



Review

Synthetic design of functional boron imidazolate frameworks



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Contents

1. Introduction	255
1.1. Framework design principles	256
1.2. The charge distribution	256
1.3. Two-step synthetic strategy of BIFs	258
2. Various types of BIFs	258
2.1. BIFs based on the four-connected boron imidazolate ligands	258
2.1.1. 4-Coordinate and 4-connected structures	258
2.1.2. 6-Coordinate and 4-connected structures	260
2.1.3. Other structures	260
2.2. BIFs based on the three-connected boron-imidazolate ligands	262
3. Others issues for BIFs	265
4. Summary and prospective	265
Acknowledgements	265
References	266

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ABSTRACT

Boron imidazolate frameworks (BIFs) are a family of metal–organic frameworks (MOFs) that based on the cross-linking of predetermined boron–imidazolate complexes by metal cations. One fundamental feature of BIFs is that both three-connected tripodal ligands and four-connected tetrahedral ligands can be readily synthesized prior to solvothermal synthesis. In this review, we focus on the recent advances in BIFs that possess zeolite and other types of topological nets based on the three- or four- connected boron imidazolate ligands. In particular, we emphasize the basic design principles of the synthetic methodology to construct specifically topological BIFs, especially, towards the zeolitic topologies.

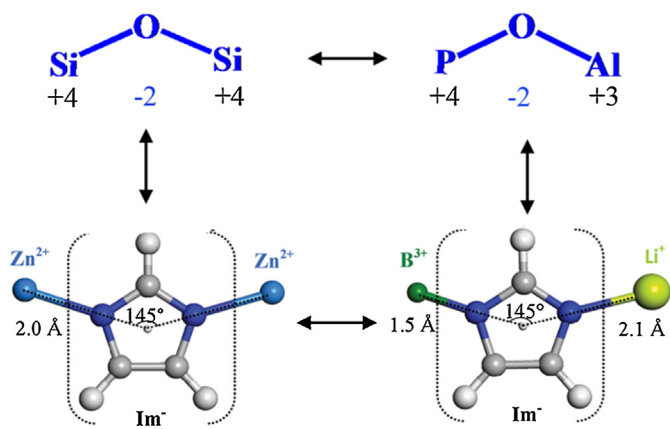
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1. Introduction

Zeolites are one of humanity's most important microporous materials [1–3]. In fact, a major part of the global economy currently relies on the use of these aluminosilicates in many industrial processes. These materials are comprised of Si and/or Al tetrahedral metal ions (T), bridged by oxygen atoms (O, technically oxide ions) at approximately 145° T–O–T angles. A major current goal in chemistry is to create structures that mimic features of zeolites in which organic units and transition metals are

introduced into the backbone of these types of zeolite [4–9]. The recent decades has witnessed an explosive growth of metal–organic frameworks (MOFs) which are built from organic linkers and inorganic metal nodes [10–17]. To some extent, MOFs have a higher degree of designability and adjustability in their structures and functions. Due to their easily controllable synthesis and modification, the search for new zeolite-like structures is extended to metal–organic frameworks. Attributed to the similarity of coordination geometries between tetrahedral metal imidazolate and aluminosilicates, metal–organic zeolites based on imidazolate ligands with different substituents, have been studied extensively [18–23]. Metal–organic zeolites represent a unique subclass of MOF material that combines the remarkable chemical and thermal stability of inorganic zeolites with the rich topological

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Scheme 1. The similarity of coordination geometries between tetrahedral metal imidazolate and aluminosilicates. **ZIFs** (left) versus **BIFs** (right) in terms of metal–imidazole–metal angles and distances.

diversity characteristic of **MOFs**. Zeolitic imidazolate frameworks (**ZIFs**) constitute an important sub-class of metal organic frameworks (**MOFs**). Boron imidazolate frameworks (**BIFs**) is a new class of metal–organic zeolite materials based on the crosslinking of various pre-synthesized boron-imidazolate complexes by metal cations [24–28].

1.1. Framework design principles

Imidazolate, the five-membered aromatic nitrogen heterocycles, is an important building block of many metal–organic zeolites, because of the two nitrogen donors oriented at an angle of ca. 135–145° [29]. For assembly of imidazolates with differently charged tetrahedral nodes, two important types of zeolite crystalline materials, zeolitic imidazolate frameworks (**ZIFs**) and boron imidazolate frameworks (**BIFs**), have been widely studied. As for **ZIFs** with the general framework composition of $M(\text{im})_2$ ($M = \text{Zn}, \text{Co}$ or Cd , $\text{im} = \text{imidazolate}$), the typical construction strategy is inspired by the similarity between the Si–O–Si angle (145°) in zeolitic SiO_2 and the $M\text{–Im–M}$ angle in metal imidazolate (Scheme 1). Tetrahedral metal cations (usually Zn^{2+} , Co^{2+} or Cd^{2+}) are linked by imidazolate derivatives to create topologies that are analogous to those of aluminosilicate zeolites. In these materials, the metal ions form the tetrahedral centers play the role of silicon and the imidazolate anions form bridges mimic the role of oxygen. Because of their exceptional chemical and thermal stability, **ZIFs** hold great promise as porous materials for a variety of applications (i.e. separation, storage, and catalysis) [30–33].

