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Review

When defects turn into virtues: The curious case of zirconium-based metal-organic frameworks

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ABSTRACT

Zirconium-based metal-organic frameworks (Zr-MOFs) are one of the most attractive classes of MOF materials, due to their superior thermal, chemical and mechanical stability. Recently, Zr-MOFs have been shown to feature an unusually high concentration of defects without suffering from severe loss of stability. This feature makes Zr-MOFs unique among MOF materials and is generating additional interest around them. Defects have a significant impact on porosity, thermal properties, mechanical properties, Lewis and Brønsted acidity. Researchers have quickly recognized that defects can be engineered to tune the physical-chemical properties of Zr-MOFs, opening up new avenues for their practical application. The scope of the present review article is to provide a comprehensive account of the progress made in this field since the discovery of defects in Zr-MOFs in 2011 and to point out some relevant controversies and open issues of fundamental nature that need to be addressed to improve the understanding of the very nature of defects.

Contents

Abbreviations: MOF, metal-organic framework; Zr-MOF, zirconium-based metal-organic framework; H_2bdc, terephthalic acid; H_2bpdc, 4,4′-biphenyldicarboxylic acid; H_2tpdc, 4,4′-terphenyldicarboxylic acid; SBU, secondary building unit; H_3btc, 1,3,5-benzenetricarboxylic acid; H_4tbaPy, 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene; H_2pzdc, 1*H*-pyrazole-3,5-dicarboxylate; DMF, *N*,*N*-dimethylformamide; PSM, post-synthetic modification; TGA, thermogravimetric analysis; AA, acetic acid; SCXRD, single-crystal X-ray diffraction; BA, benzoic acid; PXRD, powder X-ray diffraction; FA, formic acid; PDF, pair distribution function; BET, Brunauer-Emmett-Teller; PA, propionic acid; *Qst*, isosteric heat of adsorption; DFT, density functional theory; DFA, difluoroacetic acid; TFA, trifluoroacetic acid; NMR, nuclear magnetic resonance; NTE, negative thermal expansion; CA, chloroacetic acid; CUS, coordinatively unsaturated site; SA, stearic acid; RH, relative humidity; AC, alternate current; Gly, glycine; L-Pro, L-proline; L-Phe, L-phenylalanine; DRIFTS, diffuse reflectance infrared Fourier transform spectroscopy; EDS, energy dispersive X-ray spectroscopy; PSE, post-synthetic exchange; H_4tcpp, tetrakis(4-carboxyphenyl)porphyrin; SALI, solvent assisted ligand incorporation; SLI, sequential linker installation; H_2Me_2-bpdc, 2,2′-dimethylbiphenyl-4,4′-dicarboxylic acid; H_2Me_2-tpdc, 2′,5′-dimethylterphenyl-4,4″-dicarboxylic acid; PSDH, post-synthetic defect healing; PSDG, post-synthetic defect generation; PSDE, post-synthetic defect exchange; H_3sbdc, 2-sulfoterephthalic acid; SAXS, small angle X-ray scattering; WAXS, wide angle X-ray scattering; MOMO, metalorganic molecular orbital; L-Ser, L-serine.

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1. Introduction

The discovery of zirconium-based metal-organic frameworks (Zr-MOFs) UiO-66, UiO-67 and UiO-68 in 2008 represented a milestone in MOF chemistry [1]. These MOFs have general formula $Zr_6O_4(OH)_4(L)_6$, where *L* can be either terephthalate (bdc^{2-}, UiO-66, Chart 1), 4,4′-biphenyldicarboxylate ($bpdc^{2-}$, UiO-67, Chart 1) or 4,4′-terphenyldicarboxylate ($tpdc^{2-}$, UiO-68, Chart 1), and their crystal structure is based on the connection of hexanuclear $[Zr_6O_4(OH)_4]^{12+}$ clusters *via* the bridging organic linkers, with each cluster connected to twelve other clusters (Fig. 1). Since 2008, the same $[Zr_6O_4(OH)_4]^{12+}$ clusters have been combined with organic linkers having diverse geometrical and symmetrical features, giving rise to a large family of Zr-MOFs featuring a wide range of topologies (Fig. 2) [2–7].

Zr-MOFs display outstanding stability when compared to most of the known MOFs based on different metal ions or clusters: they are thermally stable up to 450 °C [1,3,5], can be soaked in many organic solvents and acidic aqueous solutions without suffering any significant damage [8,9] and retain their crystal structure under high pressure [10,11]. Such superior stability has been attributed to the strength of the carboxylate-Zr bond and to the high degree of connectivity of the metal clusters and is extremely attractive for practical applications. These applications include gas sorption/separation [12–16], heterogeneous catalysis [17–21], drug delivery [22–26], sensing [27–32] and electrochemistry [33–36].

