Cr^{3+} , usually have high chemical stability [65].

In comparison with other metal-based MOFs, for example, Zr-MOFs, Fe-MOFs, or Cu-MOFs, the titanium-based MOFs exhibit richer structural and topological diversity, due to the variable nuclearity of titanium cores.

Owing to the low-level control of titanium chemistry and highly unpredictable polycondensation of titanium cation, titanium-based MOF structures are less commonly reported compared with the Zr-MOFs, Fe-MOFs, or Cu-MOFs.

4.1.6.1.4 Stability

The stability of M^{4+} -MOFs makes them an appealing choice to concentrate on. Many factors are involved in the stability of MOFs, such as metal nodes, organic ligands, metal–ligand coordination, operating environment, hydrophobicity of the pore surface, and defects [92–94]. Thermodynamic stability of MOFs is affected by

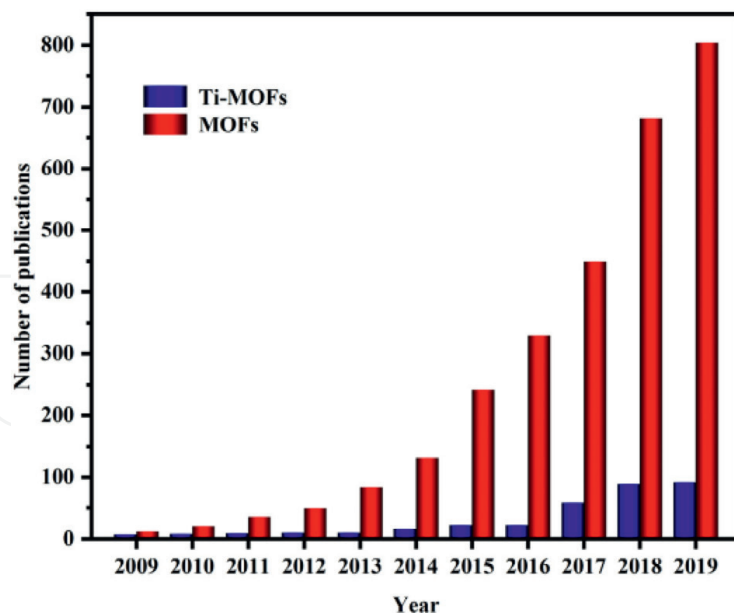


Figure 3.
The number of photocatalytic publications on MOFs and Ti-MOFs reported annually from 2009 to 2019.

metal–ligand coordination. Based on Pearson’s hard/soft acid/base (HSAB) theory, strong bonds are formed between hard Lewis’s acids and bases or soft Lewis’s acids and bases. Carboxylate-based ligands are hard bases that can generate stable MOFs with group 4 metal cations such as Ti^{4+} [66]. Likewise, kinetic factors have an important role in the stability of MOFs. Strong connection between metal-oxo clusters and rigid ligands leads to dense and rigid frameworks, which increase the stability of MOFs. Hence, good stability in M^{4+} -based MOFs is expected because M^{4+} cations tend to have more ligands to balance their charges. Another factor that affects the stability of MOFs is the operating environment. For instance, the resistance of carboxylate-based ligands in acids and bases is completely different. They show excellent stability in acids, while their stability is quite weak in bases [95].

4.1.6.1.5 The coordination behavior of titanium ions

Generally, each metal ion prefers to coordinate with other components in a special way. For example, Cu^{2+} ions tend to assemble with four carboxylate groups to form $\text{Cu}(\text{COO})_4$ paddle-wheel geometry [44] and zirconium ions construct the clusters like $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CO}_2)_{12}$ as 6-C, 8-C, 10-C, or 12-C nodes [49]. With regard to titanium ions, the coordination with other components changes with reaction systems. The diversity in titanium-oxo clusters makes it hard to predict the topology of titanium-based MOFs. Ti^{4+} constructs octahedrally six-coordinated structures by O forming TiO_6 units that are bridged by $\mu_2\text{-O}$ or $\mu_3\text{-O}$ atoms. They lead to the creation of titanium-oxo clusters that vary based on their synthetic conditions. For instance, the cluster in MIL-125 or $\text{NH}_2\text{-MIL-125}$, $\text{Ti}_8\text{O}_8(\text{OH})_4$ is completely different from $\text{Ti}_3(\mu_3\text{-O})$ cluster in its polymorph Ti-MIL-101 [69, 71].

4.1.6.1.6 Applications

Most of the investigations have demonstrated that Ti-MOFs have several applications due to their diversity of stable structures, including photocatalytic reactions and organic transformations such as H_2 productions [96], CO_2 conversion [97], H_2O_2

production [98], pollutant degradation [99], and many other organic reactions. As an example, in 2018, an efficient photocatalytic H₂ production, accomplished by a Ti-MOF known as MIL-125-(SCH₃)₂, was reported by Han et al. [100]. In 2018, Yamashita and coworkers reported the first example of a Ti-based MOF, MIL-125-NH₂ with NiO nanoparticles (NPs), used in photocatalytic H₂O₂ production [101]. The photocatalytic reduction of CO₂ with Co/NH₂-MIL-125(Ti) was reported by Fu et al. under visible light irradiation [102].

4.1.6.2 Titanium precursor for MOF synthesis

Titanium precursors used in MOFs synthesis include hydrous TiO₂, titanium chlorides, titanium alkoxides, titanium complexes, and titanium-oxo-clusters.

MIL-25 [103] and MIL-22 [81], two Ti natural phosphonates, were the first structures that were formed by hydrous TiO₂ as a precursor. Hydrous forms of TiO₂ are rarely used for the synthesis of MOFs due to their limitations, such as high reaction temperature (>200 C), long reaction time (3–4 d), and highly corrosive and toxic reaction media (40% HF aqueous solution) [104].

Titanium chlorides extremely hydrolyze and release hydrochloride fumes in the reaction medium [105]. This is the reason why they are seldom used in Ti-MOFs synthesis. TiCl₃ is an exception in the construction of di or trivalent Ti-MOFs. Whereas Ti⁴⁺ is not a suitable selection because of the imbalanced charge and ionic range. According to the reductive nature of Ti³⁺, exposure to air inhibits the synthesis [106].

In terms of titanium alkoxides, Ti(OR)₄, hydrophobic character and hindrance of alkoxy groups cause them less hydrolyzed than TiCl₄. The construction of complexes of Ti cations with bidentate ligands, such as carboxylates, diketonates, catecholates, and phosphonates, leads to a stable structure [64].

An efficient way to control the reaction degree of MOF synthesis is the utilization of stable six-coordinated Ti compounds (Ti-oxo-clusters) [80]. Owing to the different sizes, geometry, and coordination numbers of Ti clusters, they have the potential to be chosen as building blocks of MOFs. The original cluster might be transformed during the reaction. For instance, in the synthesis of PCN-22 by Ti₆O₆(iOPr)₆(abz)₆ as Ti precursor, this cluster was completely transformed to Ti₇O₆-oxo SBU in the final MOFs [107]. In comparison with Ti alkoxides, Ti clusters are useful to adjust the reaction rates and obtain larger single crystals [106].

