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Zeolitic Boron Imidazolate Frameworks**

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Abstract

From porous AlPO_4 to porous BIFs Reported here are a family of crystalline materials based on boron imidazolate frameworks (BIFs). It is demonstrated that the synthetic method, which is based on the crosslinking of various pre-synthesized boron imidazolates by monovalent cations (Li^+ and Cu^+), is capable of generating a large variety of open frameworks ranging from the 4-connected zeolitic sodalite type to the 3-connected chiral (10,3)-a type.

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Keywords

Boron; metal-organic framework; imidazolate; zeolite; crystal structure

Low-connectivity (4- or 3-connected) of the basic structural building block is closely associated with the open architecture and porosity in 3-D framework materials. The synthetic development of low-connectivity frameworks with new composition and topology continues to attract much attention because applications of such materials depend on the unique composition or topology of each material.[1–6]

Currently, the synthesis of metal-organic frameworks (MOFs) is an active research area.[1,7] The vast majority of new microporous materials synthesized in the past decade belong to this family.[8–13] Among numerous known MOFs, a family of materials that closely resemble zeolite topologies are those based on divalent metal (M^{2+}) imidazolates (im^-) in which M^{2+} and im^- replace Si^{4+} (Al^{3+}) and O^{2-} , respectively, resulting in the general framework composition $M(im)_2$, just like SiO_2 . [8–11] The success in generating new zeolitic topologies is attributed to structure-directing effects of imidazolate ligands and other conditions such as solvents.

Here we demonstrate a versatile synthetic method capable of generating a large family of low-connectivity framework materials. This method is based on the crosslinking of various pre-synthesized boron imidazolate complexes by monovalent cations (e.g., Li^+ and Cu^+) into extended frameworks. One advantage of this method is that it allows the use of ultra-light chemical elements (i.e., Li and B) as framework vertices. Furthermore, unlike the Zn-im system in which it is difficult to pre-synthesize 3-connected $Zn(im)_3^-$ unit, both 4-connected B ($im)_4^-$ and 3-connected HB($im)_3^-$ can be readily synthesized (Scheme 1) prior to solvothermal synthesis, which further increases the diversity of materials accessible through this method. For the creation of 4-connected topologies, our strategy is reminiscent of the strategy that led to the discovery of microporous $AlPO_4$ by analogy with porous silica.[2] Just as Al^{3+} and P^{5+} can replace two Si^{4+} sites in a porous silicalite, Li^+ and B^{3+} can replace two Zn^{2+} sites in a $Zn(im)_2$ type framework.

A total of eleven boron imidazolate framework materials have been made (Table 1). In addition to 4-connected topologies, 3-connected and mixed (3,4)-connected 3-D framework topologies have also been realized. These materials exhibit eight distinct topological features (Table 1). Three particularly interesting materials are the unprecedented 4-connected framework materials (**BIF-1-Li**, **BIF-2-Li** and **BIF-3-Li**) based on the lightest possible tetrahedral nodes in the Periodic Table: Li and B (excluding Be which is not studied in this work because of its toxicity).

BIF-1-Li exhibits a 3D tetrahedral framework in which each Li^+ or B^{3+} center is connected to four imidazoly (denoted as im) ligands to create a SiO_4 -like tetrahedron (i.e., $Li(im)_4$ and $B(im)_4$) (Figure 1a). Each im^- linker bridges one Li^+ center and one B^{3+} center with the $Li...B$ distance ranging from 5.585 to 5.683 Å. The $Li(im)_4$ and $B(im)_4$ tetrahedra alternate through corner-sharing into a 4-connected 3-D zni-type framework containing 4-, 6-, and 12-membered rings (Figure 1b, Figure S2).

BIF-2-Li, another 3-D 4-connected Li-B imidazolate framework, was synthesized by using 2-methylene-imidazolate (mim) as the crosslinking ligand and it possesses the non-interpenetrating diamond (dia) topology (Figure S3).

To demonstrate the general applicability of our synthetic strategy, we have also explored other M^+/M^{3+} combinations. We have found that the same framework topology present in **BIF-1-Li** and **BIF-2-Li** can also be made by using Cu^+ in place of Li^+ (Table 1)

Prior to this work, some polymeric materials based on $[B(im)_4]^-$ and divalent metals (e.g., Pb, Mg, Ca, Sr) are known.[14] However, it was observed that such combinations between $[B(im)_4]^-$ and M^{2+} have a tendency to produce layered materials. There is one known Li-B-im structure, however, half of the lithium sites in this phase contain terminal H_2O and CH_3OH ligands.[15]

Two of the most interesting materials reported here are isostructural $LiB(mim)_4$ (**BIF-3-Li**) and $CuB(mim)_4$ (**BIF-3-Cu**) with neutral sodalite (SOD) topology containing 4- and 6-rings formed by alternating corner-sharing $Li(mim)_4$ (or $Cu(mim)_4$) and $B(mim)_4$ tetrahedra (Figure 1c and 1d).

