

# Hydrogen-bonded boron imidazolate frameworks†

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The research on tetrahedral imidazolate frameworks takes on a new direction into the supramolecular area through the synthesis of three hydrogen-bonded boron imidazolate ( $B[im]_4^-$ ) frameworks (HBIFs) that show distinct three- and two-dimensional supramolecular architectures: (1) the ionic diamond net containing the first reported  $Li^+$  complex with ethylene glycol, (2) four-connected double-layers built from a new neutral  $Li(tea)B(im)_4$  ( $tea =$  triethanolamine) complex, and (3) three-connected (6,3) layer of  $H_3O \cdot BH(eim)_3$ .

Designed synthesis of zeolitic imidazolate frameworks has attracted much attention in recent years due to their potential applications in gas storage and separation *etc.*<sup>1–6</sup> In these materials, tetrahedrally coordinated atoms (T atoms) are cross-linked by various imidazolate-type ligands to form a four-connected network. Inspired by the similarity between T–im–T angles (im = imidazolate) in metal imidazolates and T–O–T angles in zeolitic  $SiO_2$  and  $AlPO_4$  frameworks, two general strategies have been developed. One is based on divalent metal ( $M^{2+} = Zn^{2+}$  or  $Co^{2+}$ ) imidazolates in which  $M^{2+}$  and  $im^-$  replace  $Si^{4+}$  and  $O^{2-}$ , respectively, resulting in the general framework composition  $M(im)_2$  (denoted ZIFs), just like  $SiO_2$ .<sup>2–5</sup> Another is based on the use of pre-synthesized boron imidazolate ligands that are subsequently linked through monovalent cations (*e.g.*,  $M^+ = Li^+$  and  $Cu^+$ ) into extended frameworks with the general framework composition  $MB(im)_4$  (denoted BIFs), similar to  $AlPO_4$ .<sup>6</sup>

The use of lightweight elements (*e.g.*, Li and B) as framework vertices has a great potential for the creation of low-density and high porosity adsorbents. Because of this, we are interested in developing strategies to create Li–B–imidazolates that extend beyond the  $LiB(im)_4$ -type covalent frameworks to include supramolecular frameworks (denoted HBIFs) based on hydrogen-bonding interactions. Such materials should be able to broaden the type of materials that can be constructed from the lightweight second-row elements.

The Li–B–imidazolate system has an inherent advantage for creating hydrogen-bonded frameworks because of the unique hydrogen-bonding capability of the tetrahedrally distributed N donors in the pre-synthesized boron imidazolate ligands. With  $B(im)_4^-$  as the ready hydrogen-bonding acceptor, the challenge then becomes the creation of hydrogen-bonding donors that can form suitable framework vertices. In the system with the  $Li^+$  ions, one strategy to create hydrogen-bonding donors is to employ a

ligand that has a hard donor atom to solvate  $Li^+$  ions and in the meantime also provides suitable hydrogen for hydrogen bond formation.

We have studied the coordination behavior of  $Li^+$  ions in various solvents in the presence of  $B(im)_4^-$  type ligands.<sup>6</sup> When solvent molecules (*e.g.*,  $H_2O$ , MeOH, DMF, 2-aminobutanol) contain only one oxygen donor atom, these solvent molecules are not competitive in their binding with  $Li^+$  ions against negatively charged  $B(im)_4^-$  type donors. The crystallization in such solvents usually proceeds to generate  $LiB(im)_4$  covalent frameworks with direct Li–imidazolate linkages. Only under special conditions, such as the use of tripodal  $BH(im)_3^-$  ligands or  $B(bim)_4^-$  ( $bim =$  benzimidazolate) with bulky substituents, are solvent molecules found to bind to  $Li^+$  ions in the crystalline products. But solvent molecules usually occupy only one Li coordination site (per lithium ion) with other three sites still being coordinated to imidazolates.<sup>6c</sup>