4.1.6.2.1 Synthesis methods

New synthetic methods of Ti-MOFs have been proposed to remove the restrictions. In this section, we have introduced some strategies to synthesize these structures, including direct synthesis, cooperative self-assembly strategy, and vapor-assisted crystallization method. Besides, the synthetic strategies of Ti-MOF composites and derived porous materials are discussed [85].

4.1.6.2.1.1 Direct synthesis

Most of the Ti-MOFs have been synthesized by direct methods, such as hydrothermal/solvothermal, microwave, and ultrasonic synthesis. The most conventional method for direct synthesis of Ti-MOFs is the hydrothermal/solvothermal technique, which includes the interaction between metal–salt and an organic linker in a suitable

solvent(s) and autoclave conditions. Choosing the proper solvent and concentration of reactants are two important factors that affected the crystallinity and morphology of Ti-MOFs [106]. As an example, the morphology of NH₂-MIL-125 microcrystals could be changed from circular plate to octahedron by changing the concentration of the solution [108]. In 2015, Yaghi and coworkers reported the first three-dimensional (3D) extended Ti catecholate MOF (Ti-CAT-5) by solvothermal reaction of the Ti ion and hexatopic catecholate linker, 2,3,6,7,9,11-hexahydroxytriphenylene (H₆THO) at 180 C for 4 h [73].

Other direct methods for synthesis of Ti-MOFs are ultrasonic- and microwave-assisted techniques that have advantages including obtaining structures with different molecular sizes and shapes in short reaction time and low temperature [104]. Kim and coworkers have synthesized NH₂-MIL-125 by the microwave-assisted method in a shorter reaction time in comparison with the solvothermal technique. As an example of sonochemical synthesis, Han and coworkers have reported NH₂-MIL-125 in a uniform size distribution of around 300 nm [109].

4.1.6.2.1.2 Coordination-covalent combination method

In spite of the advantages of direct synthesis of Ti-MOFs, this methodology has some limitations like the formation of unpredicted structures and byproducts. The utilization of Ti-oxo clusters can approximately solve this problem. To obtain an ideal structure that does not disturb the Ti–O bonding in the clusters, combining the MOFs and COFs known as the coordination-covalent combination strategy was introduced [104]. The first example of this strategy was reported by Yaghi and coworkers. This reported synthesis involves *in situ* generation of an amine-functionalized titanium oxo cluster, Ti₆O₆(OCH₃)₆(AB)₆ (AB = 4-aminobenzoate), which was linked with benzene-1,4-dialdehyde using imine condensation reactions, typical of COFs. The crystal structure of MOF-901 with known structure and topology was achieved [110].

4.1.6.2.1.3 Post-synthetic cation exchange method

Another strategy to overcome the conventional methods' limitations is the cation exchange method. This technique can avoid the high reactivity and vigorous hydrolysis of Ti precursors and lead to desired pore and topography in Ti-MOFs [111]. The example for post Ti-exchange was first reported by Cohen et al. Ti ion exchange occurred in Zr-MOF, UiO-66, became a better option for Ti-MOF [112].

4.1.6.2.1.4 Vapor-assisted crystallization method

To overcome the limitations of microporous structures in catalytic applications of Ti-MOFs by creating mesopores in MOFs structures, the vapor-assisted crystallization method (VAC) was introduced by Hicks et al. [113].

4.1.6.2.1.5 Synthesis of Ti-MOF composites

According to the importance of MOFs supported metal nanoparticle compounds in catalysis, highly dispersed nanoparticle-doped Ti-MOFs were prepared. Not only noble metal nanoparticles, such as silver (Ag), gold (Au), platinum (Pt), palladium (Pd), and non-noble metal nanoparticles, such as nickel (Ni) have been successfully embedded into the pores of Ti-MOFs [114, 115] but also quantum dots, such as

graphene-like MoS₂ sheets, Ag₂S, CdS, and CuS have been deposited onto MIL-125 and a series of Ti MOFs based composites [116].

4.1.6.2.2 Different types of Ti-MOFs

Ti-MOFs can be categorized based on their structures (one-dimensional (1D) chain structures, two-dimensional (2D) layer structures, and three-dimensional (3D) network structures) and ligands in their secondary building units (phosphonates, carboxylates, salicylates, and catecholates).

4.1.6.2.2.1 Types of Ti-MOFs based on their structures

1D and 2D Ti-MOF structures are rarely reported. For instance, MIL-168 has 1D zigzag chains running parallel to each other (**Figure 4a**) [74]. To form an ordered 1D zigzag, a single bidentate ligand occupies two cis positions to create an octahedral environment around the metal ion [117].

Generally, 2D network structures can be divided into two types: “tilt penetration” and “parallel penetration” [118]. In two-dimensional MIL-169 (Ti₂(DOBDC)₄O(H₂O)₂ dimer, DOBDC₄ = 2,5-dioxido-1,4-benzenedicarboxylate), the Ti ion is chelated by two DOBDC ligands through the six-membered ring (**Figure 4b**) [74].

In terms of 3D MOFs, they possess different complicated structures. For example, Jiang et al. reported the synthesis and structure of a 3D chiral structure, a 3-connected SrSi₂ net with (10,3) topology, which exhibited a novel doubly interwoven SrSi₂ topology (**Figure 4c**) [119].

4.1.6.2.2.2 Types of Ti-MOFs based on ligands in secondary building units

It is noteworthy to discuss about the structures of Ti-MOFs based on different kinds of ligands due to their obvious directing effects toward the finally formed Ti-oxo SBU.

4.1.6.2.2.2.1 Carboxylate-based Ti-MOFs

In general, Ti-MOFs are mostly constructed from carboxylate ligands. Ti cations with polydentate carboxylate acids have a tendency to form large Ti-oxo-carboxylate clusters, leading to a wide variety of Ti-MOFs' structures. Ti-oxo-carboxylate clusters with the general formula Ti_nO_m(OR)_x(OOCR')_y can be synthesized by a solution of a

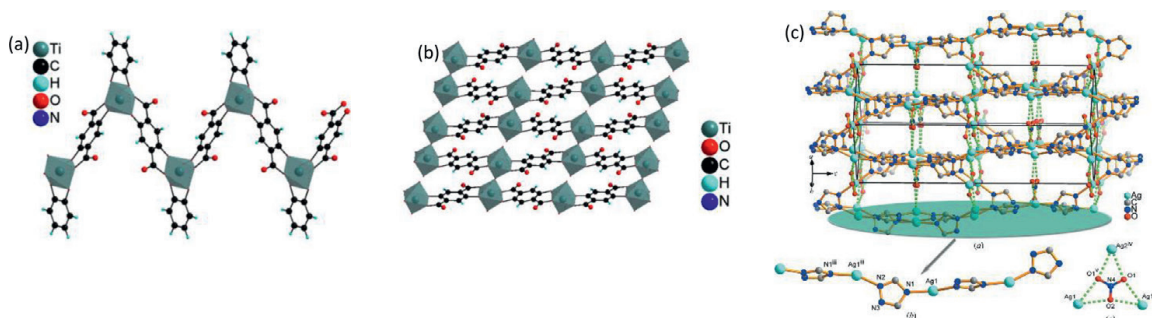


Figure 4. (a) Crystal structure of MIL-168, a 1D coordination chain. (b) Crystal structure of MIL-169, 2D coordination network. (c) a view of the structure of poly[bis(μ₃-3,5-di-ethyl-1,2,4-triazolato-κ³N⁴:N²:N⁴)trisilver nitrate] along the [110] direction, showing the three-dimensional framework.

