



## Review

## Titanium-based metal–organic frameworks for photocatalytic applications

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## ABSTRACT

Titanium-based metal–organic frameworks (Ti-MOFs) are considered one of the most appealing subclasses of the MOFs family owing to their promising optoelectronic and photocatalytic properties, high thermal and chemical stability, and unique structural features. Restricted by their challenging synthesis, however, only limited Ti-MOFs have been reported and utilized so far. In this review, we comprehensively summarize the synthesis, structures and photocatalytic applications of Ti-MOFs reported to date, particularly focusing on the synthetic strategy to develop new Ti-MOF structures and composites as photocatalysts with high sunlight harvesting efficiency and photocatalytic activity. Photocatalytic applications including photocatalytic redox reactions, water splitting, organic pollutant degradation, polymerization, deoxygenation reaction and sensors are highlighted. For wider interests, other applications of Ti-MOFs are also briefly introduced. This review aims to provide up-to-date developments of Ti-MOFs beneficial to researchers who currently work or are interested in this field.

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**Abbreviations:** AB, ammonia borane; abz, 4-aminobenzoate; AC, acetylacetone; BDA, benzene-1,4-dialdehyde; BET, Brunauer–Emmett–Teller; BMA, benzyl methacrylate; BPDA, 4,4'-biphenyldicarboxaldehyde; cat, catecholate; cdc, *trans*-1,4-cyclo-hexanedicarboxylate; COFs, covalent-organic frameworks; CPE, carbon paste electrode; [Cp<sub>2</sub>Ti<sup>IV</sup>Cl<sub>2</sub>], dicyclopentadienyl titanium(IV) dichloride; CTAB, cetyltrimethylammonium bromide; dabco, 1,4-diazabicyclo-[2.2.2]octane; DEAH, diethylammonium; DEF, N,N'-diethylformamide; DMF, N,N'-dimethylformamide; dmobpy, 4,4'-dimethoxy-2,2'-bipyridine; DSSC, dye-sensitized solar cell; EXAFS, Extended X-ray Absorption Fine Structure; GFs, graphite felts; H<sub>2</sub>cdc, *trans*-1,4-cyclo-hexanedicarboxylic acid; H<sub>3</sub>obdc, 2-hydroxyterephthalic acid; H<sub>3</sub>ondc, 3-hydroxy-2,7-naphthalenedicarboxylic acid; H<sub>4</sub>DOBDC, 2,5-dihydroxyterephthalic acid; H<sub>4</sub>L, N,N'-piperazinebismethylenephosphonic acid; H<sub>6</sub>THO, 2,3,6,7,9,11-hexahydroxytriphenylene; HVMO, high valence metathesis and oxidation; LIBs, lithium ion batteries; LMCT, ligand-to-metal charge transfer; LUMO, Lowest Unoccupied Molecular Orbital; MB, methylene blue; MMA, methyl methacrylate; MOFs, metal–organic frameworks; MOPs, metal–organic polyhedrons; NDC, 2,6-naphthalen-di-carboxylate; NIBs, Na ion batteries; NMR, Nuclear Magnetic Resonance; NTU, Nanyang Technological University; pipH<sub>2</sub>, piperazinium; PSM, post-synthetic metathesis; PXRD, powder X-ray diffraction; P123, PEG-PPG-PEG symmetric triblock copolymer; RFB, redox flow battery; rGO, reduced graphene oxide; RhB, rhodamine B; RSD, relative standard deviation; SBUs, secondary building blocks; TBOT, tetrabutyl titanate; TCPP, tetrakis(4-carboxyphenyl) porphyrin; TEOA, triethanolamine; Ti(iOPr)<sub>4</sub>, titanium tetraisopropoxide; Ti-MOFs, titanium-based metal–organic frameworks; Ti(OR)<sub>4</sub>, titanium alkoxides; TOF, turn-over frequency; TON, turn-over number; UV, ultraviolet; VAC, vapor-assisted crystallization; Vis-IR, visible-infrared; Vis-NIR, visible-near infrared; XRD, X-ray diffraction; 2D, bidimensional; 2-mpy, 2-mercapto-pyridyl; 3D, tridimensional.

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## 1. Introduction

Metal-organic frameworks (MOFs) have welcomed their third decade of intensive study since the early 1990s [1–4]. During the last 20 years, the MOF community has been significantly developed, attracting researchers from diverse fields including coordination chemistry [5–7], nano-engineering [8–10], gas storage and separation [11–16], catalysis [17–23], optics and optoelectronics [24–28], sensing [29–31], energy storage and conversion [32–35], biomedical science [36–39] etc. In terms of the chemistry nature of MOFs, one of the ultimate purposes of structural chemists is to construct MOFs from any metallic element in the periodic table in a well-controlled and pre-designed manner. Such efforts have partially succeeded considering the thousands of MOFs reported hitherto, mostly constructed from di- or trivalent ions of 3p metals [40], 3d transition metals [41–44] and lanthanides [45,46], while developing MOFs based on high-valent metal ions remains a big challenge [47,48]. On the other hand, increasing the charge of metal ions leads to stronger polarizing power, which significantly strengthens the metal-ligand bonds and hence improves the chemical stability of MOFs [49]. Most of the MOFs constructed from divalent metal ions (Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, etc.) including many highly porous and conventional ones (MOF-5, MOF-74, HKUST-1, etc.) suffer from poor water stability due to weak interaction between metal centers and organic ligands, limiting their wide applications [50–54]. Trivalent ions (Fe<sup>3+</sup>, Al<sup>3+</sup>, Cr<sup>3+</sup>, etc.) have proven useful in building MOFs with high stability [55,56], and the success of Zr-based MOFs, started from the prototypical UiO-66 [57], undoubtedly confirms the feasibility of such strategy.

From the structure point of view, high-valent metals are quite different from low-valent ones. Their high charge over ionic radius makes the metal precursors highly reactive and oxophilic, tending to form large and rigid multi-nuclear secondary building blocks (SBUs) with high coordination number during MOFs formation, leading to structure diversity and enhanced framework ruggedness [58,59]. For example, Zr(IV) ions in Zr-based MOFs could generate Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>12-n</sub>(-COO)<sub>n</sub> (*n* = 6, 8, 10 or 12) SBUs with different coordination numbers. Incorporating diverse Zr-based SBUs with various choices of polytopic organic ligands, such as dicarboxylic acid, tricarboxylic acid and planar tetracarboxylic acid, abundant MOFs architectures have been constructed, boosting the rapid growth of the field of Zr(VI)-based MOFs [60].

In this regard, Ti or titanium is considered a most appealing candidate for construction of MOFs with high chemical stability and structural diversity. Titanium is just above zirconium in the periodic table, thus also a typical tetravalent element in ionic form, while the much smaller ionic radius of Ti<sup>4+</sup> comparing to Zr<sup>4+</sup> grants it stronger affinity to oxygen. Actually, TiO<sub>2</sub> is only soluble in highly acidic media (pH ≤ 0). Such stability could also be inherited by Ti-based MOFs constructed from Ti-oxo-carboxylate SBUs with strong Ti–O bonds. The most fascinating feature of Ti is, however, its well-known multifunctionality, typically, redox activity (transition between Ti<sup>3+</sup> and Ti<sup>4+</sup>), photochemical property, and biocompatibility [61]. Possibility to engineer the optical band gap and integrate additional functional moieties by modification of organic ligands and nano-engineering has also attracted intensive interests from the traditional TiO<sub>2</sub> community [62–65]. Efforts to construct Ti-based MOFs could date back to the early days of MOFs, mostly failed, resulting in a wide range of amorphous and

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