To enhance the stability of Li–hydroxyl solvent complexes so that they can serve as nodes in hydrogen-bonded supramolecular assembly, it becomes necessary to use diols or triols. The chelate effect between  $Li^+$  ions and diols (or triols) would be able to enhance the stability of Li–solvent complexes to a level that is competitive against the Li–imidazolate formation. In this work, we illustrate the success of this synthetic strategy for creating hydrogen-bonded supramolecular assemblies (HBIF-1 and HBIF-2) through the use of ethylene glycol (eg) and triethanolamine (tea). A related example (HBIF-3) that contains hydrogen-bonded framework with no  $Li^+$  ions is also given to illustrate the range of hydrogen-bonded frameworks that can be prepared in the boron imidazolate system.

Three supramolecular compounds with different hydrogen donors and acceptors,  $Li(eg)_2 \cdot [B(mim)_4]$  (HBIF-1,  $mim =$  2-methylimidazolyl),  $Li(tea)[B(im)_4]$  (HBIF-2) and  $(H_3O) \cdot [BH(eim)_3]$  (HBIF-3,  $eim =$  2-ethylimidazolyl), have been synthesized‡ and structurally characterized.§

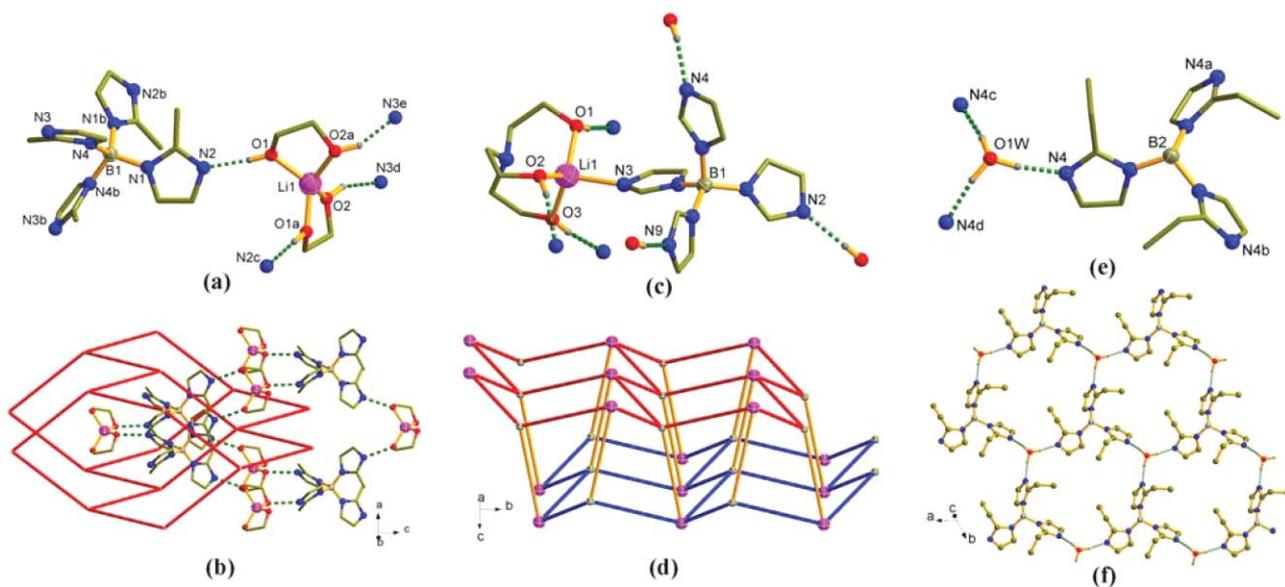
Of particular interest is the unprecedented hydrogen-bonded tetrahedral framework in HBIF-1 where the tetrahedral anionic  $[B(mim)_4]^-$  unit coexists with the tetrahedral cationic  $[Li(eg)_2]^+$  unit. Because tetrahedral connectivity is highly directional, the four-connected diamond net is usually formed from molecular building units with strongly directional bonds and the resulting framework is often covalent. It is uncommon to form the highly directional diamond net from ionic species. In our work, the requisite directionality is achieved through the formation of the  $[Li(eg)_2]^+$  complex in which four hydroxyl groups are arranged in a tetrahedral pattern.