metal cation precursor (very often $\text{Ti}(\text{OR})_4$) with carboxylate ligand and/or a controlled amount of water. It is important to control different factors such as nature and the amount of the metal cation precursor, the ligand ($\text{R}'\text{COOH}$), the solvent, and the reaction conditions (time, pressure, presence of water or not, inert conditions or not, etc.). In 2015, Bueken et al. reported a new Ti-MOF based namely COK-69 by reaction of trans-1,4-cyclo-hexanedicarboxylate (cdc) linkers and an unprecedented $[\text{Ti}^{\text{IV}}_3 - (\mu_3\text{-O})(\text{O})_2(\text{COO})_6]$ cluster. In COK-69, three neighboring Ti atoms joined by a $\mu_3\text{-O}^{2-}$ ion and six carboxylates give the formation of the Ti_3O_3 cluster. Subsequently, the porous framework is formed by a connection between the cluster and six cdc^{2-} linkers [120].

4.1.6.2.2.2.2 Phosphonate-based Ti-MOFs

A series of different phosphonate-based Ti-MOFs, typically MIL-22 [81], MIL-25_n ($n = 2, 3$) [103], and MIL-91(Ti) [68], has been introduced by Férey et al. For example, the monoclinic MIL-22 is synthesized by corner-shared trimers of Ti-oxo octahedrals and PO_4 from diphosphonic linkers, forming a 2D array of microporous channels.

4.1.6.2.2.2.3 Salicylate-based Ti-MOFs

As an example of using salicylate organic linkers in the structure of MOF, in 2013 Hong et al. introduced Ti-salicylate MOF, namely ZTOF-1. Under solvothermal conditions, the reaction of zinc and titanium precursors with asymmetrical dicarboxylate ligand, 2-hydroxyterephthalic acid (H_3obdc) leads to orange crystals of ZTOF-1. In this structure, Ti coordinates with the “salicylate” end of the ligand, while Zn coordinates with the carboxylate end [121].

4.1.6.2.2.2.4 Catecholate-based Ti-MOFs

Up to now only one Ti-MOF based on polycatecholate ligand known as Ti-CAT-5 was reported, in spite of the richness of Ti-catecholate clusters and the potential of these structures to apply in different fields. Ti-CAT-5 was constructed by the connection of isolated Ti-centers and the tritopic catechol derivative ligand, H_6THO [73].

5. Conclusion

Metal-organic frameworks, composed of metal ions or well-defined secondary building units and organic linkers, are utilized in different fields, such as gas storage and separation, liquid separation and purification, electrochemical energy storage, catalysis, and sensing, due to their unique properties. According to the features of titanium, such as different oxidation states, high coordination number of Ti^{4+} , and the ability to form strong bonds with oxygen and different ligands, it is used as a metal node in MOF design. Titanium-based MOFs, as a branch of metal-organic frameworks, have recently attracted the researchers' attention because of their special properties, including high thermal and chemical stability, novel structural diversity, photocatalytic properties, low cost, and low toxicity. In this regard, the characteristics, types of Ti-MOFs, methods of synthesis, applications, and comparison of Ti-MOFs with other MOFs are discussed in this chapter. In comparison with other metal-based MOFs, for example, Zr-MOFs, Fe-MOFs, or Cu-MOFs, the titanium-based MOFs exhibit richer structural and topological diversity, high thermal and chemical stability, and high photocatalytic activity.

Conflict of interest

The authors declare no conflict of interest.


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References

- [1] Corma A, García H, Llabrés FX, Xamena I. Engineering metal organic frameworks for heterogeneous catalysis. *Chemical Reviews*. 2010;**110**:4606-4655. DOI: 10.1021/CR9003924/ASSET/CR9003924.FP.PNG_V03
- [2] Tomic EA. Thermal stability of coordination polymers. *Journal of Applied Polymer Science*. 1965;**9**:3745-3752. DOI: 10.1002/APP.1965.070091121
- [3] Sowerby DB, Audrieth LF. Inorganic polymerization reactions III. Coordination polymerization. *Journal of Chemical Education*. 1960;**37**:134-137. DOI: 10.1021/ED037P134
- [4] Berlin AA, Matveeva NG. Polymeric chelate compounds. *Russian Chemical Reviews*. 1960;**29**:119-128. DOI: 10.1070/rc1960v029n03abeh001223
- [5] Hoskins BF, Robson R. Design and construction of a new class of scaffolding-like materials comprising infinite Polymeric frameworks of 3D-linked molecular rods. A reappraisal of the Zn(CN)₂ and Cd(CN)₂ structures and the synthesis and structure of the diamond-related frameworks [N(CH₃)₄][CuI₂ZnII(CN)₄] and CuI[4,4',4'',4'''-tetracyanotetraphenylmethane]BF₄·x C₆H₅NO₂. *Journal of the American Chemical Society*. 1990;**112**:1546-1554. DOI: 10.1021/JA00160A038/SUPPL_FILE/JA00160A038_SI_001.PDF
- [6] Batten SR, Hoskins BF, Robson R. Two interpenetrating 3D networks which generate spacious sealed-off compartments enclosing of the order of 20 solvent molecules in the structures of Zn(CN)(NO₃)(tpt)_{2/3}·solv (tpt = 2,4,6-tri(4-pyridyl)-1,3,5-triazine, solv = ~3/4 C₂H₂Cl₄·3/4 CH₃OH or ~3/2 CHCl₃·1/3 CH₃OH). *Journal of the American Chemical Society*. 1995;**117**:5385-5386. DOI: 10.1021/JA00124A032/SUPPL_FILE/JA5385.PDF
- [7] Yaghi OM, Li H. Hydrothermal synthesis of a metal-organic framework containing large rectangular channels. *Journal of the American Chemical Society*. 1995;**117**:10401-10402. DOI: 10.1021/JA00146A033/SUPPL_FILE/JA10401.PDF
- [8] Li H, Eddaoudi M, O'Keeffe M, Yaghi OM. Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature*. 1999;**402**:276-279. DOI: 10.1038/46248
- [9] Kumar S, Jain S, Nehra M, Dilbaghi N, Marrazza G, Kim KH. Green synthesis of metal-organic frameworks: A state-of-the-art review of potential environmental and medical applications. *Coordination Chemistry Reviews*. 2020;**420**:213407. DOI: 10.1016/J.CCR.2020.213407
- [10] Yuan S, Qin JS, Lollar CT, Zhou HC. Stable metal-organic frameworks with group 4 metals: Current status and trends. *ACS Central Science*. 2018;**4**:440-450. DOI: 10.1021/ACSCENTSCI.8B00073/ASSET/IMAGES/LARGE/OC-2018-000738_0005.JPEG
- [11] Howarth AJ, Liu Y, Li P, Li Z, Wang TC, Hupp JT, et al. Chemical, thermal and mechanical stabilities of metal-organic frameworks. *Nature Reviews Materials*. 2016;**1**(3):1-15. DOI: 10.1038/natrevmats.2015.18
- [12] Lee YR, Kim J, Ahn WS. Synthesis of metal-organic frameworks: A mini review. *Korean Journal of Chemical*

