Metal–Organic Frameworks

DOI: 10.1002/anie.200804169

Zeolitic Boron Imidazolate Frameworks**

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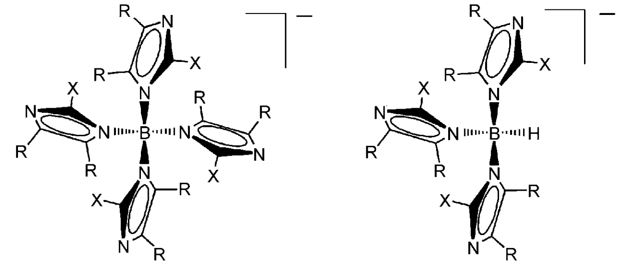
Low connectivity (four- or three-connectivity) of the basic structural building block is closely associated with the open architecture and porosity in 3D framework materials. The synthetic development of low-connectivity frameworks with new composition and topology continues to attract much attention, 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^- ions replace zeolite Si^{4+} (Al^{3+}) and O^{2-} ions, 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.

Herein we demonstrate a versatile synthetic method capable of generating a large family of low-connectivity framework materials. This method is based on the cross-linking of various presynthesized boron imidazolate complexes with monovalent cations (e.g., Li^+ and Cu^+) into extended frameworks. One advantage of this method is that it allows the use of ultralight chemical elements (i.e., Li and B) as framework vertices. Furthermore, unlike the zinc imidazolate system, in which it is difficult to presynthesize three-connected $Zn(im)_3^-$ units, both four-connected $B(im)_4^-$ and three-connected $HB(im)_3^-$ can be readily synthesized prior to solvothermal synthesis (Scheme 1), thus further increasing the diversity of materials accessible through this method. For the creation of four-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+} ions can replace two Si^{4+} sites in a porous silicalite, Li^+ and B^{3+} ions can replace two Zn^{2+} sites in a $[Zn(im)_2]$ framework.



R = H; X = H (BIF-1), Me (BIF-2, 3)
R = C_4H_4; X = H (BIF-4, 5)

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

Scheme 1. The presynthesized four- and three-connected boron-centered ligands. The framework for which each ligand is used is shown in parentheses.

A total of eleven boron imidazolate framework materials have been made (Table 1). In addition to four-connected topologies, three-connected and mixed (3,4)-connected 3D framework topologies have also been realized. These materials exhibit eight distinct topological features (Table 1). Three particularly interesting materials are the unprecedented four-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 herein because of its toxicity).

BIF-1-Li exhibits a 3D tetrahedral framework in which each Li^+ or B^{3+} ion is connected to four imidazolyl ligands to create a SiO_4-like tetrahedron (i.e., $Li(im)_4$ or $B(im)_4$; Figure 1 a). Each im^- linker bridges one Li^+ center and one B^{3+} center, with Li···B distances ranging from 5.585 to 5.683 Å. The $Li(im)_4$ and $B(im)_4$ tetrahedra alternate through corner sharing to form a four-connected 3D zni-type framework containing four-, six-, and twelve-rings (i.e., rings with a total of four, six, or twelve boron and lithium atoms; Figure 1 b and Figure S2 in the Supporting Information). BIF-2-Li, another 3D four-connected Li–B imidazolate framework, was synthesized by using 2-methylane-imidazolate (mim) as the crosslinking ligand; it possesses the non-interpenetrating diamond (dia) topology (Figure S3 in the Supporting Information).

To demonstrate the general applicability of our synthetic strategy, we also explored other M^+/M^{3+} combinations. We 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 the $B(im)_4^-$ ion and divalent metals (e.g., Pb, Mg, Ca, Sr) were known.[14] However, it was observed that such combinations of $B(im)_4^-$ and M^{2+} ions have a tendency to produce layered

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[**] We thank the support of this work by the National Institutes of Health (X.B.; 2 S06 GM063119-05) and NSF (P.F.).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200804169.