Unlike the previously reported lithium-based covalent BIFs, the tetrahedral  $Li^+$  ion in HBIF-1 is not directly coordinated to the  $[B(mim)_4]^-$  unit. Instead,  $Li^+$  is complexed to two symmetry-related ethylene glycol ligands (Fig. 1(a)). Each glycol ligand

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**Fig. 1** (a) The molecular structure of **HBIF-1**, showing the O–H···N hydrogen-bonding interactions (green dashed lines) between the ionic pair; (b) the hydrogen-bonding structural fragment of the two-fold interpenetrating diamond-type framework of **HBIF-1**; (c) the molecular structure of **HBIF-2**, showing the O–H···N hydrogen-bonding interactions (green dashed lines) with its adjacent groups; (d) topological representation of the four-connected hydrogen-bonding double layer from two (6,3) layers (highlighted as red and blue) in **HBIF-2**; (e) the molecular structure of **HBIF-3**, showing the O–H···N hydrogen-bonding interactions (green dashed lines); (f) the three-connected hydrogen-bonding (6,3) layer in **HBIF-3**.

chelates one  $\text{Li}^+$  ion and also simultaneously forms two kinds of O–H···N hydrogen bonds with two  $[\text{B}(\text{mim})_4]^-$  units. The O···N hydrogen-bonding distances are 2.678(5) Å and 2.690(5) Å, respectively, which illustrates strong hydrogen-bonding interactions between the hydrogen donor  $[\text{Li}(\text{eg})_2]^+$  and the hydrogen acceptor  $[\text{B}(\text{mim})_4]^-$ .

The tetrahedral cationic hydrogen donor  $[\text{Li}(\text{eg})_2]^+$  has, to our knowledge, not been reported before. Its formation is closely associated with the tetrahedral geometry adopted by the  $\text{Li}^+$  ion, its high affinity for hard O atoms, and the chelate effect. In **HBIF-1**,  $[\text{Li}(\text{eg})_2]^+$  and  $[\text{B}(\text{mim})_4]^-$  tetrahedra are alternately linked up through the O–H···N hydrogen-bonding interactions, generating a 3-D diamondoid framework with a large void that is further occupied by another interpenetrating lattice (Fig. 1(b)).

Compared to the reported covalent and non-interpenetrating diamond-type framework  $\text{LiB}(\text{mim})_4$  (**BIF-2**), the one-atom Li tetrahedral site in **BIF-2** is replaced by a new bulky tetrahedral building block  $[\text{Li}(\text{eg})_2]^+$  in **HBIF-1**. As a result, the distance between the tetrahedral B and Li nodes is increased from approximately 5.7 Å in covalently bonded **BIF-2** to 7.857 Å in hydrogen-bonded **HBIF-1**. Clearly, hydrogen-bonded frameworks have the potential for the generation of large porosity and low density, as compared to covalent BIFs with comparable topologies. In **HBIF-1**, however, the extra porosity is lost due to the formation of two-fold interpenetration.

The use of different hydroxyl solvents represents one way to tune the nature of the hydrogen-bonded framework. When a triol, triethanolamine, is used in place of ethylene glycol, a new hydrogen-bonded framework, **HBIF-2**, is obtained. **HBIF-2** is fundamentally different from **HBIF-1**, because **HBIF-2** is based on a discrete neutral molecular complex with a formula of  $\text{Li}(\text{tea})[\text{B}(\text{im})_4]$ .