- Engineering. 2013;**309**(30):1667-1680. DOI: 10.1007/S11814-013-0140-6
- [13] Gangu KK, Maddila S, Mukkamala SB, Jonnalagadda SB. A review on contemporary metal–organic framework materials. *Inorganica Chimica Acta*. 2016;**446**:61-74. DOI: 10.1016/J.ICA.2016.02.062
- [14] Butova VV, Soldatov MA, Guda AA, Lomachenko KA, Lamberti C. Metal-organic frameworks: Structure, properties, methods of synthesis and characterization. *Russian Chemical Reviews*. 2016;**85**:280-307. DOI: 10.1070/rcr4554
- [15] Soni S, Bajpai PK, Arora C. A review on metal-organic framework: Synthesis, properties and application. *Characterization and Application of Nanomaterials*. 2018;**2**(2):87-106. DOI: 10.24294/CAN.V2I2.551
- [16] McKinstry C, Cathcart RJ, Cussen EJ, Fletcher AJ, Patwardhan SV, Sefcik J. Scalable continuous solvothermal synthesis of metal organic framework (MOF-5) crystals. *Chemical Engineering Journal*. 2016;**285**:718-725. DOI: 10.1016/J.CEJ.2015.10.023
- [17] Bhattacharjee S, Choi JS, Yang ST, Choi SB, Kim J, Ann WS. Solvothermal synthesis of Fe-MOF-74 and its catalytic properties in phenol hydroxylation. *Journal of Nanoscience and Nanotechnology*. 2010;**10**:135-141. DOI: 10.1166/JNN.2010.1493
- [18] R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O’Keeffe, O.M. Yaghi, High-throughput synthesis of zeolitic imidazolate frameworks and application to CO₂ capture, *Science* (80-.). 319 (2008) 939-943. doi: 10.1126/SCIENCE.1152516/SUPPL_FILE/BANERJEE.SOM.PDF
- [19] Abid HR, Tian H, Ang HM, Tade MO, Buckley CE, Wang S. Nanosize Zr-metal organic framework (UiO-66) for hydrogen and carbon dioxide storage. *Chemical Engineering Journal*. 2012;**187**:415-420. DOI: 10.1016/J.CEJ.2012.01.104
- [20] Silva P, Vilela SMF, Tomé JPC, Almeida Paz FA. Multifunctional metal–organic frameworks: From academia to industrial applications. *Chemical Society Reviews*. 2015;**44**:6774-6803. DOI: 10.1039/C5CS00307E
- [21] Klimakow M, Klobes P, Thünemann AF, Rademann K, Emmerling F. Mechanochemical synthesis of metal-organic frameworks: A fast and facile approach toward quantitative yields and high specific surface areas. *Chemistry of Materials*. 2010;**22**:5216-5221. DOI: 10.1021/CM1012119/SUPPL_FILE/CM1012119_SI_001.PDF
- [22] Beldon PJ, Fábíán L, Stein RS, Thirumurugan A, Cheetham AK, Frišćić T. Rapid room-temperature synthesis of Zeolitic Imidazolate frameworks by using Mechanochemistry. *Angewandte Chemie International Edition*. 2010;**49**:9640-9643. DOI: 10.1002/ANIE.201005547
- [23] Cho HY, Yang DA, Kim J, Jeong SY, Ahn WS. CO₂ adsorption and catalytic application of Co-MOF-74 synthesized by microwave heating. *Catalysis Today*. 2012;**185**:35-40. DOI: 10.1016/J.CATTOD.2011.08.019
- [24] Sung HJ, Lee JH, Chang JS. Microwave synthesis of a Nanoporous hybrid material, chromium Trimesate. *Bulletin of the Korean Chemical Society*. 2005;**26**:880-881. DOI: 10.5012/BKCS.2005.26.6.880
- [25] Haque E, Khan NA, Park HJ, Jung SH. Synthesis of a metal–organic

framework material, iron terephthalate, by ultrasound, microwave, and conventional electric heating: A kinetic study. *Chemistry–A European Journal*. 2010;**16**:1046-1052. DOI: 10.1002/CHEM.200902382

[26] Jung DW, Yang DA, Kim J, Kim J, Ahn WS. Facile synthesis of MOF-177 by a sonochemical method using 1-methyl-2-pyrrolidinone as a solvent. *Dalton Transactions*. 2010;**39**:2883-2887. DOI: 10.1039/B925088C

[27] Martinez Joaristi A, Juan-Alcañiz J, Serra-Crespo P, Kapteijn F, Gascon J. Electrochemical synthesis of some archetypical Zn²⁺, Cu²⁺, and Al³⁺ metal organic frameworks. *Crystal Growth & Design*. 2012;**12**:3489-3498. DOI: 10.1021/CG300552W/SUPPL_FILE/CG300552W_SI_001.PDF

[28] Li H, Li L, Lin R-B, Zhou W, Zhang Z, Xiang S, et al. Porous metal-organic frameworks for gas storage and separation: Status and challenges. *EnergyChem*. 2019;**1**:100006. DOI: 10.1016/J.ENCHEM.2019.100006

[29] Ma S, Zhou HC. Gas storage in porous metal-organic frameworks for clean energy applications. *Chemical Communications*. 2010;**46**:44-53. DOI: 10.1039/B916295J

[30] He X. Metal-Organic Framework (MOF)-Based Materials: Aerosol Synthesis and Photocatalytic Applications. Theses Dissertation. 2019. pp. 3-9. DOI: 10.25772/63GS-6W17

[31] Wang X-S, Ma S, Forster PM, Yuan D, Eckert J, López JJ, et al. Enhancing H₂ uptake by “close-packing” alignment of open copper sites in metal-organic frameworks. *Angewandte Chemie*. 2008;**120**:7373-7376. DOI: 10.1002/ANGE.200802087

[32] Furukawa H, Ko N, Go YB, Aratani N, Choi SB, Choi E, et al. Ultrahigh porosity in metal-organic frameworks. *Science* (80-.). 2010;**329**:424-428. DOI: 10.1126/SCIENCE.1192160/SUPPL_FILE/FURUKAWA-SOM.PDF

