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Supporting information for

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

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Table S1. Total energies, space-group symmetries, densities and packing indices for optimized LiB(imid)$_4$ polymorphs

Framework topology	Space group**	Total energy, eV per formula unit LiB(imid)$_4$	Energy difference, eV/LiB(imid)$_4$	Density, g/cm^3	Packing index**, %
zni*	$I4_1cd$	-4340.8759	0.0000	1.240	66.2
cag	$Pbca$	-4340.7885	0.0874	0.951	50.6
lcs	$I\bar{4}3d$	-4340.7649	0.1110	0.883	47.0
mog	$P2/c$	-4340.7490	0.1269	1.022	54.4
dia	$I\bar{4}$	-4340.7353	0.1406	0.994	52.8
zec	$P2/c$	-4340.7247	0.1512	0.816	43.4
rho	$P432$	-4340.7233	0.1526	0.566	30.1
gis	$Fdd2$	-4340.7176	0.1583	0.627	33.4
neb	Cc	-4340.7173	0.1586	0.978	52.1
mer	$P4/nnc$	-4340.7062	0.1697	0.635	33.8
gme	$P\bar{3}1c$	-4340.6972	0.1787	0.577	30.7
dft	$P4_22_12$	-4340.6926	0.1833	0.730	38.9
lta	$F432$	-4340.6923	0.1836	0.559	29.7
pcb	$I222$	-4340.6778	0.1981	0.673	35.8
coi	$I4_1$	-4340.6757	0.2002	1.229	65.4
fau	$Fd\bar{3}$	-4340.6516	0.2243	0.492	26.2
irl	$P1$	-4340.6480	0.2279	1.000	53.3
sod	$P\bar{4}3n$	-4340.6368	0.2391	0.702	37.4
pcl	$P2_1$	-4340.5979	0.2780	0.707	37.7
cfc	$P2_1$	-4340.5636	0.3123	0.895	47.7
crb	$P2_1/c$	-4340.5348	0.3411	0.805	42.9
sra	Pc	-4340.5492	0.3267	0.716	38.1
uni	$P3_1$	-4340.5130	0.3629	0.874	46.6
unc	$P2_1$	-4340.4746	0.4013	0.956	51.0
lon	$P2_1$	-4340.4719	0.4040	0.835	44.5
gsi	$P1$	-4340.4489	0.4270	1.002	53.3
ana	$R32$	-4340.3589	0.5170	0.706	37.7
frl	$I222$	-4340.3310	0.5449	0.888	47.3
mmt	$P2_1$	-4340.2866	0.5893	0.928	49.6
qtz	$P6_222$	-4340.0485	0.8274	0.896	47.6

* Experimentally characterized LiB(imid)$_4$ polymorph [1].

** Computed with the PLATON program [2].

Table S2. Selected distances and angles in the optimized LiB(imid)$_4$ structures

