Electronic Supplementary Material (ESI) for CrystEngComm

Supplementary Information

Comparison of the relative stability of zinc and lithium-boron zeolitic imidazolate frameworks

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Table S1. Parameters of CP2K/Quickstep simulations.

Parameter	Value
Energy and atomic forces evaluation	
Method	Mixed Gaussian and plane-wave (GPW)
Functional	PBE
Pseudo-potential	Goedecker-Teter-Hutter (GTH)
Gaussian-type basis sets	Molecular optimized double zetha-valence basis sets with a polarization function (DZVP-MOLOPT)
Plane-wave cut-off	400 Ry
k-point sampling	Gamma-point only
SCF optimizer	Orbital transformation with the direct inverse in the iterative subspace optimizer (OT/DIIS)
Electron density convergence criteria	1.0×10^{-7}
Dispersive interaction correction	DFT-D2: $s_6 = 0.75$; $d = 20$; $R_{cut\text{-}off} = 12.0$ Å. DFT-D3: $s_6 = 1.000$; $s_{r6} = 1.127$; $s_8 = 0.722$; $R_{cut\text{-}off} = 12.0$ Å.
Atomic positions optimization	
Optimizer	Broyden-Fletcher-Goldfarb-Shanno (BFGS)
Constrains	no symmetry constrains on atomic positions
Convergence criteria	maximum force 4.5×10^{-5} Hartree/Bohr RMS force 3.0×10^{-5} Hartree/Bohr maximum coordinate change 3.0×10^{-4} Bohr RMS coordinate change 1.5×10^{-4} Bohr
Unit-cell parameters optimization	
Optimizer	Conjugate gradient (CG; each cell optimization step is followed by geometry optimization at current cell parameters)
Constrains	external hydrostatic pressure 1 bar
Convergence criteria	maximum force 4.5×10^{-4} Hartree/Bohr RMS force 3.0×10^{-4} Hartree/Bohr maximum parameter change 3.0×10^{-3} Bohr RMS parameter change 1.5×10^{-3} Bohr maximum pressure deviation 100 bar

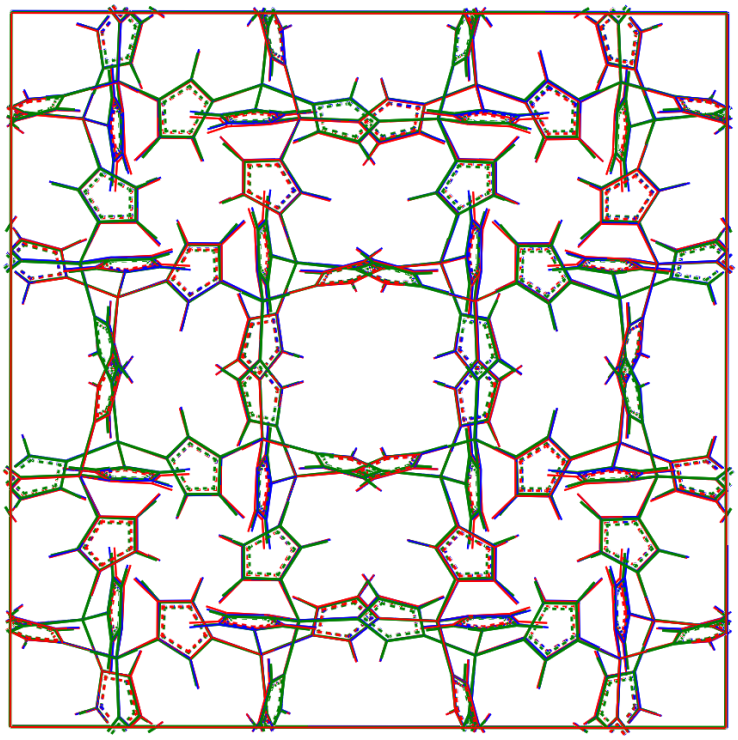
Table S2. Structure parameters and total energies for $Zn(Im)_2$ and $LiB(Im)_4$. ZIFs obtained from DFT-D simulations with CP2K.