[33] Farha OK, Yazaydin AÖ, Eryazici I, Malliakas CD, Hauser BG, Kanatzidis MG, et al. De novo synthesis of a metal-organic framework material featuring ultrahigh surface area and gas storage capacities. *Nature Chemistry*. 2010;**211**(2):944-948. DOI: 10.1038/nchem.834

[34] Yang S, Ramirez-Cuesta AJ, Newby R, Garcia-Sakai V, Manuel P, Callear SK, et al. Supramolecular binding and separation of hydrocarbons within a functionalized porous metal-organic framework. *Nature Chemistry*. 2014;**72**(7):121-129. DOI: 10.1038/nchem.2114

[35] Jiao L, Wang Y, Jiang HL, Xu Q. Metal-organic frameworks as platforms for catalytic applications. *Advanced Materials*. 2018;**30**:1703663. DOI: 10.1002/ADMA.201703663

[36] Fujita M, Washizu S, Ogura K, Kwon YJ. Preparation, Clathration ability, and catalysis of a two-Dimensional Square network material composed of cadmium(II) and 4, 4'-Bipyridine. *Journal of the American Chemical Society*. 1994;**116**:1151-1152. DOI: 10.1021/JA00082A055/SUPPL_FILE/JA1151.PDF

[37] Alvaro M, Carbonell E, Ferrer B, Lladrés FX, Xamena I, Garcia H. Semiconductor behavior of a metal-organic framework (MOF). *Chemistry–A European Journal*. 2007;**13**:5106-5112. DOI: 10.1002/CHEM.200601003

[38] Leng F, Liu H, Ding M, Lin QP, Jiang HL. Boosting photocatalytic

- hydrogen production of Porphyrinic MOFs: The metal location in Metalloporphyrin matters. *ACS Catalysis*. 2018;**8**:4583-4590. DOI: 10.1021/ACSCATAL.8B00764/SUPPL_FILE/CS8B00764_SI_006.CIF
- [39] Keskin S, Kizilel S. Biomedical applications of metal organic frameworks. *Industrial and Engineering Chemistry Research*. 2011;**50**:1799-1812. DOI: 10.1021/IE101312K
- [40] Horcajada P, Serre C, Vallet-Regí M, Sebbañ M, Taulelle F, Férey G. Metal-organic frameworks as efficient materials for drug delivery. *Angewandte Chemie International Edition*. 2006;**45**:5974-5978. DOI: 10.1002/ANIE.200601878
- [41] Cai G, Jiang H-L. A modulator-induced defect-formation strategy to hierarchically porous metal-organic frameworks with high stability. *Angewandte Chemie International Edition*. 2017;**129**:578-582. DOI: 10.1002/ANGE.201610914
- [42] Vermoortele F, Bueken B, Le Bars G, Van De Voorde B, Vandichel M, Houthoofd K, et al. Synthesis modulation as a tool to increase the catalytic activity of metal-organic frameworks: The unique case of UiO-66(Zr). *Journal of the American Chemical Society*. 2013;**135**:11465-11468. DOI: 10.1021/JA405078U/SUPPL_FILE/JA405078U_SI_001.PDF
- [43] Sun CY, Liu SX, Liang DD, Shao KZ, Ren YH, Su ZM. Highly stable crystalline catalysts based on a microporous metal-organic framework and polyoxometalates. *Journal of the American Chemical Society*. 2009;**131**:1883-1888. DOI: 10.1021/JA807357R/SUPPL_FILE/JA807357R_SI_007.CIF
- [44] Chui SSY, Lo SMF, Charmant JPH, Orpen AG, Williams ID. A chemically functionalizable nanoporous material [Cu₃(TMA)₂(H₂O)₃](n). *Science* (80-.). 1999;**283**:1148-1150. DOI: 10.1126/SCIENCE.283.5405.1148/SUPPL_FILE/986116S4_THUMB.GIF
- [45] An Y, Liu Y, An P, Dong J, Xu B, Dai Y, et al. NiII coordination to an Al-based metal-organic framework made from 2-Aminoterephthalate for photocatalytic overall water splitting. *Angewandte Chemie*. 2017;**129**:3082-3086. DOI: 10.1002/ANGE.201612423
- [46] Wang C, Wang JL, Lin W. Elucidating molecular iridium water oxidation catalysts using metal-organic frameworks: A comprehensive structural, catalytic, spectroscopic, and kinetic study. *Journal of the American Chemical Society*. 2012;**134**:19895-19908. DOI: 10.1021/JA310074J/SUPPL_FILE/JA310074J_SI_001.PDF
- [47] Ravon U, Domine ME, Gaudillère C, Desmartin-Chomel A, Farrusseng D. MOFs as acid catalysts with shape selectivity properties. *New Journal of Chemistry*. 2008;**32**:937-940. DOI: 10.1039/B803953B
- [48] Alnaqbi MA, Alzamly A, Ahmed SH, Bakiro M, Kegere J, Nguyen HL. Chemistry and applications of s-block metal-organic frameworks. *Journal of Materials Chemistry A*. 2021;**9**:3828-3854. DOI: 10.1039/D0TA09678D
- [49] Bai Y, Dou Y, Xie LH, Rutledge W, Li JR, Zhou HC. Zr-based metal-organic frameworks: Design, synthesis, structure, and applications. *Chemical Society Reviews*. 2016;**45**:2327-2367. DOI: 10.1039/C5CS00837A
- [50] Feng D, Jiang HL, Chen YP, Gu ZY, Wei Z, Zhou HC. Metal-organic frameworks based on previously unknown Zr₈/Hf₈ cubic clusters. *Inorganic Chemistry*.

2013;52:12661-12667. DOI: 10.1021/IC4018536/SUPPL_FILE/IC4018536_SI_005.PDF

[51] Cavka JH, Jakobsen S, Olsbye U, Guillou N, Lamberti C, Bordiga S, et al. A new zirconium inorganic building brick forming metal organic frameworks with exceptional stability. *Journal of the American Chemical Society*. 2008;130:13850-13851. DOI: 10.1021/JA8057953/SUPPL_FILE/JA8057953_SI_001.PDF

[52] Janczarek M, Kowalska E. On the origin of enhanced photocatalytic activity of copper-modified Titania in the oxidative reaction systems. *Catal*. 2017;7:317. DOI: 10.3390/CATAL7110317

[53] Kurisingal JF, Rachuri Y, Gu Y, Chitumalla RK, Vuppala S, Jang J, et al. Facile green synthesis of new copper-based metal-organic frameworks: Experimental and theoretical study of the CO₂Fixation reaction. *ACS Sustainable Chemistry & Engineering*. 2020;8:10822-10832. DOI: 10.1021/ACSSUSCHEMENG.0C02749/SUPPL_FILE/SC0C02749_SI_001.PDF

[54] Wu ZL, Wang CH, Zhao B, Dong J, Lu F, Wang WH, et al. A semi-conductive copper-organic framework with two types of photocatalytic activity. *Angewandte Chemie International Edition*. 2016;55:4938-4942. DOI: 10.1002/ANIE.201508325