Boron imidazolate frameworks (**BIFs**) are a series of lightweight **ZIF** analogues based on predetermined tetrahedral boron-imidazolate complexes. So far, the vast majority of reported porous **MOFs** are based on transition (or post-transition) metals that are beyond the third period of the periodic table. Recently, there has been a surge of interest in replacement of these metals with lightweight, main-group metals (e.g. Li , Mg , and Al) to produce a lower framework density, which is desirable for enhancing gravimetric energy storage capacity of gas-storage materials [34–36]. The use of B as the framework polyhedral node is very attractive because boron is one of the lightest elements. Besides, ultralight chemical elements Li can be used as vertices for constructing **BIF** frameworks, **BIFs** are of outstanding interest for developing lower-density **MOFs**.

A variety of preparative approaches of **MOFs** have been undertaken in the last two decades, such as hydro(solvo)thermal, ionothermal, urothermal and surfactant-thermal methods [37–40]. Generally, **ZIFs** are synthesized under one-pot hydro(solvo)thermal

conditions between imidazolate ligands and metal salts at temperatures ranging between 85 and 150 °C. Different from **ZIFs**, **BIFs** can be synthesized with two-step synthetic strategy. These boron-imidazolate ligands are synthesized prior to the **MOF** process and then they are linked by tetrahedral metal cations. Therefore, **BIFs** have two different tetrahedral cations (e.g., Li^+ and B^{3+}) with the general framework composition $\text{MB}(\text{im})_4$, which are comparable to zeolitic AlPO_4 (Scheme 1). One advantage of **BIFs** is that they can use ultralight chemical elements (e.g., Li^+ and B^{3+}) as vertices for constructing low-density frameworks. The **BIF** materials seamlessly combined the coordinate bonds of metal organic frameworks (**MOFs**) and covalent bonds of covalent organic frameworks (**COFs**) by using the pre-synthesized boron-imidazolate ligands. Furthermore, with the two-step synthetic strategy, the connectivity of boron imidazolate ligands can be controlled through the first-step chemical synthesis. As a result, both four-connected tetrahedral $\text{B}(\text{im})_4^-$ ligand and three-connected tetrahedral $\text{BH}(\text{im})_3^-$ ligands can be readily synthesized prior to solvothermal assembly, thus further increasing the diversity of materials accessible. The strategy affords materials with the typical 4-connected zeolitic topologies, but also other types of nets. Therefore, the interrupted **BIFs** have been developed with 3-connected nodes in these zeolite type topologies, which still remain a synthetic challenge in the one-pot hydro(solvo)thermal synthetic system in **ZIFs** [27].

So far, a total of 45 **BIF** materials have been made (Table 1). Among the 45 **BIFs**, four distinct 4-coordinated topologies purely based on boron-imidazolate ligands and metal cations: two dense structures, **zni** (**BIF-1**) [24] and **dia** (**BIF-2**) [24] and two zeotypes, **SOD** (**BIF-3**, **BIF-11**) [24] and **RHO** (**BIF-9**) [25]. Other four structures form zeotype materials those are synthesized by introduction of auxiliary ligands into the boron-imidazolate system, such as interrupted-LTA (**BIF-20**) [27], interrupted-ATN (**BIF-21**) [27], **ACO** (**BIF-22**) [28] and **ABW** (**BIF-23**) [28]. In other cases, the boron-imidazolate precursors are 3-connected, resulting in mixed (3,4)-connected or 3-connected nets [24,41,42]. For comparison, in the case of **ZIFs**, more than 105 new **ZIFs** with 25 distinct structure types have been reported so far [43,44]. The factors causing such difference between the two families are not yet fully understood. It is worth mentioning that Leoni et al. have studied 30 topological diversity of **BIFs** by DFT calculations. They have concluded that the structures based on zeolitic **RHO**, **GME** and **FAU** nets are shown to be stable which are the most promising candidates for hydrogen storage applications [45].

1.2. The charge distribution

In the imidazolate system, the charge distribution is one of key factors needs to be analyzed in the process of synthesis. The valence sum (vs) from 4-connected cationic nodes to the anionic species are generally not higher than or significantly below the valence of the anion. Thus, for the binary metal imidazolate frameworks in **ZIFs**, the most widely used tetrahedral cations are divalent metal ions (Zn^{2+} , Co^{2+}) which are connected through ditopic imidazolate with linkages $M\text{–Im–M}$ ($\text{vs} = 1$) to a neutral framework (Scheme 2a). In **BIFs**, owing to the existence of B^{3+} in boron imidazolate ligand, a +1 charged tetrahedral node is required to preserve the neutral framework feature (Scheme 2b). So in the initial works, a system of zeolitic boron imidazolate frameworks are constructed based on monovalent Li^+ and Cu^+ as tetrahedral cations [24,25]. To go beyond the limiting of Li^+ and Cu^+ ions, judicious decoration of metal centers is the key approach for desired structures and functions. By adopting terminal ligands or one chelating ligand to cover some coordination sites of the metal center, the distorted tetrahedral building node was obtained from the octahedral metal center and two zeolitic **BIFs** with **ACO**-type and **ABW**-type topologies were reported [28]. Besides that, the introduction of negatively charged

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