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Polymorphs of lithium-boron imidazolates: energy landscape and hydrogen storage properties†

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The topological diversity of lithium-boron imidazolates $\text{LiB}(\text{imid})_4$ was studied by combining topological enumeration and *ab initio* DFT calculations. The structures based on zeolitic rho, gme and fau nets are shown to be stable and have high total hydrogen uptake (6.9–7.8 wt.%) comparable with that of MOF-177.

In the last years porous framework materials have attracted much interest due to their applications in gas storage, gas purification and segregation, or catalysis. Zeolites, metal–organic frameworks (MOFs) and more recently covalent organic frameworks (COFs) represent the main classes of porous materials being at the focus of research nowadays.¹ In such technology-relevant areas there is a large need for synthetic strategies able to rapidly indicate useful prototypes. Topology has served as a blueprint for directing the assembly of novel solid-state materials from molecular fragments, a principal example thereof being the reticular synthesis of MOFs. A topological *reticulum* represents a structural prototype transferable across chemical compositions, a powerful paradigm for structural variety and property optimization. Features of MOFs and COFs can be combined by using the lightest elements (Li, B) as framework nodes and imidazolate-anions as linkers which lead to the formation of lithium-boron imidazolates (BIFs).² The synthesis of isomorphous structures $\text{M}^1\text{B}(4\text{-mim})_4$ ($\text{M}^1 = \text{Li}$, Cu; 4-mim = 4-methylimidazolate; sp. gr. *P*432) with the topology of zeolite RHO^{2b} can be considered as a successful combination of MOF and COF chemistry. In a recent Account, Yaghi *et al.* gave a comprehensive review of framework topologies and properties of zeolitic imidazolate frames (ZIFs).³ ZIFs owe their structural variety to their geometric similarity with zeolites, locally very close to SiO_4 tetrahedra. This prompted us to have a closer look at the seemingly much restricted polymorphism of lithium-boron imidazolate $\text{LiB}(\text{imid})_4$ (imid = imidazolate), for which only a dense, non-porous polymorph with the topology of the *zni* net (for the nomenclature see <http://rcsr.anu.edu.au>) is known.^{2a} Like Al^{3+} and P^{5+} formally replace Si^{4+} in going from SiO_2 to microporous AlPO_4 , Li^+ and B^{3+} are punctual replacements for Me^{2+} ($\text{Me} = \text{Zn}$, Cd, Co, *etc.*) in deriving BIFs from ZIFs. Just as for aluminophosphates, this should in principle allow for a much richer boron reticular chemistry than found up to now. In this communication we present a systematic topological scan of

structure candidates for $\text{LiB}(\text{imid})_4$. We extend the catalogue of lithium-boron imidazolates and we identify some BIF topologies as solid material candidates with promising nominal hydrogen uptake properties.

The task of extending the catalogue of BIFs consisted of two major steps: topological enumeration followed by DFT-GGA (PBE) calculations, to assess the relative stability and experimental accessibility of BIF candidates. For generating $\text{LiB}(\text{imid})_4$ polymorphs we considered all 4-coordinated nets found in imidazolate-based frameworks so far.³ In addition, not-yet discovered topologies considered in an earlier study on $\text{Zn}(\text{imid})_2$ polymorphs⁴ were included. It should be noted that some of the therein proposed structures have by now been synthesized.³

In BIF structures each M^1 atom ($\text{M}^1 = \text{Li}$, Cu) is connected *via* imidazolate ligands to the four B atoms and *vice versa* (Fig. 1). This means that the underlying net (graph) of the structure is *bipartite*. As is known from graph theory, all cycles in bipartite graphs are even-membered.⁵ In other words, this requires the formal replacement of tetrahedral nodes by Li and B to be compatible with the net topology, that is adjacent B or Li atoms are not allowed. This criterion immediately ruled out the topologies of **nog**, **moz** and **poz** nets recently found in ZIFs.³

Fig. 1 Charge substitution: going from ZIFs to BIFs. Zinc atoms are black, lithium, boron, carbon and nitrogen atoms are shown in green, red, pink and blue, respectively. Hydrogen atoms are omitted for clarity.