[55] Tasleem S, Tahir M, Khalifa WA. Current trends in structural development and modification strategies for metal-organic frameworks (MOFs) towards photocatalytic H₂ production: A review. *International Journal of Hydrogen Energy*. 2021;46:14148-14189. DOI: 10.1016/J.IJHYDENE.2021.01.162

[56] Wang D, Song Y, Cai J, Wu L, Li Z. Effective photo-reduction to deposit

Pt nanoparticles on MIL-100(Fe) for visible-light-induced hydrogen evolution. *New Journal of Chemistry*. 2016;40:9170-9175. DOI: 10.1039/C6NJ01989G

[57] Cai X, Peng F, Luo X, Ye X, Zhou J, Lang X, et al. Understanding the evolution of cobalt-based metal-organic frameworks in Electrocatalysis for the oxygen evolution reaction. *ChemSusChem*. 2021;14:3163-3173. DOI: 10.1002/CSSC.202100851

[58] Han W, Huang X, Lu G, Tang Z. Research progresses in the preparation of Co-based catalyst derived from Co-MOFs and application in the catalytic oxidation reaction. *Catalysis Surveys from Asia*. 2018;232(23):64-89. DOI: 10.1007/S10563-018-9258-1

[59] Zhang W, Huang R, Song L, Shi X. Cobalt-based metal-organic frameworks for the photocatalytic reduction of carbon dioxide. *Nanoscale*. 2021;13:9075-9090. DOI: 10.1039/D1NR00617G

[60] Yang S, Pattengale B, Kovrigin EL, Huang J. Photoactive Zeolitic Imidazolate framework as intrinsic heterogeneous catalysts for light-driven hydrogen generation. *ACS Energy Letters*. 2017;2:75-80. DOI: 10.1021/ACSENERGYLETT.6B00540/SUPPL_FILE/NZ6B00540_SI_001.PDF

[61] Tonigold M, Tu Y, Bredenkötter B, Rieger B, Bahnmüller S, Hitzbleck J, et al. Heterogeneous catalytic oxidation by MFU-1: A cobalt(II)-containing metal-organic framework. *Angewandte Chemie International Edition*. 2009;48:7546-7550. DOI: 10.1002/ANIE.200901241

[62] Kyogoku K, Yamada C, Suzuki Y, Nishiyama S, Fukumoto K, Yamamoto H, et al. Syntheses of metal-organic framework compounds containing Ni-bipyridyl complex for oligomerization of ethylene. *Journal of the Japan*

Petroleum Institute. 2010;**53**:308-312.
DOI: 10.1627/JPI.53.308

[63] Ran J, Qu J, Zhang H, Wen T, Wang H, Chen S, et al. 2D metal organic framework Nanosheet: A universal platform promoting highly efficient visible-light-induced hydrogen production. *Advanced Energy Materials*. 2019;**9**:1803402. DOI: 10.1002/AENM.201803402

[64] Assi H, Mouchaham G, Steunou N, Devic T, Serre C. Titanium coordination compounds: From discrete metal complexes to metal–organic frameworks. *Chemical Society Reviews*. 2017;**46**:3431-3452. DOI: 10.1039/C7CS00001D

[65] Li L, Wang X, Liu T, Ye J. Titanium-based MOF materials: From crystal engineering to Photocatalysis. *Small Methods*. 2020;**4**:2000486. DOI: 10.1002/smt.202000486

[66] Scarpi-Luttenauer M, Mobian P, Barloy L. Synthesis, structure and functions of discrete titanium-based multinuclear architectures. *Coordination Chemistry Reviews*. 2022;**459**:214439. DOI: 10.1016/J.CCR.2022.214439

[67] Buettner KM, Valentine AM. Bioinorganic chemistry of titanium. *Chemical Reviews*. 2012;**112**:1863-1881. DOI: 10.1021/cr1002886

[68] Serre C, Groves JA, Lightfoot P, Slawin AMZ, Wright PA, Stock N, et al. Synthesis, structure and properties of related microporous N,N'-piperazinebis(methylenephosphonates) of aluminum and titanium. *Chemistry of Materials*. 2006;**18**:1451-1457. DOI: 10.1021/cm052149l

[69] Dan-Hardi M, Serre C, Frot T, Rozes L, Maurin G, Sanchez C, et al. A new photoactive crystalline highly porous titanium(IV) dicarboxylate.

Journal of the American Chemical Society. 2009;**131**:10857-10859. DOI: 10.1021/JA903726M/SUPPL_FILE/JA903726M_SI_002.CIF

[70] Gao J, Miao J, Li PZ, Teng WY, Yang L, Zhao Y, et al. A p-type Ti(IV)-based metal–organic framework with visible-light photo-response. *Chemical Communications*. 2014;**50**:3786-3788. DOI: 10.1039/C3CC49440C

[71] Mason JA, Darago LE, Lukens WW, Long JR. Synthesis and O₂ reactivity of a titanium(III) metal-organic framework. *Inorganic Chemistry*. 2015;**54**:10096-10104. DOI: 10.1021/ACS.INORGCHEM.5B02046/SUPPL_FILE/IC5B02046_SI_001.PDF

[72] Bueken B, Vermoortele F, Vanpoucke DEP, Reinsch H, Tsou CC, Valvekens P, et al. A flexible photoactive titanium metal–organic framework based on a [TiIV₃(μ₃-O)(O)₂(COO)₆] cluster. *Angewandte Chemie International Edition*. 2015;**54**:13912-13917. DOI: 10.1002/ANIE.201505512

[73] Nguyen NTT, Furukawa H, Gándara F, Trickett CA, Jeong HM, Cordova KE, et al. Three-dimensional metal-Catecholate frameworks and their ultrahigh proton conductivity. *Journal of the American Chemical Society*. 2015;**137**:15394-15397. DOI: 10.1021/JACS.5B10999/SUPPL_FILE/JA5B10999_SI_004.CIF

[74] Assi H, Pardo Pérez LC, Mouchaham G, Ragon F, Nasalevich M, Guillou N, et al. Investigating the case of titanium(IV) Carboxyphenolate photoactive coordination polymers. *Inorganic Chemistry*. 2016;**55**:7192-7199. DOI: 10.1021/ACS.INORGCHEM.6B01060/SUPPL_FILE/IC6B01060_SI_004.CIF

[75] Wang S, Wang H, Ding WX. Pyroptosis, a novel player for alcoholic

hepatitis? *Hepatology*. 2018;**67**:1660-1662. DOI: 10.1002/HEP.29725

[76] Castells-Gil J, Padiál NM, Almora-Barrios N, Da Silva I, Mateo D, Albero J, et al. De novo synthesis of mesoporous photoactive titanium(IV)-organic frameworks with MIL-100 topology. *Chemical Science*. 2019;**10**:4313-4321. DOI: 10.1039/C8SC05218B

[77] Lan G, Ni K, Veroneau SS, Feng X, Nash GT, Luo T, et al. Titanium-based nanoscale metal-organic framework for type I photodynamic therapy. *Journal of the American Chemical Society*. 2019;**141**:4204-4208. DOI: 10.1021/JACS.8B13804/SUPPL_FILE/JA8B13804_SI_002.PDF