Table 1: Summary of crystal data and refinement results.[a]

Compound	Formula	Space group	*a* [Å]	*b* [Å]	*c* [Å]	α [°]/γ [°]	β [°]	*R*(F)	Net[b]
BIF-1-Li	$[LiB(im)]_4$	$I4_1cd$	22.5041(3)	22.5041(3)	11.5147(4)	90.00	90.00	0.0344	zni
BIF-1-Cu	$[Cu^IB(im)]_4$	$I4_1cd$	22.3798(2)	22.3798(2)	11.4888(2)	90.00	90.00	0.0259	zni
BIF-2-Li	$[LiB(mim)_4]$	$I\bar{4}$	7.5817(2)	7.5817(2)	16.4284(9)	90.00	90.00	0.0461	dia
BIF-2-Cu	$[CuB(mim)_4]$	$I\bar{4}$	7.6593(2)	7.6593(2)	16.4028(4)	90.00	90.00	0.0220	dia
BIF-3-Li	$[LiB(mim)_4]\cdot x$ solvent	$P\bar{4}3n$	16.0311(1)	16.0311(1)	16.0311(1)	90.00	90.00	0.0338	SOD
BIF-3-Cu	$[Cu^IB(mim)_4(solvent)_x]$	$P\bar{4}3n$	16.0184(2)	16.0184(2)	16.0184(2)	90.00	90.00	0.0605	SOD
BIF-4	$[Cu^I_2\{B(bim)_4\}_2(CH_3CN)]\cdot CH_3CN$	$P\bar{1}$	13.548(3)	14.627(3)	15.318(3)	73.73(1) 68.95(1)	73.79(1)	0.0654	sqc1436
BIF-5	$[Cu^I_3I\{B(bim)_4\}_2]\cdot CH_3OH$	$C2/c$	24.0260(9)	18.0135(6)	15.4627(5)	90.00	109.47(1)	0.0674	$(4.6.8)(4.6^2.8^3)$
BIF-6	$[Cu^IBH(im)_3]$	$P2_1/c$	8.0101(1)	14.0853(3)	10.0845(2)	90.00	94.25(1)	0.0339	fes (4.8^2)
BIF-7	$[Cu^IBH(mim)_3]$	Cc	13.3048(5)	13.4544(5)	18.2388(6)	90.00	111.373(2)	0.0993	ths
BIF-8	$[Cu^IBH(eim)_3]$	$Pa\bar{3}$	15.1296(6)	15.1296(6)	15.1296(6)	90.00	90.00	0.0445	srs

[a] im = imidazolate; mim = 2-methylane-imidazolate; eim = 2-ethylane-imidazolate; bim = benzimidazolate. [b] For definitions of three-letter abbreviations, see Reticular Chemistry Structure Resource (http://rcsr.anu.edu.au/).

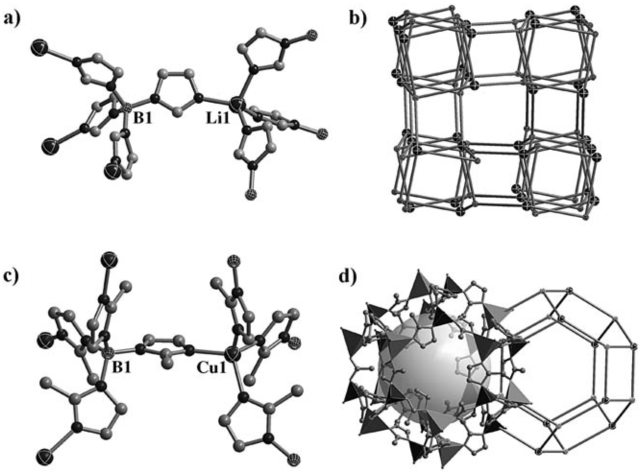

Figure 1. View of the coordination environment in a) BIF-1-Li and c) BIF-3-Cu showing the connectivity between the Li$^+$ and B^{3+} tetrahedra or the Cu$^+$ and B^{3+} tetrahedra. b) The zni net of BIF-1-Li and d) the sodalite net of BIF-3-Cu; dark and light tetrahedra represent boron and copper sites, respectively.