With this guiding principle, 30 topologically different $\text{LiB}(\text{imid})_4$ frameworks were constructed and optimized at the DFT-GGA (PBE) level with the facilities of the SIESTA program package.⁶ On the most porous structures we performed molecular simulations in order to estimate their hydrogen storage capacity (for computational details see supporting information†).

To judge the accessibility of a given $\text{LiB}(\text{imid})_4$ polymorph candidate its relative stability on a total energy scale represents a sensitive parameter. BIFs closely resemble $\text{Zn}(\text{imid})_2$ ZIF in terms of their energetic landscape, lending further support to the chemical formal replacement step. This is apparent on comparing

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† Electronic supplementary information (ESI) available: Coordinates of optimized structures in the form of cif-files, selected distances and angles, total energies and computational details. See DOI: 10.1039/c0dt01441a

the relative stability of experimentally characterized $\text{Zn}(\text{imid})_2$ polymorphs to the stability sequence of BIFs with the same topology. For $\text{Zn}(\text{imid})_2$ ZIFs the following energetic score results: **zni** $\approx$ **coi** < **nog** $\approx$ **zec** $\approx$ **cag** < **gis** $\approx$ **mer** $\approx$ **dft** < **crb** (see ESI†). In BIFs: **zni** < **cag** < **zec** < **gis** $\approx$ **mer** $\approx$ **dft** < **coi** < **crb** (Fig. 2). The ground state stays the same, while the intermediate region roughly maintains the same sequence. Rather unexpectedly, the *tetranodal coi* net in $\text{LiB}(\text{imid})_4$ is much less stable than the ‘ground state’ structure with the **zni** topology. We notice that recently a single-crystal-to-single-crystal, pressure induced phase transition was observed between $\text{Zn}(\text{imid})_2$ polymorphs having **zni** and **coi** underlying nets, respectively.⁷ Given the larger energy difference between analogous $\text{LiB}(\text{imid})_4$ structures, a similar phase transition seems to be less probable. This indicates subtle differences between ZIFs and BIFs, which may complicate the access to novel topologies, requiring e.g. further ligand functionalization, a still elusive factor of MOF topology control.

Fig. 2 Relative stabilities and densities of all $\text{LiB}(\text{imid})_4$ polymorphs included in our study.

Structures based on highly porous **rho**, **gme**, **lta** and **fau** nets (the first one being more favorable) are energetically very close to much more dense frameworks (e.g. **cag**, **dia**, **mog**, **neb**). This is manifested in the recent successful synthesis of lithium-boron 4-methylimidazolate with the **rho** topology.^{2b} As in the case of $\text{Zn}(\text{imid})_2$, the framework with the quartz topology (**qtz**) is the least stable. Shortened Li–B separations (around 5.5 Å) compared to Zn–Zn in $\text{Zn}(\text{imid})_2$ (around 6.0 Å) do not imply any additional shortening of non-bonded distances like H...H contacts (see ESI†), which govern structure stability at the supramolecular level.⁸

The estimation of hydrogen uptake in MOFs, COFs and ZIFs materials can be reliably calculated using Grand canonical Monte Carlo molecular simulations,⁹ which indicate $\text{LiB}(\text{imid})_4$ structures based on **fau**, **rho**, and **gme** nets as promising candidates for hydrogen storage applications. Their total hydrogen uptake at 77 K amounts to 7.8, 6.9 and 6.9 wt.%, respectively (Fig. 3). Note that hydrogen uptake of the **fau**-based $\text{LiB}(\text{imid})_4$ is comparable to that of MOF-177 (~10.0 wt. %), which is a reference material among experimentally characterized compounds.¹⁰ We expect that using more elongated linkers could improve storage capacities of BIFs.