The success of Zr-MOFs is also due to the ease and versatility of their synthesis [37]. This is demonstrated by the large number of new procedures that have been developed since the first solvothermal synthesis in *N,N*-dimethylformamide (DMF) [1]: water- [38–41], acetone- [42] and cyrene-based [43] synthesis, microwave-assisted synthesis [44–47], mechanochemical synthesis [48,49], chemical vapor deposition [50], spray-drying [51], continuous flow synthesis [38,52–56]. The use of monocarboxylic acids (Chart 2) or inorganic acids (HCl, HF) as modulators during synthesis is a powerful tool that allows to obtain crystals with sizes ranging from the micrometer to the low nanometer range [57–63]. Compounds that

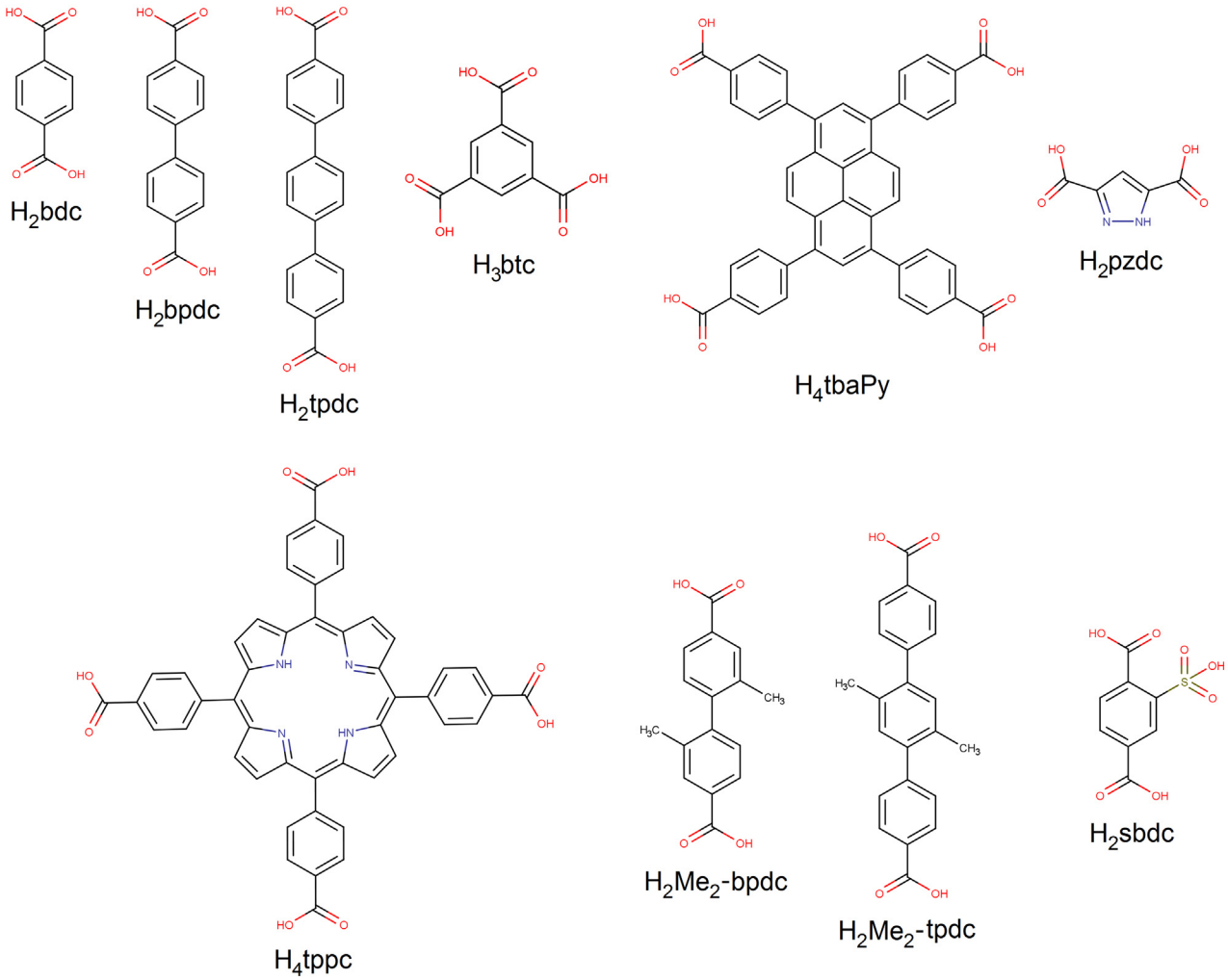

Chart 1. Molecular structure of the organic linkers cited in this review.