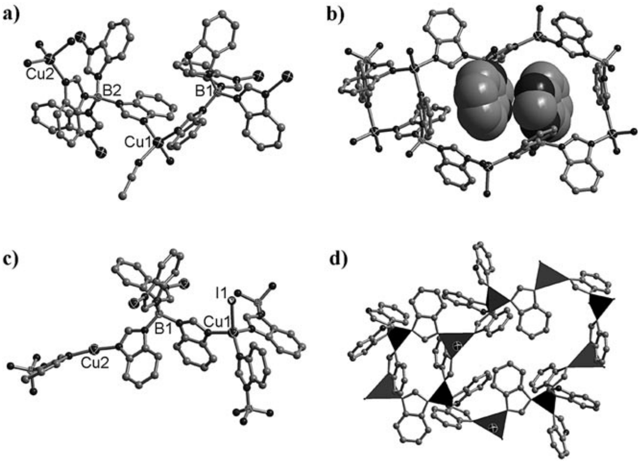

Figure 2. a) The coordination environment in BIF-4. b) View of the four-ring and the eight-ring in BIF-4; the terminal bim groups in the B(bim)$_4^-$ ligands are highlighted in the eight-ring. c) The coordination environment in BIF-5. d) View of the four-ring and eight-ring in BIF-5; the large dark triangles represent copper sites and the small dark tetrahedra represent boron sites.

materials. There is one known Li/B/im structure, but half of the lithium sites in this phase contain terminal H_2O and CH_3OH ligands.[15]

Two of the most interesting materials reported herein are isostructural $[LiB(mim)_4]$ (BIF-3-Li) and $[CuB(mim)_4]$ (BIF-3-Cu). These materials have neutral sodalite (SOD) topology and contain four- and six-rings formed by alternating corner-sharing $Li(mim)_4$ (or $Cu(mim)_4$) and $B(mim)_4$ tetrahedra (Figure 1 c,d).

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

In BIF-5, the B(bim)$_4^-$ ligand is four-connected to four Cu$^+$ ions. However, two independent Cu$^+$ ions show two different coordination environments: $CuIN_3$ tetrahedra and linear CuN_2 units are present (Figure 2 c; the iodide anion in $CuIN_3$ is a terminal ligand). The three-connected Cu1 sites are linked by the B(bim)$_4^-$ ligands into a layer with four- and eight-rings (Figure 2 d). The linear Cu2 centers 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 four-connected nodes and the Cu1 sites as the three-connected nodes (Figure S4 in the Supporting Information).

By employing three-connected boron imidazolate ligands, three-connected frameworks (BIF-6 to BIF-8) have also been prepared. In BIF-6 with the formula $[Cu^IBH(im)_3]$, tripodal

$BH(im)_3^-$ ligands are linked through planar three-coordinate Cu^+ ions into a 2D 4.8^2 layer (Figure 3a and Figure S5 in the Supporting Information). In BIF-7, the planar three-connected Cu^+ ions are bridged by the tripodal $BH(mim)_3^-$ ligands into a 3D two-fold interpenetrating framework with the (10,3)-b topology (also called the ths net; Figure 3b and Figure S6 in the Supporting Information). In comparison, BIF-8 features a three-connected 3D two-fold interpenetrating framework with the chiral (10,3)-a topology (also called the srs net; Figure 3e).

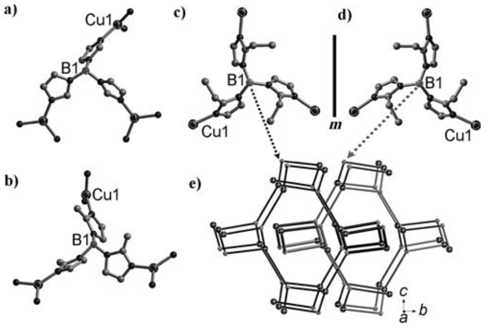

Figure 3. View of the tripodal ligands in a) BIF-6, b) BIF-7, and c, d) BIF-8. In BIF-8, the racemic $BH(eim)_3^-$ ligands (c and d) act as three-connected building blocks in a two-fold interpenetrating srs net of opposite handedness (e).