Structure	a, Å	b, Å	c, Å	α, °	β, °	γ, °	V, Å^3	d,* nm^{-3}	Energy, kJ/mol***
$Zn(Im)_2$ with PBE-D2									
cag (ZIF-4**)	15.601	14.958	18.086	90.0	90.0	90.0	4220.3	3.79	-362544.08
DFT (ZIF-3**)	19.137	19.137	16.867	90.0	90.0	90.0	6177.2	2.59	-362530.02
dia	7.969	7.969	16.647	90.0	90.0	90.0	1057.3	3.78	-362531.59
GIS (ZIF-6**)	18.483	18.483	20.678	90.0	90.0	90.0	7064.2	2.26	-362529.73
MER (ZIF-10**)	27.250	27.250	19.330	90.0	90.0	90.0	14354.0	2.23	-362529.47
SOD (ZIF-8**)	17.018	17.018	17.018	90.0	90.0	90.0	4928.2	2.43	-362530.57
zni	23.508	23.488	12.468	90.0	90.0	90.0	6884.6	4.65	-362560.07
$Zn(Im)_2$ with PBE-D3									
cag (ZIF-4**)	15.475	14.958	18.196	90.1	90.0	89.8	4211.9	3.80	-362529.57
DFT (ZIF-3**)	19.124	19.124	16.837	90.0	90.0	90.0	6158.0	2.60	-362515.44
dia	7.803	7.801	16.964	90.0	90.0	90.0	1032.7	3.87	-362518.67
GIS (ZIF-6**)	18.489	18.490	20.663	90.0	90.0	90.1	7063.8	2.27	-362514.34
MER (ZIF-10**)	27.239	27.239	19.308	90.0	90.0	90.0	14326.5	2.23	-362514.53
SOD (ZIF-8**)	17.017	17.017	17.017	90.0	90.0	90.0	4927.8	2.44	-362516.53
zni	23.552	23.522	12.458	90.0	90.0	90.0	6901.5	4.64	-362546.90
$LiB(Im)_4$ with PBE-D2									
cag	14.228	14.178	16.892	90.0	90.0	90.0	3407.7	4.70	-217258.77
DFT	18.257	18.257	15.782	90.0	90.0	90.0	5260.2	3.04	-217245.66
dia	7.583	7.592	14.981	90.0	90.0	90.0	862.4	4.64	-217257.42
GIS	25.460	18.710	24.677	90.0	90.0	90.0	11754.9	2.72	-217245.22
MER	25.729	25.729	17.738	90.0	90.0	90.0	11742.4	2.73	-217245.73
SOD	15.833	15.832	15.832	90.0	90.0	90.0	3968.3	3.02	-217245.14
zni (BIF-1)	22.375	22.375	11.331	90.0	90.0	90.0	5672.8	5.64	-217278.59
$LiB(Im)_4$ with PBE-D3									
cag	14.245	14.205	16.884	90.0	90.0	90.0	3416.3	4.68	-217232.80
DFT	18.238	18.238	15.750	90.0	90.0	90.0	5238.6	3.05	-217221.24
dia	7.520	7.521	15.145	90.0	90.0	90.0	856.6	4.67	-217232.59
GIS	25.451	18.709	24.687	90.0	90.0	90.0	11755.1	2.72	-217219.98
MER	25.734	25.734	17.723	90.0	90.0	90.0	11736.8	2.73	-217220.60
SOD	15.875	15.852	15.858	90.0	90.0	90.0	3990.5	3.01	-217220.57
zni (BIF-1)	22.410	22.415	11.419	90.0	90.0	90.0	5736.1	5.58	-217252.61

* Framework densities are expressed as the number of tetrahedral T sites per unit volume, nm^{-3}.
** The experimental structure contains guest molecules.
*** We are aware that our computations refer to internal energies (being comparable to enthalpies, assuming the volumes changes are small at the given pressure). Turning to thermodynamics, stability is determined by free energy, which requires the knowledge of entropy, which is not computed here.