Fig. 3 The most prominent $\text{LiB}(\text{imid})_4$ polymorphs for hydrogen storage and their adsorption isotherms at 77 K. Periodic nodal surfaces¹¹ (PNS) are used to separate BIF networks from the cavity space.

$\text{LiB}(\text{imid})_4$ materials are insulators with band gaps around 4.5 eV. Carbon and nitrogen 2p-states mainly contribute to the states near the Fermi level. Lithium 2p-states are highly antibonding and contribute mainly to the conduction band. Bader charges amount to +0.95 for lithium and +2.2 for boron, with a net charge on the imidazolate ligand of −0.8. While in agreement with the formal replacement step, the reduced charge on boron indicates a substantial covalent component which is absent on the Li side. Accordingly, the formula can be rewritten as $\text{Li}^+[\text{B}(\text{imid})_4]^-$. The presence of the complex boron imidazolate anion suggests further cation replacement steps, and the anion itself should be considered as a whole secondary building unit in reticular synthesis of BIFs.

In conclusion, we investigated the energy landscape of $\text{LiB}(\text{imid})_4$ polymorphs in detail and analyzed their hydrogen storage capacities as well as electronic properties. A comparison with the $\text{Zn}(\text{imid})_2$ system revealed an important difference in the stability of polymorphs with **zni** and **coi** underlying networks. The structure with the **fau** topology was shown to be one of the promising materials for hydrogen storage. Electronic structure calculations showed the different nature of the B–N and Li–N bonds, covalent and coordinative, respectively.

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Notes and references

- (a) see e.g. the metal–organic frameworks themed issue (5) of 2009 of *Chem. Soc. Rev.* edited by J. Long and O. M. Yaghi; (b) A. P. Côté, A. Benin, N. Ockwig, A. Matzger, M. O’Keeffe and O. M. Yaghi, *Science*, 2005, **310**, 1166; (c) R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O’Keeffe and O. M. Yaghi, *Science*, 2008, **319**, 939.
- (a) J. Zhang, T. Wu, C. Zhou, S. Chen, P. Feng and X. Bu, *Angew. Chem., Int. Ed.*, 2009, **48**, 2542; (b) T. Wu, J. Zhang, C. Zhou, L. Wang, X. Bu and P. Feng, *J. Am. Chem. Soc.*, 2009, **131**, 6111.
- A. Phan, C. J. Doonan, F. J. Uribe-Romo, C. B. Knobler, M. O’Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2010, **43**, 58.

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- 4 I. A. Baburin, S. Leoni and G. Seifert, *J. Phys. Chem. B*, 2008, **112**, 9437.
- 5 J. M. Harris, J. L. Hirst and M. J. Mossinghoff, *Combinatorics and Graph Theory*, 2nd ed. Springer, 2008.
- 6 J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón and D. Sánchez-Portal, *J. Phys.: Condens. Matter*, 2002, **14**, 2745.
- 7 E. C. Spencer, R. J. Angel, N. L. Ross, B. E. Hanson and J. A. K. Howard, *J. Am. Chem. Soc.*, 2009, **131**, 4022.
- 8 I. A. Baburin and S. Leoni, *CrystEngComm*, 2010, **12**, 2809.
- 9 A. Gupta, S. Chempath, M. J. Sanborn, L. A. Clark and R. Q. Snurr, *Mol. Simul.*, 2003, **29**, 29.
- 10 (a) H. Furukawa, M. A. Miller and O. M. Yaghi, *J. Mater. Chem.*, 2007, **17**, 3197; (b) R. Zacharia, D. Cossement, L. Lafit and R. Chahine, *J. Mater. Chem.*, 2010, **20**, 2145.
- 11 H.-G. von Schnering and R. Nesper, *Z. Phys. B: Condens. Matter*, 1991, **83**, 407.