In BIF-8, one prominent feature is the spontaneous resolution of the racemic $BH(eim)_3^-$ ligands into two interpenetrating three-connected chiral subnets with opposite handedness. The $BH(eim)_3^-$ ligand is chiral because of the conformation of the ethyl groups (Figure 3c, d). It is worth noting that there are two sources of chirality: 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 $BH(eim)_3^-$, 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 a 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 isotherms, indicating their microporous nature. The Langmuir surface areas are 182.3 and 726.5 $m^2 g^{-1}$ for BIF-3-Cu and BIF-3-Li, respectively (Figure 4 and Figure S13 in the Supporting Information). The CO_2 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 approximately 1 atm are 21.9 and 34.5 $cm^3 g^{-1}$ for BIF-3-Cu and BIF-3-Li, respectively.

In conclusion, we have synthesized a family of boron imidazolate framework materials by crosslinking three- or four-connected boron imidazolate complexes (e.g., $B(im)_4^-$ or $HB(im)_3^-$ ions) with three- or four-connected Li^+ or Cu^+ ions.

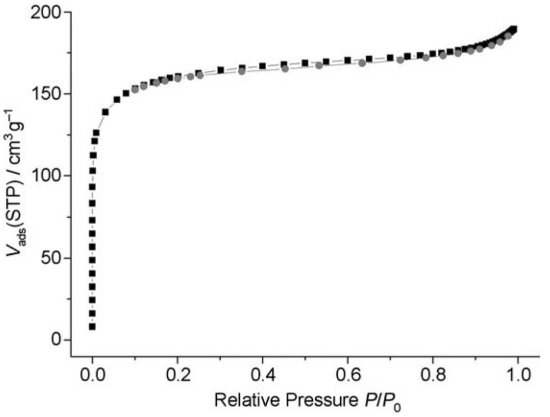

Figure 4. N_2 gas sorption isotherm of BIF-3-Li at 77 K. P/P_0 is the ratio of gas pressure (P) to saturation pressure (P_0), with $P_0 = 769$ torr (■ adsorption; ● desorption).

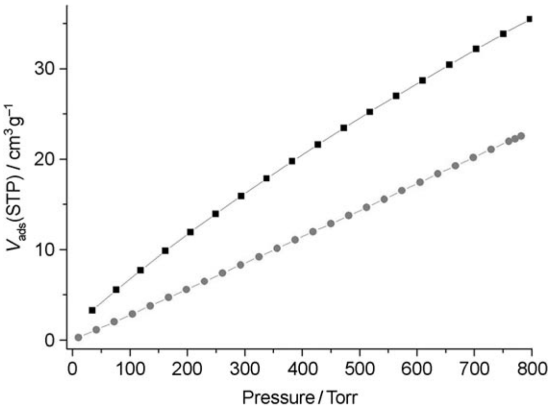

Figure 5. CO_2 adsorption isotherms of BIF-3-Li (■) and BIF-3-Cu (●) at 273 K.

These materials possess various four-connected, mixed (3,4)-connected, and three-connected 3D open frameworks with topologies ranging from zeolitic sodalite type to chiral (10,3)-a type. Permanent microporosity has been demonstrated for BIF-3-Cu and BIF-3-Li, which have sodalite topology. These materials represent a unique family of materials that border between MOFs and covalent frameworks because of the coexistence 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 $[CuB(mim)_4]\cdot x$solvent (BIF-3-Cu): Sodium tetrakis(2-methylane-imidazoly)borate (0.0981 g, 0.32 mmol) and CuI (0.0779 g, 0.41 mmol) in a mixed 2-amino-1-butanol (1.1660 g)/CH_3CN (1.5 mL) solution were placed in a 20 mL vial. The sample was heated at 120 °C for five days and then cooled to room temperature. After washing with ethanol (10 mL) and distilled water (10 mL), colorless crystals were obtained (0.1121 g, 0.26 mmol, 80 % yield).

The detailed synthesis conditions of other compounds are included in the Supporting Information.

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, 697961, 697962, 697963, 697964 (BIF-4 to BIF-8) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: August 23, 2008
Revised: December 9, 2008

Keywords: boron · imidazolates · metal–organic frameworks · microporous materials · zeolites

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