

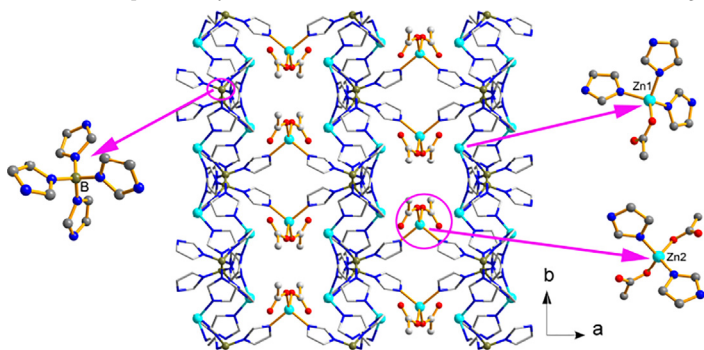
Short communication

One unique neutral boron imidazolate framework with fluorescent property

Qin-Long Hong^{a,b}, Hai-Xia Zhang^{b,*}, Yi-Hang Wen^{a,*}, Jian Zhang^b^a Zhejiang Key Laboratory for Reactive Chemistry on Solid Surfaces, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua, Zhejiang 321004, PR China^b State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China

GRAPHICAL ABSTRACT

One novel 3D pillared-layer boron imidazolate framework based on the in situ generated +1 and 0 charged metal units was hydrothermally synthesized.



ARTICLE INFO

Keywords:

Metal-organic frameworks
Boron imidazolate frameworks
Crystal structure

ABSTRACT

One unique boron imidazolate framework (BIF-95) based on the assembly of $B(im)_4^-$ and two types of metal units have been prepared, and it features a 3D pillared-layer structure. This work represents the feasibility towards the construction of new neutral BIFs by employing a wider variety of metal ions.

Currently, metal-organic frameworks (MOFs) have attracted intense attentions due to their aesthetically appealing structures and potential applications in catalysis, gas storage/separation and photoluminescence [1–15]. Of particular interest is that some of these MOFs mimic compositional and topological features of zeolites to obtain 4-connected zeolitic metal-organic frameworks [16–19], such as zeolitic imidazolate frameworks (ZIFs) [20–23] and boron imidazolate frameworks (BIFs) [24–34]. Resemblance to inorganic zeolites $AlPO_4$, BIFs with two different tetrahedral nodes (e.g., B^{3+} and M^+) are newly developed zeolitic metal-organic frameworks [25,26]. These materials combine the ultra-lightweight element B together with the strong covalent bond (B–N), holding great promise for the development of stable low density porous frameworks.

For the construction of BIFs, the most typical method is based on the crosslinking of presynthesized monocharged boron imidazolate complexes with various metal cations. In order to design neutral BIFs, monovalent cation or unit is the optimum selection to keep the charge balancing of the framework. Firstly, monovalent metal ions (e.g., Cu^+ / Li^+) were widely used for constructing a series of zeolitic BIFs (e.g., SOD and RHO) [25,26,28]. Then, the employing of some +1 charged metal units has greatly enriched the families of BIFs. By combination of divalent metal ions and auxiliary uninegative ligand (e.g., CH_3COO^- , Br^-) to assembly +1 charged units, a series of neutral BIFs have been created, including the zeolite type nets (e.g., ACO, ABW) [30,31]. However, most of these structures contain only one type of +1 charged metal units generated in situ, metal centers with two different

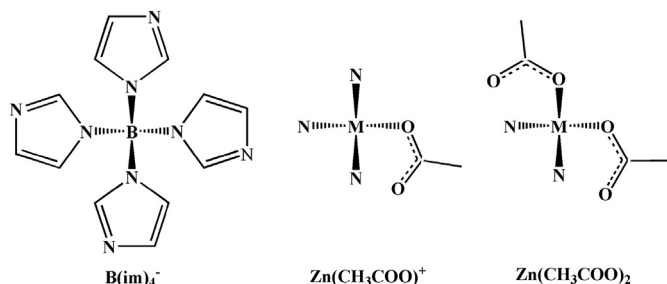
* Corresponding authors.

E-mail addresses: wyh@zjnu.cn (H.-X. Zhang), zhanghaixia@fjirsm.ac.cn (Y.-H. Wen).<https://doi.org/10.1016/j.inoche.2018.07.023>

Received 21 June 2018; Received in revised form 13 July 2018; Accepted 16 July 2018

Available online 17 July 2018

1387-7003/ © 2018 Published by Elsevier B.V.



Scheme 1. The assembly between $B(im)_4^-$ and two different metal units.