[78] Li C, Xu H, Gao J, Du W, Shangguan L, Zhang X, et al. Tunable titanium metal-organic frameworks with infinite 1D Ti-O rods for efficient visible-light-driven photocatalytic H₂ evolution. *Journal of Materials Chemistry A*. 2019;**7**:11928-11933. DOI: 10.1039/C9TA01942A

[79] Zou L, Feng D, Liu TF, Chen YP, Yuan S, Wang K, et al. A versatile synthetic route for the preparation of titanium metal-organic frameworks. *Chemical Science*. 2016;**7**:1063-1069. DOI: 10.1039/c5sc03620h

[80] Rozes L, Sanchez C. Titanium oxo-clusters: Precursors for a Lego-like construction of nanostructured hybrid materials. *Chemical Society Reviews*. 2011;**40**:1006-1030. DOI: 10.1039/C0CS00137F

[81] Serre C, Férey G. Hybrid open frameworks. 8. Hydrothermal synthesis, crystal structure, and thermal behavior of the first three-dimensional titanium(IV) diphosphonate with an open structure: Ti₃O₂(H₂O)₂(O₃P-(CH

2)-PO₃)₂·(H₂O)₂, or MIL-22. *Inorganic Chemistry*. 1999;**38**:5370-5373. DOI: 10.1021/IC990345M/SUPPL_FILE/IC990345M_S.PDF

[82] Nguyen HL. Perspectives on titanium-based metal-organic frameworks. *Journal of Physics: Energy*. IOP Publishing Ltd. April 1, 2021:021003. DOI: 10.1088/2515-7655/abe3c9

[83] Fang WH, Zhang L, Zhang J. Synthetic strategies, diverse structures and tuneable properties of polyoxo-titanium clusters. *Chemical Society Reviews*. 2018;**47**:404-421. DOI: 10.1039/C7CS00511C

[84] Li Y, Yang B, Liu B. MOF assisted synthesis of TiO₂/Au/Fe₂O₃ hybrids with enhanced photocatalytic hydrogen production and simultaneous removal of toxic phenolic compounds. *Journal of Molecular Liquids*. 2021;**322**:114815. DOI: 10.1016/J.MOLLIQ.2020.114815

[85] Chen X, Peng X, Jiang L, Yuan X, Yu H, Wang H, et al. Recent advances in titanium metal-organic frameworks and their derived materials: Features, fabrication, and photocatalytic applications. *Chemical Engineering Journal*. 2020;**395**:125080. DOI: 10.1016/J.CEJ.2020.125080

[86] Qiu LG, Xu T, Li ZQ, Wang W, Wu Y, Jiang X, et al. Hierarchically micro- and mesoporous metal-organic frameworks with tunable porosity. *Angewandte Chemie International Edition*. 2008;**47**:9487-9491. DOI: 10.1002/ANIE.200803640

[87] Sun D, Li Z. Robust Ti- and Zr-based metal-organic frameworks for photocatalysis. *Chinese Journal of Chemistry*. 2017;**35**:135-147. DOI: 10.1002/CJOC.201600647

- [88] Brozek CK, Dincă M. Ti³⁺-, V^{2+/3+}-, Cr^{2+/3+}-, Mn²⁺-, and Fe²⁺-substituted MOF-5 and redox reactivity in Cr- and Fe-MOF-5. *Journal of the American Chemical Society*. 2013;**135**:12886-12891. DOI: 10.1021/JA4064475/SUPPL_FILE/JA4064475_SI_001.PDF
- [89] Nguyen HL, Vu TT, Le D, Doan TLH, Nguyen VQ, Phan NTS. A titanium-organic framework: Engineering of the band-gap energy for photocatalytic property enhancement. *ACS Catalysis*. 2017;**7**:338-342. DOI: 10.1021/ACSCATAL.6B02642/SUPPL_FILE/CS6B02642_SI_001.PDF
- [90] Visible-Light-Active Photocatalysis: Nanostructured Catalyst Design, Mechanisms, and Applications | Wiley. n.d. <https://www.wiley.com/en-ie/Visible+Light+Active+Photocatalysis:+Nanostructured+Catalyst+Design,+Mechanisms,+and+Application+s-p-9783527342938> [Accessed: July 24, 2022]
- [91] Hendon CH, Tiana D, Fontecave M, Sanchez C, D'Arras L, Sassoey C, et al. Engineering the optical response of the titanium-MIL-125 metal-organic framework through ligand functionalization. *Journal of the American Chemical Society*. 2013;**135**:10942-10945. DOI: 10.1021/ja405350u
- [92] Canivet J, Fateeva A, Guo Y, Coasne B, Farrusseng D. Water adsorption in MOFs: Fundamentals and applications. *Chemical Society Reviews*. 2014;**43**:5594-5617. DOI: 10.1039/C4CS00078A
- [93] Burtch NC, Jasuja H, Walton KS. Water stability and adsorption in metal-organic frameworks. *Chemical Reviews*. 2014;**114**:10575-10612. DOI: 10.1021/cr5002589
- [94] Wang C, Liu X, Keser Demir N, Chen JP, Li K. Applications of water stable metal-organic frameworks. *Chemical Society Reviews*. 2016;**45**:5107-5134. DOI: 10.1039/C6CS00362A
- [95] Wang K, Lv XL, Feng D, Li J, Chen S, Sun J, et al. Pyrazolate-based Porphyrinic metal-organic framework with extraordinary base-resistance. *Journal of the American Chemical Society*. 2016;**138**:914-919. DOI: 10.1021/JACS.5B10881/SUPPL_FILE/JA5B10881_SI_002.CIF
- [96] Zhang G, Lan ZA, Wang X. Conjugated polymers: Catalysts for photocatalytic hydrogen evolution. *Angewandte Chemie International Edition*. 2016;**55**:15712-15727. DOI: 10.1002/ANIE.201607375
- [97] Yu J, Low J, Xiao W, Zhou P, Jaroniec M. Enhanced photocatalytic CO₂-reduction activity of anatase TiO₂ by Coexposed {001} and {101} facets. *Journal of the American Chemical Society*. 2014;**136**:8839-8842. DOI: 10.1021/JA5044787/SUPPL_FILE/JA5044787_SI_001.PDF
- [98] Liao X, Wei W, Zhou Y, Zhang M, Cai Y, Liu H, et al. A Ti-based bi-MOF for the tandem reaction of H₂O₂ generation and catalytic oxidative desulfurization. *Catalysis Science & Technology*. 2020;**10**:1015-1022. DOI: 10.1039/C9CY02318F
- [99] Li SL, Xu Q. Metal-organic frameworks as platforms for clean energy. *Energy & Environmental Science*. 2013;**6**:1656-1683. DOI: 10.1039/C3EE40507A
- [100] Han SY, Pan DL, Chen H, Bu XB, Gao YX, Gao H, et al. A Methylthio-functionalized-MOF Photocatalyst with high performance for visible-light-driven H₂ evolution. *Angewandte Chemie*