Figure S1. Experimental (green), simulated with PBE-D2 (red) and PBE-D3 (blue) structures of $Zn(Im)_2$ **zni** (a) and $LiB(Im)_4$ **zni** (b). The unit cells are viewed down the [001] direction. Excellent agreement is observed for the other experimental structures.

(a)



(b)

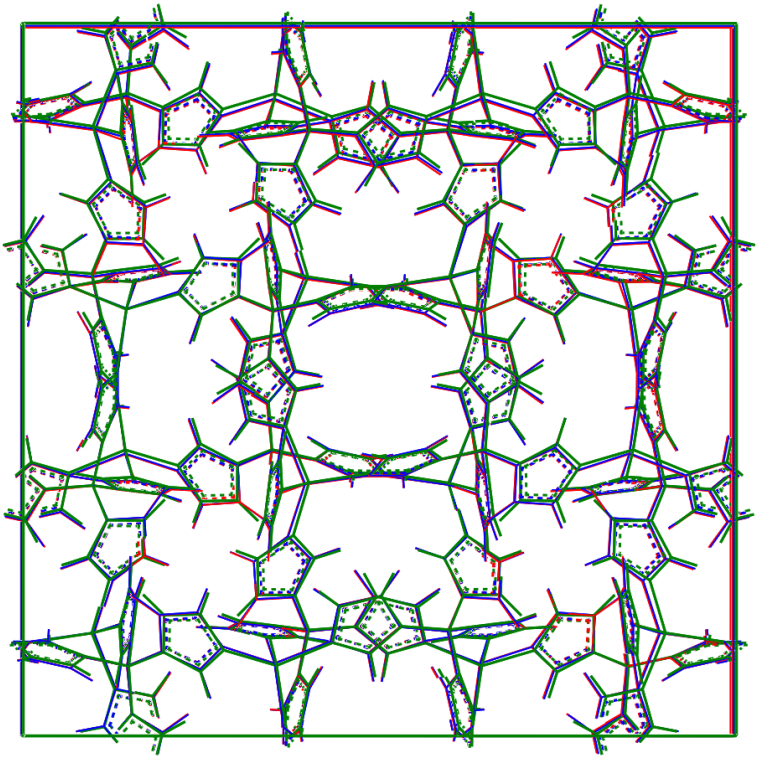


Table S3. The comparison of ZIFs' unitcell parameters and relative energies as simulated with CP2K/Quickstep and CASTEP using PBE-D2. For comparison with CP2K calculations, plane-wave calculations were performed on both **MER** and **zni** structures, considered here as benchmarks. These calculations used the PBE functional, a cut-off of 350 eV (or 25.7 Ry) and sampling at the Γ point. Energy differences at the DFT-D2 level between **MER** and **zni** were found to be 27.45 kJ/mol and 29.87 kJ/mol for the Zn-based and LiB-based structures, respectively, confirming the veracity of the CP2K results.

	Zn-based				LiB-based			
Topology	**zni**		**MER**		**zni**		**MER**	
Code	CP2K*	CASTEP	CP2K*	CASTEP	CP2K*	CASTEP	CP2K*	CASTEP
a, Å	23.508	23.502	27.250	27.093	22.375	22.419	25.729	25.730
b, Å	23.488	23.494	27.250	27.0923	22.375	22.392	25.729	25.730
c, Å	12.468	12.382	19.330	19.473	11.331	11.386	17.738	17.720
Volume, $Å^{-3}$	6884.6	6836.4	14354.0	14293.9	5672.8	5715.9	11742.4	11731.0
Energy,** kJ/mol	0.000	0.000	30.596	27.444	0.000	0.000	32.861	29.870

* CP2K/Quickstep DFT module
** The relative energy is measured with respect to **zni** and normalized per tetrahedral site (Zn or Li/B).