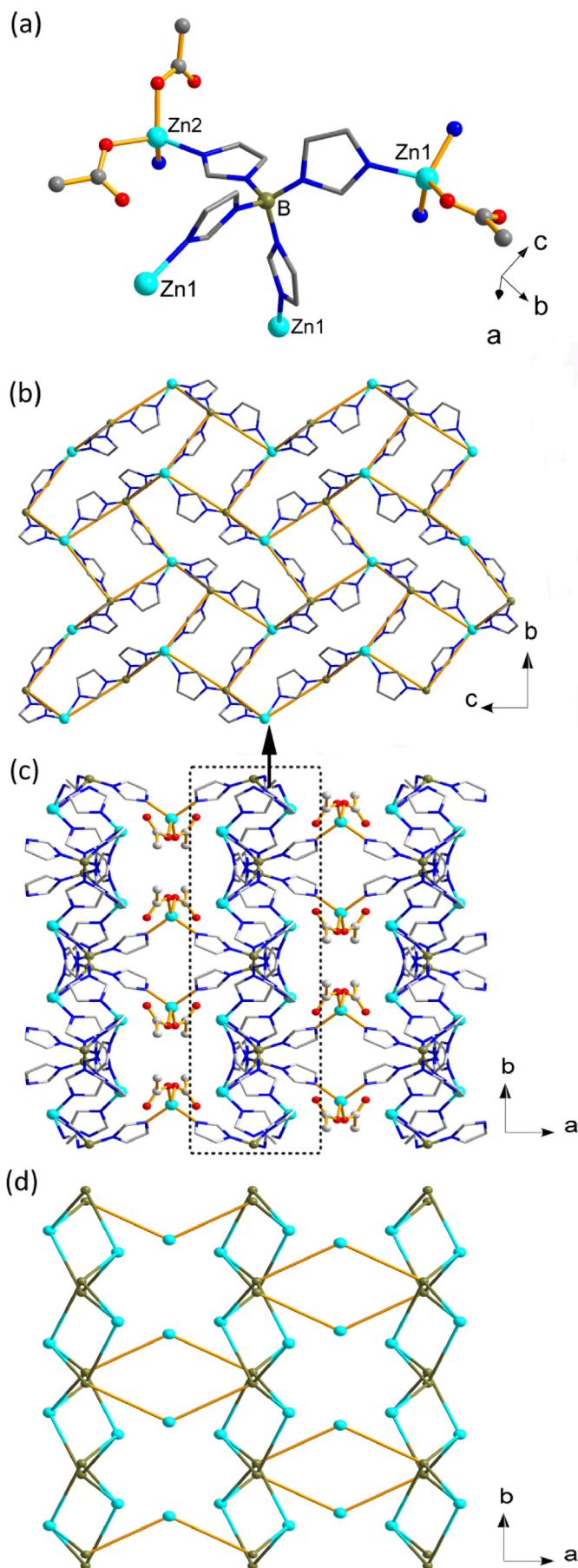
coordination environments are rarely reported in BIFs system. Considering the charge matching principle in the neutral frameworks, it is required to introduce 0 charged metal center to this assembly system of boron imidazolate ligands and +1 charged metal units. Here we report such a crystal (**BIF-95**) with a 3D neutral extended framework structure which is based on the in situ generated +1 and 0 charged metal units (**Scheme 1**).

BIF-95 was solvothermally synthesized by mixing tetrahedral ligands $KB(im)_4$ and $Zn(CH_3COO)_2 \cdot 4H_2O$ in a mixed solvent of ethylene glycol/ H_2O . The structure was fully characterized by X-ray single crystal diffraction. To study the structure of the powder sample, its powder X-ray diffraction pattern was measured (Fig. S5) [35]. The crystals are stable in air and insoluble in common solvents, such as H_2O , alcohol and DMF.

Single crystal X-ray structure analysis reveals that **BIF-95** crystallizes in the monoclinic space group $C2/c$. As shown in Fig. 1a, the asymmetric unit contains one Zn1 ion, a half Zn2 ion, one $BH(im)_4^-$ ligand and two $HCOO^-$ ligands. Both independent Zn centers show a tetrahedral coordination environment, although each one has different coordination atoms from the ligands. Zn1 ion is coordinated by three nitrogen atoms from three $B(im)_4^-$ ligands and one oxygen atom from a terminal ligand $HCOO^-$, resulting the three-connectivity center (Fig. S2). Zn2 is surrounded by two nitrogen atoms from $B(im)_4^-$ ligands and two oxygen atoms from $HCOO^-$, showing a neutral linear ZnN_2 units (Fig. S3). The Zn–N bond lengths range from 1.987 to 2.012 Å and the Zn–O bond lengths range from 1.937 to 1.941 Å, respectively. Each B atom is covalently bonded to four N atoms from imidazolate ligands with B–N bond lengths from 1.473 to 1.601 Å. The tetrahedral $B(im)_4^-$ ligands act as μ_4 -bridging ligands linked four Zn centers into 3D framework, with the Zn...B distances range from 5.4340 to 5.6143 Å.

The main structural feature of **BIF-95** is the linear metal center as supported-rod linked 2-D layer into the 3D pillared-layer frameworks. Therein, the three-connected Zn1 ions are linked by three imidazolate groups of $B(im)_4^-$ ligands into a 3-connected *fes* type layer with four- and eight-rings in the *bc* plane (Fig. 1b). Then, the linear Zn2 ions further pillar the layers into a 3D pillared-layer framework by connecting these layers through the fourth imidazolate group of $B(im)_4^-$ ligands (Fig. 1c). As a result the whole framework can be topologically regarded as (3, 4)-connected net with a vertex symbol of (4.6.8) ($4.6^2.8^3$), by considering the $B(im)_4^-$ ligands as the 4-connected nodes and Zn1 sites as the 3-connected nodes (Fig. 1d). Although pillared-layer frameworks are common in MOFs, most of them are pillared by organic ligands or coordination anions. The structures pillared by 0 charged metal center are rarely reported [36–38]. The framework shows rectangle pores with dimensions of 6.3125×5.6250 Å along *c* axis, which are blocked by terminal coordinated ligand $HCOO^-$. As a result, the framework contains small the total potential solvent-accessible volume ca. 474.9 \AA^3 per unit cell volume, and the pore volume ratio is 10.4%, as calculated with the PLATON program.

Thermogravimetric analysis (TGA) was studied to investigate the thermal stability of **BIF-95**. The TGA experiment was carried out from room temperature to 800 °C in a flowing N_2 atmosphere (Fig. S6). TGA curve of **BIF-95** indicated a weight loss of 7% before 250 °C,



(caption on next page)

Download English Version:

<https://daneshyari.com/en/article/7748368>

Download Persian Version:

<https://daneshyari.com/article/7748368>

[Daneshyari.com](https://daneshyari.com)