Framework topology	Li–N distances, Å	B–N distances, Å	N–Li–N angles, degr.	N–B–N angles, degr.	Closest H...H contact, Å
zni*	2.087-2.127	1.553-561	103.92-116.83	107.85-111.16	2.228
cag*	2.047-2.065	1.555-1.557	106.66-112.21	107.74-110.96	2.447
lcs	2.043-2.054	1.555-1.556	104.05-112.79	107.21-110.70	2.669
mog	2.041-2.086	1.553-1.559	101.22-118.81	107.01-111.85	2.542
dia	2.045-2.046	1.556	106.84-110.81	107.75-110.35	2.633
zec*	2.040-2.101	1.552-1.565	102.98-115.34	106.99-112.00	2.176
rho	2.049-2.080	1.555-1.557	104.45-117.94	107.22-112.14	2.499
gis	2.059-2.071	1.556-1.557	101.70-114.03	107.74-110.22	2.657
neb	2.060-2.134	1.553-1.565	104.48-115.21	107.69-110.47	2.296
mer*	2.055-2.079	1.555-1.558	104.08-116.30	107.26-110.80	2.585
gme	2.053-2.068	1.555-1.560	102.63-116.26	107.47-111.11	2.635
dft*	2.051-2.086	1.555-1.558	106.94-111.80	107.60-111.81	2.489
lta	2.046-2.074	1.553-1.559	104.91-114.72	107.14-112.44	2.350
pcb	2.068-2.075	1.554-1.559	101.64-125.57	108.05-111.01	2.513
coi*	2.024-2.142	1.553-1.571	98.77-120.98	104.95-114.93	2.128
fau	2.038-2.083	1.553-1.564	100.38-114.35	107.18-111.42	2.415
irl	2.053-2.142	1.547-1.563	99.02-129.64	107.35-111.71	2.307
sod	2.067-2.069	1.557-1.559	103.83-112.36	108.18-110.16	2.407
pcl	2.059-2.151	1.554-1.565	97.00-124.44	107.31-111.58	2.382
cfc	2.038-2.140	1.555-1.561	100.43-120.17	107.45-111.27	2.378
crb*	2.048-2.107	1.554-1.565	102.44-119.27	106.75-111.99	2.246
sra	1.998-2.133	1.556-1.563	103.69-116.81	105.25-112.72	2.421
uni	2.025-2.139	1.554-1.562	98.14-122.04	107.69-112.11	2.179
unc	2.047-2.123	1.552-1.572	98.34-119.56	104.55-113.35	2.245
lon	2.055-2.139	1.554-1.561	93.38-125.81	107.30-111.89	2.272
gsi	2.011-2.197	1.548-1.566	95.19-130.38	106.42-114.20	2.003
ana	2.107-2.170	1.556-1.561	103.14-112.18	105.89-111.96	1.871
frl	2.053-2.149	1.556-1.570	97.83-120.14	105.32-114.21	1.942
mmt	2.061-2.219	1.557-1.564	98.88-139.32	105.75-115.65	2.156
qtz	2.122-2.147	1.563-1.565	99.66-118.38	105.85-114.89	1.841

*Analogues of experimentally characterized Zn(imid)$_2$ polymorphs.

Table S3. Total energies of experimentally characterized Zn(imid)$_2$ polymorphs*

Framework topology	Space group	Total energy, eV per formula unit Zn(imid)$_2$
zni	$I4_1cd$	-3764.8735
coi	$I4_1$	-3764.8717
nog	$P2_1/c$	-3764.8220
zec	$C2/c$	-3764.8212
cag	$Pbca$	-3764.8200
gis	$I4_1/amd$	-3764.7927
mer	$I4/mmm$	-3764.7887
dft	$P4_2/mnm$	-3764.7748
crb	$Pbca$	-3764.7071

* Referred to the basis set developed in [3].

Computational details

I. Structure optimization

The SIESTA program package [4] was used to perform conjugate-gradient relaxations on $LiB(imid)_4$ structures (BIFs). During relaxation, both atomic coordinates and cell shape were allowed to change. The metric of the crystal family was initially constrained to improve convergence, by controlling angle deviations from those required by crystal symmetry. The geometry was relaxed to residual forces smaller than 0.03 eV/Å with a stress tolerance less than 0.1 GPa. Convergence of the total energy with respect to the number of *k*-points was carefully checked. Calculations including 8 *k*-points with an energy cutoff of 250 Ry ensured convergence of the electronic part for most structures. For porous structures with large unit cells Γ-point approximation was sufficient. The calculations were performed within the GGA approximation using Perdew-Burke-Ernzerhof exchange-correlation functional [5]. Norm-conserving Trouiller-Martins pseudopotentials were applied to represent core electrons [6]. For H, C, N atoms we used the same basis set as developed in our previous paper on $Zn(imid)_2$ diamondoid conformers [3], for Li and B atoms we used DZP basis.

II. Simulation of hydrogen adsorption

The hydrogen adsorption in the BIF structures was modelled with Grand canonical Monte Carlo simulations (GCMC) using the multipurpose simulation code Music [7]. The sorbent (BIF) is described by a periodic 2x2x2 supercell to eliminate boundary effects. BIFs were treated as rigid structures. The calculations of adsorption isotherms were carried out at T=77 K throughout a wide range of pressure, from low pressure ($P=10^{-3}$ bar) up to high pressure (P=100 bar) to get a complete picture of the adsorption properties. For each point on the isotherm, the simulations were equilibrated for five million steps, and a further five million steps were used to sample the data. Each Monte Carlo step consisted of (i) an insertion attempt of a new molecule, (ii) a deletion attempt of an existing molecule, (iii) translation, or (iv) rotation of an existing molecule, with equal probabilities.