In **HBIF-2**, the tetrahedral  $\text{Li}^+$  ion is bonded by three O atoms from the tea ligand and one N atom from the  $[\text{B}(\text{im})_4]^-$  ligand (Fig. 1(c)), which leads to the formation of a neutral complex with two tetrahedral centers (Li and B). **HBIF-2** clearly shows that the strength of bonding between  $\text{Li}^+$  and chelating hydroxyl solvent molecules and that between  $\text{Li}^+$  and  $[\text{B}(\text{im})_4]^-$  is comparable.

Interestingly, the  $[\text{B}(\text{im})_4]^-$  ligand in **HBIF-2** has two different coordination modes. One of its imidazolate rings coordinates to one  $\text{Li}^+$  ion while the three remaining imidazolate rings form O–H···N hydrogen bonds with the tea ligands from three adjacent molecules. Each tea ligand chelates one  $\text{Li}^+$  ion and hydrogen bonds to three  $[\text{B}(\text{im})_4]^-$  ligands. Three O···N hydrogen-bonding distances are 2.756(3) Å, 2.708(3) Å, and 2.743(3) Å, respectively, which are slightly longer than those in **HBIF-1**. This is expected because **HBIF-1** also involves electrostatic interactions between hydrogen donors and hydrogen acceptors. In comparison, hydrogen donors and hydrogen acceptors in **HBIF-2** are two different ends of the same neutral complex.

The hydrogen-bonding interactions between the neutral molecules in **HBIF-2** result in a 2-D double layer structure. Treating Li and B sites as the four-connected nodes, the framework can be topologically represented as a four-connected bilayer containing two linked honeycomb-like (6,3) sheets (Fig. 1(d)).

Because of the inherent hydrogen-bonding capability of boron imidazolate complexes, hydrogen-bonded supramolecular assemblies can occur under other conditions as shown by the synthesis of **HBIF-3** in which the O–H···N hydrogen-bonding interactions between two trigonal units (the protonated  $\text{H}_3\text{O}^+$  cation and the  $[\text{BH}(\text{eim})_3]^-$  anion) lead to a 2-D honeycomb-like (6,3) sheet

(Fig. 1(e) and 1(f)). Both the O site and B site are located at special positions with three-fold symmetry. The O...N hydrogen-bonding distance is 2.701 Å. The adjacent (6,3) sheets are further stacked up without supramolecular interactions between them.

The CO<sub>2</sub> gas adsorption measurement was performed on a Micromeritics ASAP 2010 surface area and pore size analyzer, which confirms the permanent microporosity of **HBIF-2**. The sample was degassed at 80 °C for 1 day under vacuum prior to the measurement. A significant increase in the amount of CO<sub>2</sub> gas adsorbed by **HBIF-2** was observed as the pressure of CO<sub>2</sub> increased (Fig. 2), indicating the diffusion of CO<sub>2</sub> molecules into the channels.

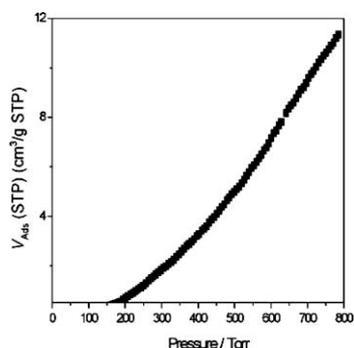


Fig. 2 The CO<sub>2</sub> adsorption isotherm of **HBIF-2** at 273 K.

In summary, it is shown here that the use of chelating hydroxylic ligands provides a new path for the creation of supramolecular hydrogen-bonded assemblies with potential for open-framework architectures that supplement covalent BIFs reported earlier. In **HBIF-1**, the cationic tetrahedral lithium complex [Li(eg)<sub>2</sub>]<sup>+</sup> forms a 3-D hydrogen-bonded tetrahedral framework with anionic [B(mim)<sub>4</sub>]<sup>-</sup>. In **HBIF-2**, large neutral molecules formed from the coupling between cationic Li(tea)<sup>+</sup> and anionic [B(im)<sub>4</sub>]<sup>-</sup> are further cross-linked through hydrogen-bonding into a double-layer assembly. **HBIF-3** further illustrates the potential diversity of hydrogen-bonded supramolecular assemblies that are accessible in the boron imidazolate system. These results provide a new synthetic strategy for the construction of imidazolate frameworks based on supramolecular interactions.