The synthetic method described here can also lead to the synthesis of framework materials with the mixed (3,4) connectivity. The solvothermal reaction of CuI and sodium tetrakis (benzimidazolyl)borate ($NaB(bim)_4$) at 85 °C or 120 °C led to the crystallization of **BIF-4** and **BIF-5** with (3,4)-connected nets, respectively. In the asymmetric unit of **BIF-4**, two independent tetrahedral Cu^+ ions show 4- and 3-connectivity due to one terminal acetonitrile ligand at the $Cu1$ site, and two independent $B(bim)_4^-$ ligands show μ_4 - and μ_3 -coordination modes, respectively (Figure 2a). **BIF-4** features a unique (3,4)-connected framework with sqc1436 topology containing 4- and 8-membered rings (Figure 2b). The uncoordinated bim ligand in μ_3 - $B(bim)_4^-$ is located in the 8-membered ring.

In **BIF-5**, the $B(bim)_4^-$ ligand is 4-connected to four Cu^+ ions. However, two independent Cu^+ ions show two different coordination environments: $CuIN_3$ tetrahedron and linear CuN_2 (Figure 2c) (iodide anion in $CuIN_3$ is a terminal ligand). The 3-connected $Cu1$ sites are linked by the $B(bim)_4^-$ ligands into a layer with 4- and 8-rings (Figure 2d). The linear $Cu2$ centres further connect these layers through the additional coordination of the $B(bim)_4^-$ ligands, generating a $(4.6.8)(4.6^2.8^3)$ net by considering the $B(bim)_4^-$ ligands as the 4-connected nodes and the $Cu1$ sites as the 3-connected nodes (Figure S4).

By employing 3-connected boron-imidazolate ligands, 3-connected frameworks (**BIF-6** to **BIF-8**) have also been prepared. In **BIF-6** with the formula $Cu^I BH(im)_3$, tripodal $BH(im)_3^-$ ligands are linked through planar 3-coordinate Cu^+ ions into a 2D 4.8^2 layer (Figure 3a and Figure S5). In **BIF-7**, the planar 3-connected Cu^+ ions are bridged by the tripodal $BH(mim)_3^-$ ligands into a 3D 2-fold interpenetrating framework with the (10,3)-b topology (also called the *ths* net) (Figure 3b and Figure S6). In comparison, **BIF-8** features a 3-connected 3-D 2-fold interpenetrating framework with the chiral (10,3)-a topology (also called the *srs* net) (Figure 3e).

In **BIF-8**, one prominent feature is the spontaneous resolution of the racemic $BH(eim)_3^-$ ligands into two interpenetrating 3-connected chiral sub-nets with opposite handedness. The $BH(eim)_3^-$ ligand is chiral because of the conformation of the ethyl groups (Figure 3c and 3d). It is worth noting that there are two sources of chirality here: chiral $BH(eim)_3^-$ ligands (R- and S-configurations) and chiral *srs* nets (denoted $+\gamma^*$ and $-\gamma^*$ for two enantiomeric forms). Because each intrinsically chiral *srs* net selects only one enantiomer of $BH(eim)_3^-$ ligands, the spontaneous resolution of racemic $BH(eim)_3^-$ ligands into two independent but interpenetrating frameworks is observed (Figure 3e).

To determine zeolitic properties of such materials, **BIF-3-Cu** and **BIF-3-Li** with the sodalite topology were studied by gas adsorption measurements performed on Micromeritics ASAP 2010 surface area and pore size analyzer. The permanent porosity was confirmed by N_2

adsorption measurements. The samples were degassed at 200°C prior to the measurement. They exhibit type I isotherm, indicating the microporous nature. The Langmuir surface areas are 182.3 and 726.5 m²/g for **BIF-3-Cu** and **BIF-3-Li**, respectively (Figure 4, Figure S13). The CO₂ adsorption isotherms of **BIF-3-Cu** and **BIF-3-Li** at 273 K were also evaluated. As shown in Figure 5, the maximum adsorptions at ~1 atm are 21.9 and 34.5 cm³.g⁻¹ for **BIF-3-Cu** and **BIF-3-Li**, respectively.

In conclusion, we have synthesized a family of boron imidazolate framework materials by crosslinking 3- or 4-connected boron imidazolate complexes (e.g., B(im)₄⁻ or HB(im)₃⁻) with 3- or 4-connected Li⁺ or Cu⁺ centers. These materials possess various 4-connected, mixed (3,4)-connected, and 3-connected 3-D open frameworks with topologies ranging from zeolitic sodalite type to chiral (10,3)-a type. The permanent microporosity has been demonstrated for **BIF-3-Cu** and **BIF-3-Li** with the sodalite topology. These materials represent a unique family of materials that border between MOFs and covalent frameworks because of the co-existence of covalent (B–N) and coordination bonds (Li–N and Cu–N).

Experimental Section

Boron imidazolate complexes were synthesized according to the literature procedure.[16]

Typical synthesis of CuB(mim)₄.(solvent)_x (BIF-3-Cu)

Sodium tetrakis(2-methylane-imidazoly)borate (0.0981 g) and CuI (0.0779 g) in a mixed 2-amino-1-butanol (1.1660 g)/CH₃CN (1.5 mL) solution were placed in a 20 ml vial. The sample was heated at 120 °C for 5 days, and then cooled to room-temperature. After washed by ethanol and distilled water, the colorless crystals were obtained.