International Edition. 2018;57:9864-9869. DOI: 10.1002/ANIE.201806077

[101] Isaka Y, Kondo Y, Kawase Y, Kuwahara Y, Mori K, Yamashita H. Photocatalytic production of hydrogen peroxide through selective two-electron reduction of dioxygen utilizing amine-functionalized MIL-125 deposited with nickel oxide nanoparticles. *Chemical Communications*. 2018;54:9270-9273. DOI: 10.1039/C8CC02679C

[102] Fu Y, Yang H, Du R, Tu G, Xu C, Zhang F, et al. Enhanced photocatalytic CO₂ reduction over Co-doped NH₂-MIL-125(Ti) under visible light. *RSC Advances*. 2017;7:42819-42825. DOI: 10.1039/C7RA06324E

[103] Serre C, Férey G. Hydrothermal synthesis and structure determination from powder data of new three-dimensional titanium(IV) diphosphonates Ti(O₃P-(CH₂)_n-PO₃) or MIL-25n (n=2, 3). *Inorganic Chemistry*. 2001;40:5350-5353. DOI: 10.1021/IC010260X/ASSET/IMAGES/MEDIUM/IC010260XN00001.GIF

[104] Ratnamala A, Reddy GD, Noorjahaan M, Manjunatha H, Janardan S, Kumar NS, et al. Titanium-based metal-organic frameworks for photocatalytic applications. *Metal-Organic Frameworks for Chemical Reactions*. 2021:37-63. DOI: 10.1016/B978-0-12-822099-3.00003-4

[105] Cassaignon S, Koelsch M, Jolivet JP. Selective synthesis of brookite, anatase and rutile nanoparticles: Thermolysis of TiCl₄ in aqueous nitric acid. *Journal of Materials Science*. 2007;4216(42):6689-6695. DOI: 10.1007/S10853-007-1496-Y

[106] Zhu J, Li PZ, Guo W, Zhao Y, Zou R. Titanium-based metal-organic frameworks for photocatalytic

applications. *Coordination Chemistry Reviews*. 2018;359:80-101. DOI: 10.1016/j.ccr.2017.12.013

[107] Yuan S, Liu TF, Feng D, Tian J, Wang K, Qin J, et al. A single crystalline porphyrinic titanium metal-organic framework. *Chemical Science*. 2015;6:3926-3930. DOI: 10.1039/C5SC00916B

[108] Hu S, Liu M, Li K, Zuo Y, Zhang A, Song C, et al. Solvothermal synthesis of NH₂-MIL-125(Ti) from circular plate to octahedron. *CrystEngComm*. 2014;16:9645-9650. DOI: 10.1039/C4CE01545B

[109] Han Y, Han L, Zhang L, Dong S. Ultrasonic synthesis of highly dispersed Au nanoparticles supported on Ti-based metal-organic frameworks for electrocatalytic oxidation of hydrazine. *Journal of Materials Chemistry A*. 2015;3:14669-14674. DOI: 10.1039/C5TA03090K

[110] Nguyen HL, Gándara F, Furukawa H, Doan TLH, Cordova KE, Yaghi OM. A titanium-organic framework as an exemplar of combining the chemistry of metal- and covalent-organic frameworks. *Journal of the American Chemical Society*. 2016;138:4330-4333. DOI: 10.1021/JACS.6B01233/SUPPL_FILE/JA6B01233_SI_001.PDF

[111] Brozek CK, Dincă M. Cation exchange at the secondary building units of metal-organic frameworks. *Chemical Society Reviews*. 2014;43:5456-5467. DOI: 10.1039/C4CS00002A

[112] Kim M, Cahill JF, Fei H, Prather KA, Cohen SM. Postsynthetic ligand and cation exchange in robust metal-organic frameworks. *Journal of the American Chemical Society*. 2012;134:18082-18088.

DOI: 10.1021/JA3079219/SUPPL_FILE/JA3079219_SI_001.PDF

3773(19980619)37:11<1460::AID-ANIE1460>3.0.CO;2-Z

[113] McNamara ND, Hicks JC. Chelating agent-free, vapor-assisted crystallization method to synthesize hierarchical microporous/mesoporous MIL-125 (Ti). *ACS Applied Materials & Interfaces*. 2015;7:5338-5346. DOI: 10.1021/AM508799D/SUPPL_FILE/AM508799D_SI_001.PDF

[119] Jiang F, Dai L, Shi Y, Wang Z. A three-dimensional chiral crystal structure constructed from a chiral triazolate ligand showing an SrSi₂ topology: Poly[bis(μ -3,3,5-diethyl-1,2,4-triazolato- κ 3N1: N2: N4)trisilver nitrate]. *Acta Crystallographica Section C: Crystal Structure Communications*. 2013;69:1485-1487. DOI: 10.1107/S0108270113029788/YF3050ISUP2.HKL

[114] Shen L, Luo M, Huang L, Feng P, Wu L. A clean and general strategy to decorate a titanium metal-organic framework with noble-metal nanoparticles for versatile photocatalytic applications. *Inorganic Chemistry*. 2015;54:1191-1193. DOI: 10.1021/IC502609A/SUPPL_FILE/IC502609A_SI_001.PDF

[120] Bueken B, Vermoortele F, Vanpoucke DEP, Reinsch H, Tsou C-C, Valvekens P, et al. A flexible photoactive titanium metal-organic framework based on a [TiIV₃(μ ³-O)(O)₂(COO)₆] cluster. *Angewandte Chemie*. 2015;127:14118-14123. DOI: 10.1002/ANGE.201505512

[115] Fu Y, Sun L, Yang H, Xu L, Zhang F, Zhu W. Visible-light-induced aerobic photocatalytic oxidation of aromatic alcohols to aldehydes over Ni-doped NH₂-MIL-125(Ti). *Applied Catalysis B: Environmental*. 2016;187:212-217. DOI: 10.1016/J.APCATB.2016.01.038

[121] Hong K, Bak W, Chun H. Unique coordination-based heterometallic approach for the stoichiometric inclusion of high-valent metal ions in a porous metal-organic framework. *Inorganic Chemistry*. 2013;52:5645-5647. DOI: 10.1021/IC400607W/SUPPL_FILE/IC400607W_SI_002.PDF

[116] Wang H, Yuan X, Wu Y, Chen X, Leng L, Zeng G. Photodeposition of metal sulfides on titanium metal-organic frameworks for excellent visible-light-driven photocatalytic Cr(vi) reduction. *RSC Advances*. 2015;5:32531-32535. DOI: 10.1039/c5ra01283j

[117] Nguyen HL. The chemistry of titanium-based metal-organic frameworks. *New Journal of Chemistry*. 2017;41:14030-14043. DOI: 10.1039/C7NJ03153J

[118] Batten SR, Robson R. Interpenetrating nets: Ordered, periodic entanglement. *Angewandte Chemie International Edition*. 1998;37:1460-1494. DOI: 10.1002/(SICI)1521-