The H_2/H_2 and H_2/BIF framework interactions were described *via* a repulsion–dispersion 12-6 Lennard–Jones (LJ) potential to account for van der Waals interactions between the H_2 molecules and the BIFs structures (Eq. (1)):

$$V(r_{ij}) = 4\varepsilon^{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \qquad (1)$$

where i and j stand for the sites of the adsorbate (hydrogen molecules) and the BIF structure; r_{ij} – the distance between them; ε^{ij} and σ_{ij} – the Lennard–Jones parameters.

The H_2 molecule was modelled as a rigid diatomic molecule with a bond length 0.74 Å where each H atom represented LJ interaction site. The potential parameters for the hydrogen molecule (σ = 2.72 Å; ε = 10.0 K) were taken from [8]. These parameters reproduce satisfactorily the density of hydrogen gas as well as the experimental data on hydrogen adsorption in MOFs [8]. The potential parameters for the BIF framework atoms (except Li) were taken from the DREIDING force field [9]. For Li atoms the parameters (which are not available in [9]) from the UFF force field [10] were used. Lorentz-Berthelot mixing rules ($\sigma_{ij} = (\sigma_i + \sigma_j)/2, \varepsilon^{ij} = \sqrt{(\varepsilon^i \times \varepsilon^j)}$) were employed to calculate H_2-BIF LJ potential parameters. A cut-off of 13.0 Å was applied to the Lennard-Jones interactions.

III. Calculation of electronic density and Bader charges

The electronic density was calculated with the all-electron, full-potential local orbital (FPLO) minimal basis method [11]. In FPLO each atomic orbital *nl* with principal quantum number *n* and angular momentum *l* is represented by one basis function only. The basis functions are obtained by solving an effective Schrödinger equation which contains the spherically averaged crystal potential and an artificial confining potential [12]. The confining potential makes the basis functions more strongly localized than the atomic orbitals. The FPLO method does not have any atomic (or muffin–tin) spheres so that the whole space is treated in a uniform manner. In the scalar relativistic calculations within the LDA scheme (Perdew and Wang [13]) B(1s, 2s, 2p, 3d), Li(1s, 2s, 2p, 3d), C(2s, 2p, 3d) , N(2s, 2p, 3d) and H(1s, 2p) represented the basis sets. Lower-lying states were treated as core states.

A *k* mesh of 8 irreducible points in the Brillouin zone ensured convergence with respect to the number of *k*-points. The spatial extension of the orbitals forming the basis was optimized to minimize the total energy. For the electronic density calculation a mesh of 31250310 irreducible points were used. The Bader analysis was performed on this density with the program Dgrid [14].

References

1. J. Zhang, T. Wu, C. Zhou, S. Chen, P. Feng and X. Bu, *Angew. Chem., Int. Ed.* 2009, **48**, 2542.
2. A. L. Spek, *Acta Crystallogr. Sect. D: Biol. Crystallogr.* 2009, **65**, 148
3. I. A. Baburin and S. Leoni, *CrystEngComm* 2010, DOI:10.1039/b926717d
4. 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
5. J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* 1996, **77**, 3865.
6. N. Troullier and J. L. Martins, *Phys. Rev. B* 1991, **43**, 1993
7. A. Gupta, S. Chempath, M. J. Sanborn, L. A. Clark and R. Q. Snurr, *Mol. Simul.* 2003, **29**, 29
8. Q. Yang and C. Zhong, *J. Phys. Chem. B* 2005, **109**, 11862.
9. S. L. Mayo, B. D. Olafson and W. A. Goddard, *J. Phys. Chem.* 1990, **94**, 8897.
10. A. K. Rappé, C. J. Casewit, K. S. Colwell, W. A. Goddard, W. M. Skiff, *J. Am. Chem. Soc.*, 1992, **114**, 10024
11. K. Koepernik and H. Eschrig, *Phys. Rev. B* 1999, **59**, 1743.
12. H. Eschrig, *Optimized LCAO Methods and the Electronic Structure of Extended Systems*, Springer, Berlin, 1989.
13. J. P. Perdew and Y. Wang, *Phys. Rev. B* 2002, **45**, 13244.
14. M. Kohout, DGrid, version 4.5, Radebeul, 2009.