The detailed synthesis conditions of other compounds were included in the supporting file.

CCDC- 693499 (BIF-1-Li), 693500 (BIF-1-Cu), 699084 (BIF-2-Li), 703703 (BIF-2-Cu), 703704 (BIF-3-Li), 697959 (BIF-3-Cu), 697960 to 697964 (BIF-4 to BIF-8) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. View of the coordination environment in **BIF-1-Li** (a) and **BIF-3-Cu** (c), respectively, showing the connectivity between the Li^+ and B^{3+} tetrahedra or the Cu^+ and B^{3+} tetrahedra; and the **zni** net of **BIF-1-Li** (b) and the **sodalite** net of **BIF-3-Cu** (d).

Figure 2.

(a) The coordination environment in **BIF-4**; (b) view of the 4-ring and 8-ring in **BIF-4**, the terminal bim groups in the B(bim)₄⁻ ligands are highlighted in the 8-ring; (c) the coordination environment in **BIF-5**; (d) view of the 4-ring and 8-ring in **BIF-5**.

Figure 3.

View of the tripodal ligands in **BIF-6** (a), **BIF-7** (b) and **BIF-8** (c and d). In **BIF-8**, the racemic $\text{BH}(\text{eim})_3^-$ ligands (c and d) act as 3-connected building blocks in two-fold interpenetrating srs net of opposite handedness (e).

Figure 4.

N_2 gas sorption isotherm of **BIF-3-Li** at 77K. P/P_0 is the ratio of gas pressure (P) to saturation pressure (P_0), with $P_0=769$ torr (adsorption: dotted line; desorption: circles).

Figure 5.
CO₂ adsorption isotherms of **BIF-3-Li** (dotted line) and **BIF-3-Cu** (circles) at 273 K.

R = H; X = H (**BIF-1**), Me (**BIF-2, 3**)
R = C₄H₄; X = H (**BIF-4, 5**)

R = H; X = H (**BIF-6**), Me(**BIF-7**),
Et (**BIF-8**)

Scheme 1.

The pre-synthesized 4- and 3-connected B-centred ligands.

Table 1

A Summary of Crystal Data and Refinement Results.^[a]

	Formula	Space Group	a (Å)	b (Å)	c (Å)	$\alpha(^{\circ})/\gamma(^{\circ})$	$\beta(^{\circ})$	R(F)	N_{ref}/b
BIF-1-Li	LiB(im) ₄	<i>I4/cd</i>	22.5041(3)	22.5041(3)	11.5147(4)	90.00	90.00	0.0344	zni
BIF-1-Cu	Cu ^I B(im) ₄	<i>I4/cd</i>	22.3798(2)	22.3798(2)	11.4888(2)	90.00	90.00	0.0259	zni
BIF-2-Li	LiB(mim) ₄	<i>I-4</i>	7.5817(2)	7.5817(2)	16.4284(9)	90.00	90.00	0.0461	dia
BIF-2-Cu	CuB(mim) ₄	<i>I-4</i>	7.6593(2)	7.6593(2)	16.4028(4)	90.00	90.00	0.0220	dia
BIF-3-Li	LiB(mim) ₄ (solvent) _x	<i>P-43n</i>	16.0311(1)	16.0311(1)	16.0311(1)	90.00	90.00	0.0338	SOD
BIF-3-Cu	Cu ^I B(mim) ₄ (solvent) _x	<i>P-43n</i>	16.0184(2)	16.0184(2)	16.0184(2)	90.00	90.00	0.0605	SOD
BIF-4	Cu ^I ₂ [B(bim) ₄] ₂ (CH ₃ CN) _x	<i>P-1</i>	13.548(3)	14.627(3)	15.318(3)	73.73(1) 68.95(1)	73.79(1)	0.0654	sqc1436
BIF-5	Cu ^I ₃ [B(bim) ₄] ₂ (CH ₃ O) _H	<i>C2/c</i>	24.0260(9)	18.0135(6)	15.4627(5)	90.0	109.47(1)	0.0674	(4.6.8)(4.6 ² .8 ³)
BIF-6	Cu ^I BH(im) ₃	<i>P2₁/c</i>	8.0101(1)	14.0853(3)	10.0845(2)	90.00	94.25(1)	0.0339	fes (4.8 ²)
BIF-7	Cu ^I BH(mim) ₃	<i>Cc</i>	13.3048(5)	13.4544(5)	18.2388(6)	90.00	111.373(2)	0.0993	ths
BIF-8	Cu ^I BH(eim) ₃	<i>Pa-3</i>	15.1296(6)	15.1296(6)	15.1296(6)	90.00	90.00	0.0445	srz

^[a]im = imidazolate; mim = 2-methylene-imidazolate; eim = 2-ethylene-imidazolate; bim = benzimidazolate.

^[b]For definitions of three-letter abbreviations, see Reticular Chemistry Structure Resource (<http://rcsr.anu.edu.au/>).