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## Notes and references

‡ Synthesis of Li(glycol)<sub>2</sub>B(mim)<sub>4</sub> (**HBIF-1**): tetrakis(2-methylane-imidazoly)boric acid (0.0388 g, 0.10 mmol) and Li<sub>2</sub>S (0.0243 g, 0.5 mmol) in a mixed 2-amino-1-butanol (0.6130 g, 6.96 mmol)–CH<sub>3</sub>CN (0.9232 g, 14.2 mmol)–glycol (0.3575 g, 5.76 mmol) solution were placed in a 20 mL vial. The sample was heated at 85 °C for 5 days, and then cooled to room-temperature. After washing by ethanol, colorless crystals were obtained (yield: 0.035 g, 78%). Synthesis of Li(tea)[B(im)<sub>4</sub>] (**HBIF-2**): in a 20 mL vial, sodium tetrakis(imidazoly)borate (0.0501 g, 0.15 mmol) and LiNO<sub>3</sub> (0.0562 g, 0.82 mmol) were dissolved by 1.5233 g triethanolamine solvent, and 3 mL acetone was layered on the mixture. After keeping in the refrigerator (temperature = 5 °C) for 3 days, colorless crystals were obtained in the sealed vial (yield: 0.055 g, 85%). Synthesis of (H<sub>3</sub>O)<sub>3</sub>[BH(im)<sub>3</sub>] (**HBIF-3**): in a 20 mL vial, 0.2 mL HCl (1 mol L<sup>-1</sup>) was added into the mixed water–ethanol solution (3 mL, 1 : 1 volume ratio) of sodium trikis(2-ethylane-imidazoly)borate (0.1011 g, 0.43 mmol). After evaporation at room temperature for 3 days, colorless crystals were obtained (yield: 0.121 g, 90%).

§ Crystal data for **HBIF-1**: C<sub>20</sub>H<sub>24</sub>BLiN<sub>8</sub>O<sub>4</sub>, M<sub>r</sub> = 458.22, tetragonal, space group I4̄, a = b = 10.1374(9) Å, c = 24.286(4) Å, V = 2495.8(5) Å<sup>3</sup>, Z = 4, T = 293(2) K, D<sub>c</sub> = 1.219 g cm<sup>-3</sup>, R(int) = 0.0419, 5590 reflections collected, R1(wR2) = 0.0510 (0.1397) and S = 1.143 for 939 reflections with I > 2σ(I). Crystal data for **HBIF-2**: C<sub>18</sub>H<sub>27</sub>BLiN<sub>6</sub>O<sub>5</sub>, M<sub>r</sub> = 435.24, orthorhombic, space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, a = 7.44740(10) Å, b = 10.1434(2) Å, c = 30.0269(5) Å, V = 2268.29(7) Å<sup>3</sup>, Z = 4, T = 293(2) K, D<sub>c</sub> = 1.274 g cm<sup>-3</sup>, R(int) = 0.0491, 16 895 reflections collected, R1(wR2) = 0.0379 (0.0827) and S = 1.014 for 1629 reflections with I > 2σ(I). Crystal data for **HBIF-3**: C<sub>15</sub>H<sub>24</sub>BN<sub>6</sub>O, M<sub>r</sub> = 315.21, trigonal, space group P31c, a = b = 10.828(2) Å, c = 18.738(8) Å, V = 1902.6(10) Å<sup>3</sup>, Z = 4, T = 293(2) K, D<sub>c</sub> = 1.100 g cm<sup>-3</sup>, R(int) = 0.0673, 4854 reflections collected, R1(wR2) = 0.0541 (0.1312) and S = 1.023 for 586 reflections with I > 2σ(I).

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